SOLID STATE REACTION OF SODIUM CARBONATE WITH MONTMORILLONITE AT 550°C

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Abstract—The isothermal solid state reactions of Na_2CO_3 and other salts at 550°C with montmorillonite and with 1:1 mixtures of montmorillonite-illite and montmorillonite-chlorite were investigated. At a concentration of 20 wt. %, Na_2CO_3 caused the complete destruction of the X-ray powder diffraction (XRD) pattern of montmorillonite alone and in mixtures with other clays. Less deterioration of the XRD pattern was found for NaOH, NaF, K_2CO_3, and Li_2CO_3. NaCl, Na_2SO_4, Na_3PO_4, $MgCO_3$, and $CuCO_3$ had no effect on the XRD traces of montmorillonite. The time dependence of the Na_2CO_3-montmorillonite interaction at 550°C suggested that the reaction is diffusion controlled in three dimensions, i.e., diffusion was directed from the surface of the particle towards its center.

Key Words—Chlorite, Diffusion, Illite, Montmorillonite, Sodium carbonate, Thermal treatment.

INTRODUCTION

The isothermal reaction between sodium carbonate and montmorillonite at 550°C has been used for the detection of montmorillonite in soil clays, especially those montmorillonite materials that are difficult to identify because of the absence of basal X-ray powder diffraction (XRD) reflections (Helmy *et al.*, 1984). These workers found that such a heat treatment destroys the XRD reflections of montmorillonite, but does not affect those of illite. In a continuation of these studies concerned with the thermal stability of montmorillonite in such systems, montmorillonite alone and in 1:1 mixtures with illite or chlorite was heated in the presence of a variety of salts. The effect of time on the sodium carbonate-clay reaction was also investigated to provide insight into the mechanism of the salt-clay reaction in the solid state.

EXPERIMENTAL

The clay used in this study was montmorillonite from Río Negro, Argentina (Natale and Mandolesi, 1985). Clay particles <2 μm in diameter were obtained by sedimentation in water followed by centrifugation and air drying. In one experiment two other montmorillonites were used, one from Cerro Bandera, Argentina (Peinemann *et al.*, 1972) and the other from Wyoming.

Differential thermal analysis (DTA) of the clay was carried out in a Netzsch GmbH model 404 DTA apparatus at a heating rate of 10°C/min. A thermal gravimetric analysis (TGA) curve was also obtained at the same heating rate using a Netzsch GmbH (model 409/2) thermobalance.

For the study of salt-clay interactions, 0.07 g of salt was added together with few drops of water to 0.35 g of clay. The paste was well mixed, dried in air, and pulverized in an agate mortar. The clay-salt mixture was then heated in a porcelain crucible at 550°C for 2 hr in a muffle furnace. XRD traces of the products were obtained using Ni-filtered CuKα radiation (Rigaku-Danki model D 3F diffractometer).

Mixtures containing equal amounts of montmorillonite and illite or chlorite were also prepared and treated as above. The illite was Fithian illite, and the chlorite was from the Teniente Matienzo mine, Mendoza, Argentina.

The effect of time on the salt-clay interaction was investigated as follows. Several crucibles containing the samples were weighed before and after heating at 550°C in the furnace. The first crucible was withdrawn just as the furnace reached 550°C. The others were withdrawn at the times shown in the illustrations. The data shown in the Figures 5 and 6 are averages of triplicate runs. The difference in weight per gram between the sample withdrawn first (zero time at 550°C) and that withdrawn from the muffle furnace after 2 hr was taken as representing the complete reaction between the salt and the clay, i.e., $\alpha = 1$ in Eqs. (2) and (3). This criterion was adopted because no change in the weight of the samples was observed after the 2-hr period.

RESULTS AND DISCUSSION

Interaction of montmorillonite with Na_2CO_3

The DTA curve shown in Figure 1a is typical for montmorillonite and shows a large dehydration peak at about 110°C and a well-developed endothermic peak at 670°C, which is usually attributed to the dehydroxylation of the clay. The TGA data plotted in Figure 1b does not, however, confirm a loss of all the hydroxyls of the montmorillonite structure. The curve indicates that about 10% weight was lost on heating the sample to 200°C, probably due to the loss of water of hydration. Between 200° and 670°C, the sample lost an additional
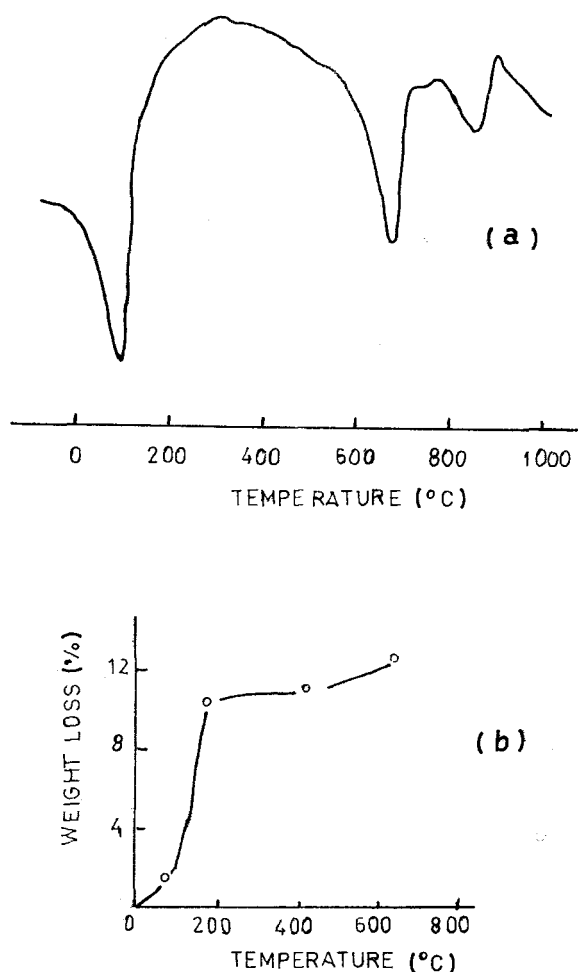
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Figure 1. (a) Differential thermal analysis curve and (b) thermogravimetric analysis curve for montmorillonite from Río Negro.
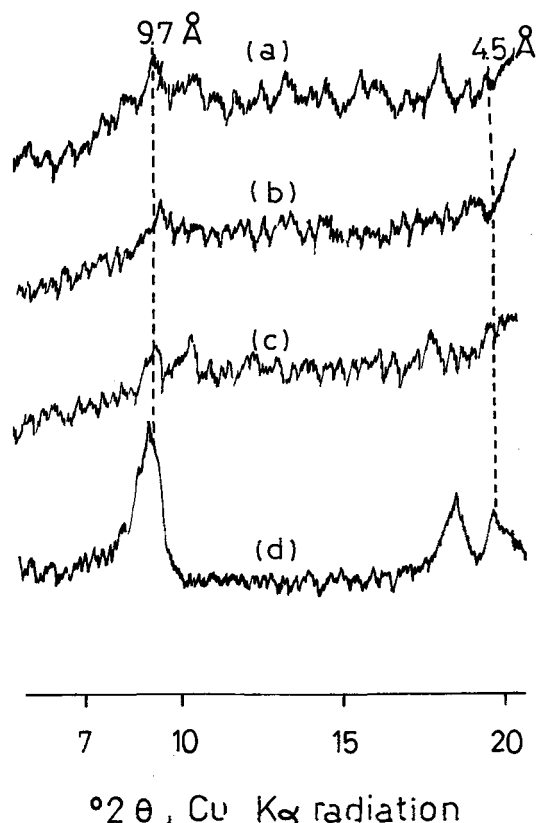

Figure 2. X-ray powder diffraction traces of montmorillonite from different localities and of samples heated at 550°C for 2 hr in the presence of 20 wt. % Na_2CO_3. (a) Cerro Bandera, (b) Wyoming, and (c) Río Negro. Trace (d) is for the Río Negro montmorillonite heated at 550°C for 2 hr.

2 wt. %, which probably corresponded to a partial dehydroxylation (*vide infra*).

The chemical composition of the clay was given by Natale and Mandolesi (1985) as:

$$(Si_{7.83}Al_{0.17})(Al_3Fe^{3+}_{0.35}Mn^{3+}_{0.05}Mg_{0.61})O_{20}(OH)_4$$

which yields a formula weight of 716. On total dehydroxylation, the clay loses 2 moles of H_2O per formula unit of clay, corresponding to a weight loss of 5.03%. Inasmuch as only 2% was lost, the clay only partially dehydroxylated on heating to 670°C. The crystal structure of montmorillonite is not destroyed by heating to 800°C, and the unit cell dimensions change only by about 0.1–0.3 Å (Bradley and Grim, 1951; Earley *et al.*, 1953). Furthermore, according to Jonas (1955), rehydroxylation of montmorillonite heated to 700°C is almost complete, further proof of the stability of the structure up to this temperature.

Heating this same clay in a small muffle furnace to 550°C for 2 hr produced a weight loss of 10.4%; an additional loss of 1.6% was recorded after 2 hr of heating at this temperature. These results compare well with those obtained by thermal gravimetry. The weight loss for the clay mixed with 20 wt. % Na_2CO_3 was 15.6% from room temperature to 550°C and an additional 1.2% after heating it for 2 hr at this temperature. This substantial weight loss suggests that some process other than dehydroxylation took place in the presence of Na_2CO_3.

According to Taylor (1962), in the absence of salts, the dehydroxylation of clays involves the migration of protons from inside the structure to surfaces or boundaries and their combination with OH groups present in these regions to form water. The reaction is facilitated by the volatilization of the water. In this process the clay structure loses one positively and one negatively charged species, hence, no charge imbalance is produced. Only some vacant OH sites are produced. This dehydroxylation is different from the reaction that was apparently operative in the presence of Na_2CO_3; here, protons migrated and volatile products formed, as follows:
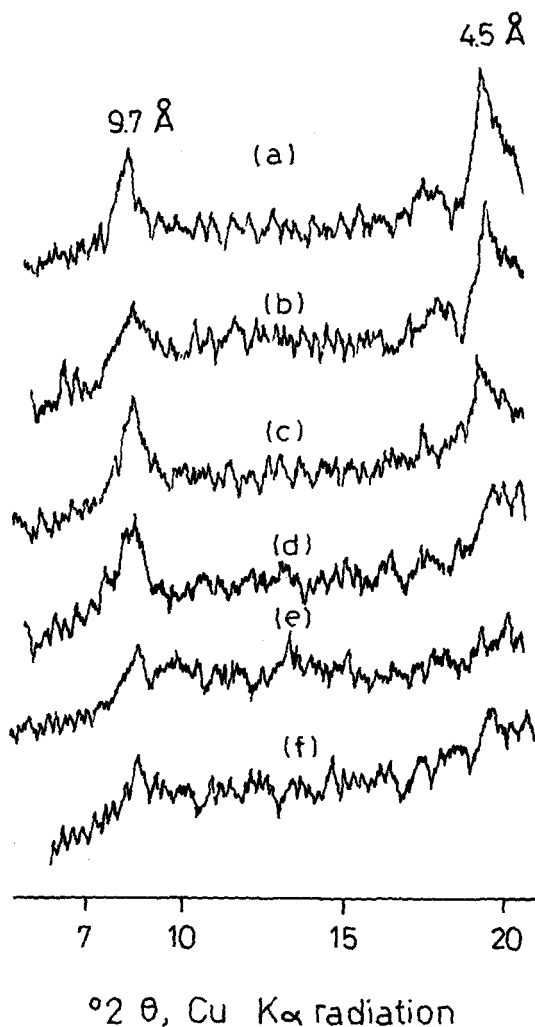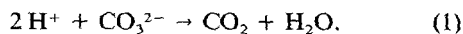
Figure 3. X-ray powder diffraction traces of montmorillonite heated for 2 hr at 550°C in the presence of 20 wt. %. (a) NaCl, (b) Na_2SO_4, (c) Na_3PO_4, (d) $NaHCO_3$, (e) NaF, and (f) NaOH.

Figure 4. X-ray powder diffraction traces of montmorillonite heated for 2 hr at 550°C in the presence of 20 wt. %. (a) $MgCO_3$, (b) $CuCO_3$, (c) K_2CO_3, and (d) Li_2CO_3.

$$2\,H^+ + CO_3^{2-} \rightarrow CO_2 + H_2O. \qquad (1)$$

In this reaction structural hydroxyls were not lost; hence, a charge imbalance and a diffusion potential were created, which forced the movement of sodium ions into the crystal along the electric potential created by the movement of the protons in the opposite direction. Because of its size (much greater than a proton) and its 8- to 10-fold coordination with oxygen in silicates, the movement of sodium into the clay structure requires drastic changes in the oxygen packing. The presence of sodium, therefore, produces a distortion of the clay structure and the loss of the crystallographic properties of the clay, namely, the production of a disordered structure and the disappearance of the XRD pattern of the mineral. This loss is shown by the XRD traces of Figure 2, in which the 001 and 02,11 reflections are missing.
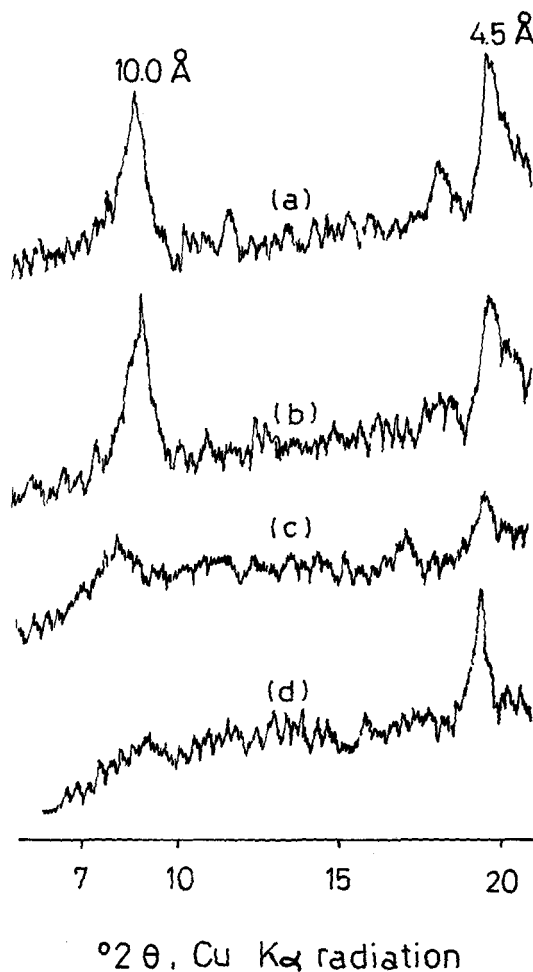
No carbonate was detected in the products of the carbonate-treated samples after they were heated at 550°C for 2 hr, supporting the reaction given by Eq. (1). The 350 mg of clay used in the experiment was equivalent to $350/716 = 0.49$ mmole of clay, containing $0.49 \times 4 = 1.96$ mmole of protons. The 1.96 mmole of protons was able to consume 0.98 mmole of Na_2CO_3 (103.6 mg), an amount greater than the amount of Na_2CO_3 added (70 mg).

Interaction of montmorillonite with salts other than Na_2CO_3

Heating montmorillonite at 550°C for 2 hr in the presence of 20 wt. % Na_2SO_4, Na_3PO_4, or NaCl produced no change in the XRD pattern of the clay, indicating the absence of salt-clay interactions (see Figure
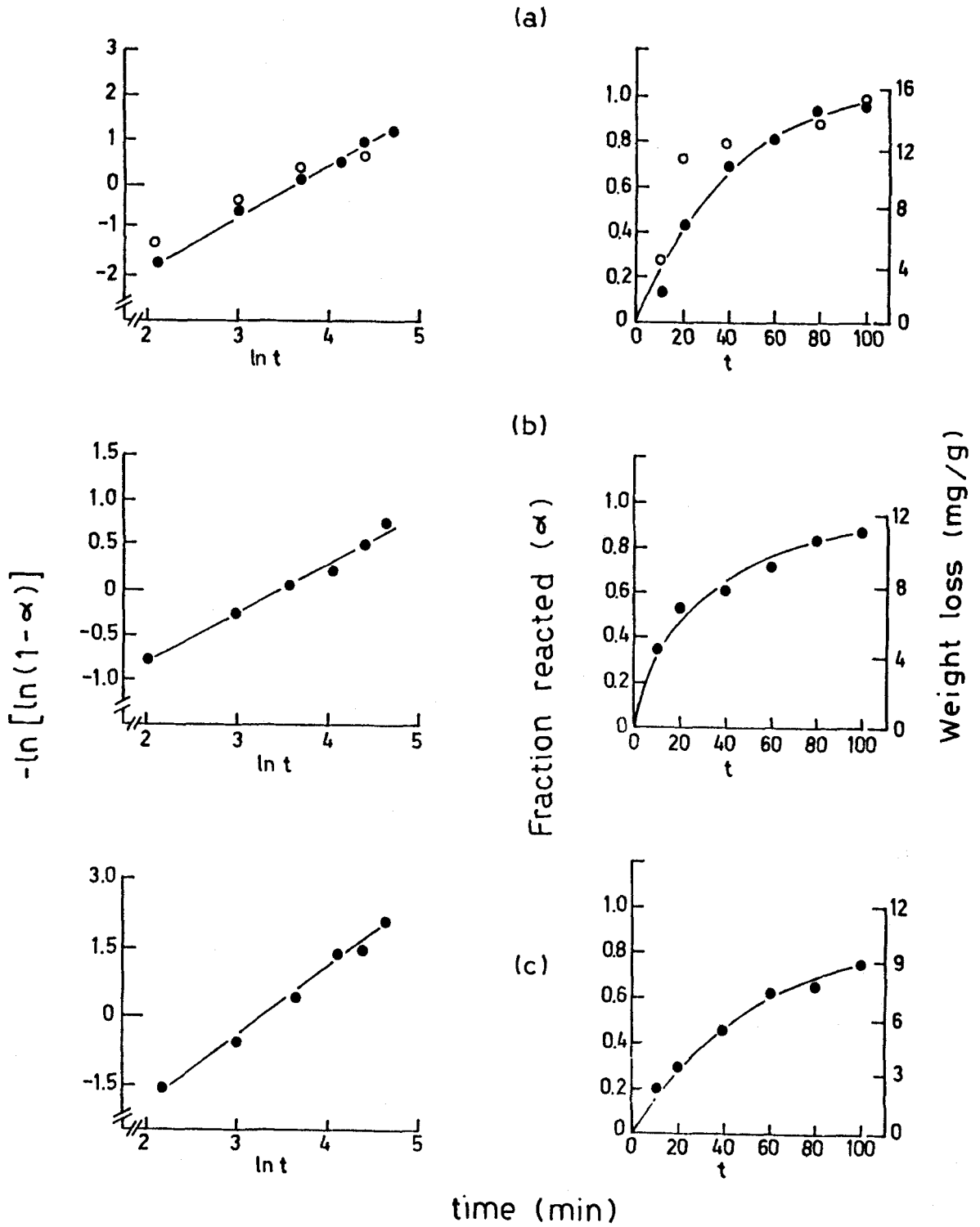
Figure 5. Plots of $-\ln\ln(1 - \alpha)$ vs. ln t and of the fraction reacted (α) vs. time for (a) dehydroxylation of montmorillonite at 550°C (●) and 670°C (○); (b) mixture of montmorillonite and Na_2CO_3 at 550°C; (c) mixture of montmorillonite and NaOH at 550°C. Extra scale of ordinates of graphs at right represent weight losses in mg/g clay.
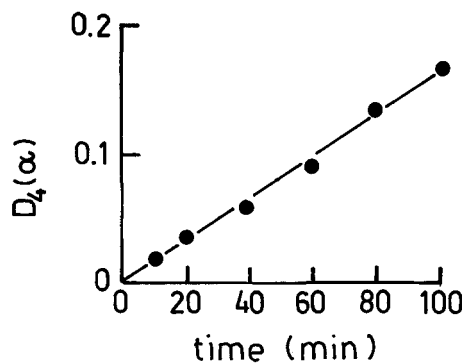
Figure 6.   Kinetic data for solid state reaction of montmorillonite with Na_2CO_3 at 550°C plotted according to Eq. (3).

3). For the sulfate and phosphate the lack of interaction may have been due to the absence of a volatile product formed from the salt anion and protons of the clay structure, hence, the detention of proton loss. In other words, the nondisappearance of reaction products usually tended to block further reaction according to the mass action principle. For NaCl, the HCl which may have been produced in the NaCl-montmorillonite interaction is a volatile compound, however, it is not inert as the CO_2 or H_2O produced in the carbonate-clay reaction. It could have reacted with the silicate, thereby blocking or interfering with the reaction between NaCl and the clay, as already mentioned.

The above explanation is supported by the observation that for fluoride and hydroxide, from which volatile products can be formed, the areas of many XRD peaks decreased (see Figure 3). The lack of interaction of the bicarbonate with the clay was due probably to the thermal instability of the bicarbonate, which releases CO_2 at 270°C; hence, a reaction similar to that given in Eq. (1) did not materialize (Na_2CO_3 is stable to 851°C).

The XRD traces in Figure 4 indicate that no solid state reaction took place between the clay and Mg and Cu carbonates. This inactivity may be attributed to the decomposition of these carbonates below 550°C and to the small diffusion coefficients of the divalent cations. According to Calvet and Chaussidon (1969), the ratio of the diffusion coefficients of Na and Ca in montmorillonite at room temperature is about 100.

Both potassium and lithium carbonates interacted with montmorillonite at 550°C, as is evidenced by the XRD traces in Figure 4. Both salts apparently interacted in a direction along the c-axis of the clay structure, inasmuch as the 02,11 reflection was unaffected; whereas the 001 reflection became broad after the Li treatment and expanded to 10.6 Å after the K_2CO_3 treatment. Normal K-saturated montmorillonite has a 001 reflection at 10 Å spacing at 500°C (Martin-Vivaldi et al., 1963).

°2θ, Cu Kα radiation
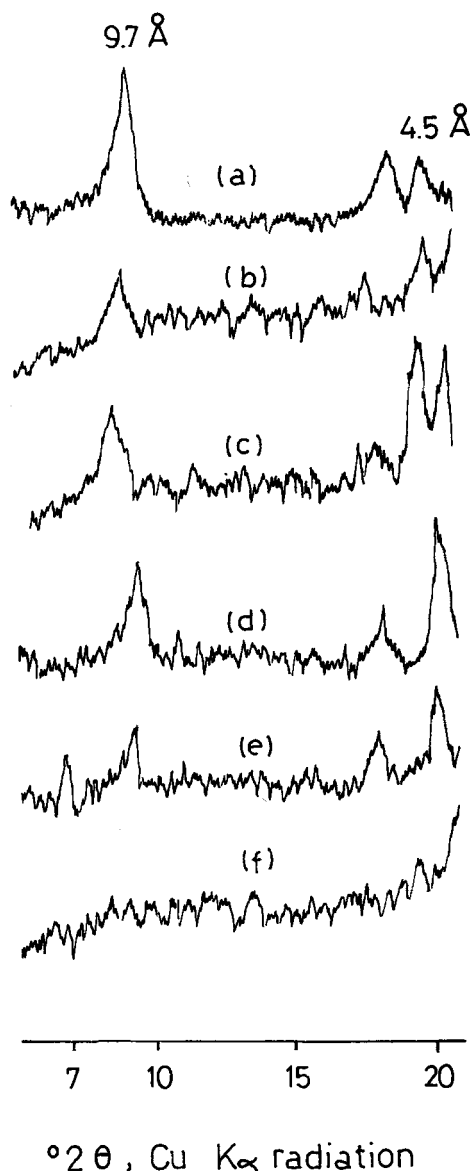
Figure 7.   X-ray powder diffraction traces of: (a) montmorillonite heated at 550°C for 2 hr; (b) 1:1 mixture of montmorillonite and illite heated at 550°C for 2 hr; (c) same as (b), but in presence of 20 wt. % Na_2CO_3; (d) illite heated at 550°C for 2 hr; (e) same as (d), but in presence of 20 wt. % Na_2CO_3; and (f) same as (d), but in presence of 50 wt. % Na_2CO_3.

Kinetics of the montmorillonite-Na_2CO_3 reaction

Models and equations used for the analysis of data of isothermal reactions of solids were compiled by Beretka and Brown (1983), and the merits of some of the equations were discussed by Brindley et al. (1967) and Hancock and Sharp (1972). According to these authors the basic equation for comparing kinetic data for solid state reactions may be written as:
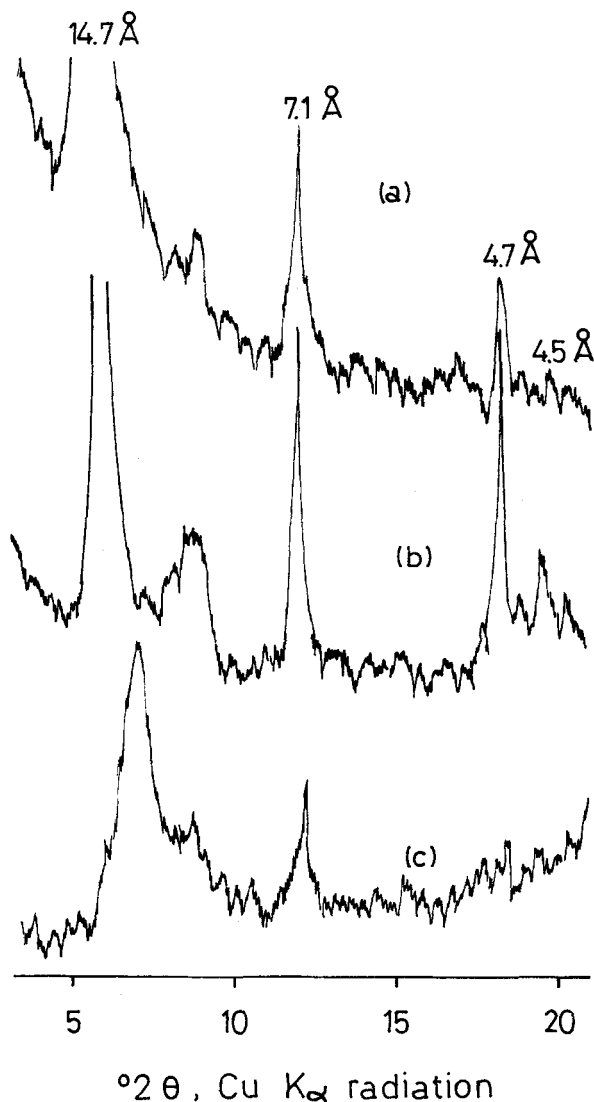
Figure 8. X-ray powder diffraction traces of: (a) chlorite heated at 550°C for 2 hr; (b) 1:1 mixture of montmorillonite and chlorite heated at 550°C for 2 hr; and (c) same as (b), but in presence of 20 wt. % Na₂CO₃.

$$-\ln \ln(1 - \alpha) = \ln B + m \ln t, \qquad (2)$$

where α is the fraction transformed and B and m are constants. The value of m varies from 0.5 to 3 and is characteristic of the mechanism that controls the transformation as diffusion controlled, first-order controlled, or phase-boundary controlled. Once the general mechanism is identified by means of the factor m, more details can be obtained by examining the fit of the data to one of the equations pertaining to the group.

The experimental data for the different treatments are plotted according to Eq. (2) in Figure 5. The values of m obtained from this figure are between 1.18 and 0.63, indicating that the dehydroxylation of mont-

morillonite and the montmorillonite-salt reaction were diffusion and/or first-order controlled (Hancock and Sharp, 1972). The best fit of the data, however, was obtained with the kinetic diffusion equation known as $D_4(\alpha)$, namely:

$$(1 - 2\alpha/3) - (1 - \alpha)^{2/3} = kt. \qquad (3)$$

Accordingly, Na⁺ diffusion started over the exterior surface of the particle and was directed toward its center, in opposite direction to H⁺ movement.

Reaction of montmorillonite and Na₂CO₃ at 550°C in presence of other clays

The montmorillonite-Na₂CO₃ reaction was investigated in 1:1 mixtures of montmorillonite and illite or chlorite. The XRD traces of the products after heating the mixtures at 550°C for 2 hr in the presence and in the absence of 20 wt. % Na₂CO₃ are shown in Figures 7 and 8, together with the traces of each untreated clay. As can be seen in Figure 7, the trace for the montmorillonite-illite-carbonate mixture is similar to that for illite alone, indicating that the carbonate interacted mainly with the montmorillonite and destroyed the structure, as evidenced by the absence of characteristic XRD peaks in the traces of the products. Increasing the proportion of Na₂CO₃ to 50 wt. % almost completely destroyed the illite structure, as evidenced by the disappearance of the 001 reflection and the reduction in the peak area of the 020 reflection (4.5 Å) (Figure 7f).

Similar results were obtained for the montmorillonite-chlorite mixture, however, the carbonate had some effect on the chlorite. The areas of the peaks corresponding to the 001 (14.4 Å), 002 (7.19 Å), and 003 (4.79 Å) reflections were slightly decreased (Figure 8).

Na₂CO₃ solid state reaction with different montmorillonite samples

The XRD traces of the three montmorillonite samples are shown in Figure 2. All the clays were heated for 2 hr at 500°C in the presence of 20 wt. % Na₂CO₃. The 001 and 02,11 reflections are absent in the traces of all three products, indicating an identical interaction of these clays with sodium carbonate.

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