

THE EXOTHERMIC REACTION OF METAKAOLINITE IN THE PRESENCE OF MINERALIZERS. INFLUENCE OF CRYSTALLINITY

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Abstract—This paper presents further results concerning the nature of the exothermic reaction of metakaolinite near 950°C. In a previous work (Lemaitre *et al.*, 1975), we proposed that the exothermic effect had a double origin: (a) direct formation of mullite, promoted by CaO and (b) formation of a segregated spinel-type phase, i.e. γ -Al₂O₃, promoted by MgO.

In this paper, we examine the influence of a further parameter on the reaction sequence, namely the crystallinity of the starting kaolinite as defined by Hinckley's index (c.i.; Hinckley, 1963). By combining X-ray and DTA techniques it is shown that the direct mullite formation path (a) occurs readily at 900°C in well-ordered kaolinite, but not in poorly ordered samples, even when fired with CaO. On the other hand, path (b) can be promoted in all samples using MgO as a mineralizer. When the indirect reaction path (b) occurs, a second exothermic effect is observed at approximately 1200°C, indicating secondary mullite formation by recombination of segregated silica and alumina phases. This effect occurs in poorly ordered kaolinites even in the presence of CaO [path (a) promotor] indicating that path (b) is the most probable reaction mechanism in very disordered kaolinites.

INTRODUCTION

The exact origin of the exothermic transformation which metakaolinite undergoes near 950°C has raised many controversial discussions in the literature. Indeed, several very different interpretations have been proposed. In a first explanation, the exothermic phenomenon is thought to be caused by a sudden recrystallization into gamma alumina, which is the first crystalline phase detected in metakaolinite fired above 900°C (Colegrave and Rigby, 1952; Richardson and Wilde, 1952; Lundin, 1958). Other workers have noted that the exothermic phenomenon persists even when kaolinite has been previously treated at 850°C, the temperature at which the characteristic X-ray lines of γ -alumina already appear. They conclude that the exothermic peak should have its origin in the nucleation of mullite (Roy *et al.*, 1955; Comeforo *et al.*, 1948). Other interpretations have been suggested. In a detailed study of the kaolinite reaction sequence, Brindley and Nakahira (1959) concluded that the exothermic phenomenon is due to a recrystallization of metakaolinite into an aluminum-silicon spinel. More recently, in a study by differential thermal calorimetry, Nicholson and Fulrath (1970) indicated the equality of the amount of heat released by the exothermic effect with the amount of heat evolved by the recrystallization of amorphous silica into high quartz.

It is known that the intensity and the position of the exothermic peak are sensitive to the presence of

chemical impurities, even when introduced in very small amounts (Prabhakaram, 1968). Furthermore, the degree of structural organization of the starting clay material also has a considerable influence on the subsequent reactivity at high temperature. In particular, the ability to develop the mullite phase (in the early stages of the reaction) depends greatly on the 'crystallinity' of the unfired kaolinite (Wahl and Grim, 1964).

In a recent paper (Lemaitre *et al.*, 1975), we attempted to correlate modifications of the exothermic peak characteristics with the nature of the various crystalline phases which develop after prolonged heating in the presence of chemical additives. Using a kaolinite of average crystallinity from Karlovy Vary, Czechoslovakia and a series of mineralizers (principally alkaline and alkaline-earth metal oxides), careful DTA measurements were made and X-ray powder diffraction diagrams were recorded for samples fired at 900°C. From this study, it was possible to classify mineralizers into three categories depending on the selectivity regarding the formation of new phases at 900°C:

- (1) mineralizers with no definite selectivity: Li₂O, Na₂O, K₂O;
- (2) mineralizers promoting the formation of a spinel type phase: MgO, ZnO;
- (3) mineralizers promoting the formation of mullite: CaO, CuO.

Groups 2 and 3 were studied in more detail by examining the influence of additive concentration on the DTA characteristics and the influence of concentration and firing time on the formation of high-temperature phases. Table 1 outlines previous results

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Table 1.* Influence of impurity content on the DTA characteristics of kaolinite 'Kolloid' (c.i. = 0.56)

| Mineralizer <i>M</i> | At. prop. <i>r</i> | Peak max. (°C) | Peak area [(°C) ² /g kaol] | Peak width (°C) |
|-------------------------|-----------------------|-------------------|--|--------------------|
| Mg | 0.0 | 970 | 676 | 13.4 |
| | 0.013 | 967 | 714 | 14.7 |
| | 0.028 | 960 | 759 | 14.9 |
| | 0.063 | 956 | 896 | 21.0 |
| Ca | 0.0 | 970 | 676 | 13.4 |
| | 0.013 | 965 | 673 | 12.9 |
| | 0.028 | 979 | 944 | 21.2 |
| | 0.063 | 981 | 1340 | 30.0 |

At. prop. $r = M/(Al + Si)$.

* Lemaitre *et al.* (1975).

(Lemaitre *et al.*, 1975), showing that the exothermic effect increases both with MgO and CaO additives. Figure 1 illustrates the effect of these additives on the transformation of kaolinite at 900°C for different firing times and concentrations. The coefficient r represents the atomic proportion of mineralizers M introduced where $r = M/(Al + Si)$. From this study, it was concluded that the exothermic effect of metakaolinite does not have a single origin. It was concluded that this effect was due both to the formation of a cubic-type phase, for instance, γ -Al₂O₃, and the nucleation of mullite. The relative amounts of each

one of these phases formed when the effect takes place, could depend on the nature of the kaolin material. By using selective mineralizers, it was possible to enhance either the formation of γ -alumina or mullite.

In the present paper, we shall examine the effect of the foregoing mineralizers on a series of kaolinites exhibiting marked differences in crystallinity as defined by the crystallinity index of Hinckley (Hinckley, 1963). DTA experiments were effected on all samples and X-ray diagrams were recorded after firing. Since high heating rates are required for DTA

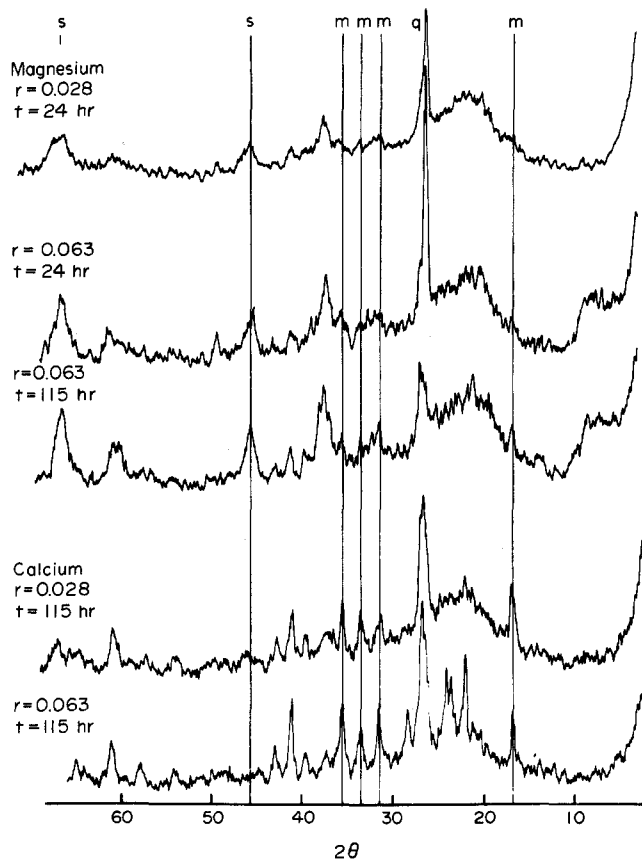


Figure 1. Influence of additive concentration and firing time (900°C) for kaolinite 'Kolloid' (c.i. = 0.56) mineralized with Ca (115 hr, $r = 0.028$ and 0.063 ; 115 hr, $r = 0.063$) s: spinel, m: mullite, q: quartz (Lemaitre *et al.*, 1975).

measurements, the resulting exothermic effect corresponds to relatively rapid reactions. Accordingly, for more selectivity in the correlative detection of phases by X-ray powder diffraction, prolonged heating (necessary for the new phases to become apparent) was conducted at a lower temperature than that corresponding to the observed DTA peak. The temperature chosen was 900°C.

EXPERIMENTAL DETAILS

Materials

Four kaolinites were selected for this study on the basis of their crystallinity. The crystallinity index (c.i.) referred to in this work is the parameter measured from an X-ray powder diffraction diagram of a non-oriented sample as described by Hinckley (1963). Two kaolinites had a very good index (c.i. ≥ 0.8), namely, the type Zettlitz from Czechoslovakia, and the type Arvor from a Bretagne deposit (France). Two other kaolinites had a poor index (c.i. ≤ 0.3), namely, the type BM1 and YBi4 from Font Bouillant, France, and Yangambi, Zaire, respectively. The Yangambi sample naturally contains 12.5% Fe₂O₃, of which 10.4% is in the free state. Accordingly, this sample was 'deferrated' to remove free iron oxides by a technique which does not affect the structure of the clay (Jackson, 1956).

The principal characteristics and crystallinity index of the samples are indicated in Table 2.

Method of introduction of mineralizers

A very efficient method of dispersing mineralizers in the kaolinite samples has been developed. The additives were incorporated in the samples by mixing the kaolinite (dried at 110°C) with analytical grade nitrates of the corresponding metals, namely, Ca(NO₃)₂·4H₂O, and Mg(NO₃)₂·6H₂O from Merck. Mixing of all samples (including pure standards) was accomplished in a clean agate planetary ball mill, rotating at 800 rev/min for 20 min. Upon heating, the nitrate precursors first melt and 'wet' the surface of the kaolinite particles. After decomposition of the nitrates, an effective dispersion of the mineralizer in oxidic form is obtained on the surface of the kaolinite particles.

Table 2. Characteristics of the kaolinite samples

| | Arvor | Zettlitz | BM1 | YBi* |
|--------------------------------|-------|----------|-------|-------|
| Al ₂ O ₃ | 39.65 | 38.50 | 35.93 | 35.56 |
| Fe ₂ O ₃ | 0.82 | 0.52 | 1.33 | 2.23 |
| MgO | 0.16 | 0.06 | 0.10 | n.d. |
| TiO ₂ | 0.07 | 0.18 | 4.38 | 1.85 |
| K ₂ O | 0.66 | 0.52 | 0.04 | 0.22 |
| Cryst. index | 1.00 | 0.85 | 0.31 | 0.02 |

* Deferrated sample.

A fixed proportion of additive *M* was used in all samples on the basis of previous results (Lemaitre *et al.*, 1975). This proportion corresponded to an atomic ratio $r = M/(Al + Si) = 0.063$.

Physico-chemical measurements

All DTA measurements were effected with a Setaram M.4 analyzer using a Pt/Pt.Rh 13% thermocouple with a Kipp BD5 (*T/ΔT*) recorder; the sensitivity corresponded to a $\Delta T'$ of 0.076° at 1000°C. The sample weight was between 15 and 20 mg. The reference sample was α -Al₂O₃ calcined 24 hr at 1100°C. The heating rate was 10°C/min. The surface area of the DTA peak was calculated by multiplying the height *h*, by the width at *h/2*. Results are expressed as °C²/g pure kaolinite. The reproducibility was better than 10%.

X-ray measurements were made by standard Debye-Scherrer techniques using Philips equipment (PW 1010 generator, PW 1050/70 Norelco goniometer) working with Cu K α , at 40 kV, 20 mA, and scanning at 1° 2 θ /min.

RESULTS

Samples of the four different kaolinites were mineralized with Ca and Mg and analyzed by DTA. The results are presented in Table 3. Typical DTA experimental curves are illustrated in Figure 2 (well-ordered kaolinites), and Figure 3 (poorly ordered kaolinites).

All samples, (mineralized and pure) were fired at 900°C for 24 and 124 hr. X-ray powder diffraction diagrams are presented in Figure 4 (pure samples), Figure 5 (samples mineralized with CaO), and Figure

Table 3. DTA results of four kaolinites mineralized with CaO and MgO additives, $r = 0.063$

| DTA data | Addit. | Arvor | Zettlitz | BM1 | YBi |
|-----------------------------|--------|-------|----------|------|------|
| Peak area | — | 581 | 721 | 975 | 870 |
| [(°C) ² /g kaol] | Mg | 678 | 1623 | 1917 | 1674 |
| | Ca | 1124 | 1582 | 2167 | 1624 |
| Peak width | — | 9.5 | 11 | 13.7 | 12.7 |
| (°C) | Mg | 15.3 | 38 | 39.5 | 38.5 |
| | Ca | 29 | 40 | 57 | 45 |
| Peak max. | — | 994 | 993 | 973 | 971 |
| (°C) | Mg | 974 | 976 | 958 | 946 |
| | Ca | 1004 | 1000 | 972 | 971 |

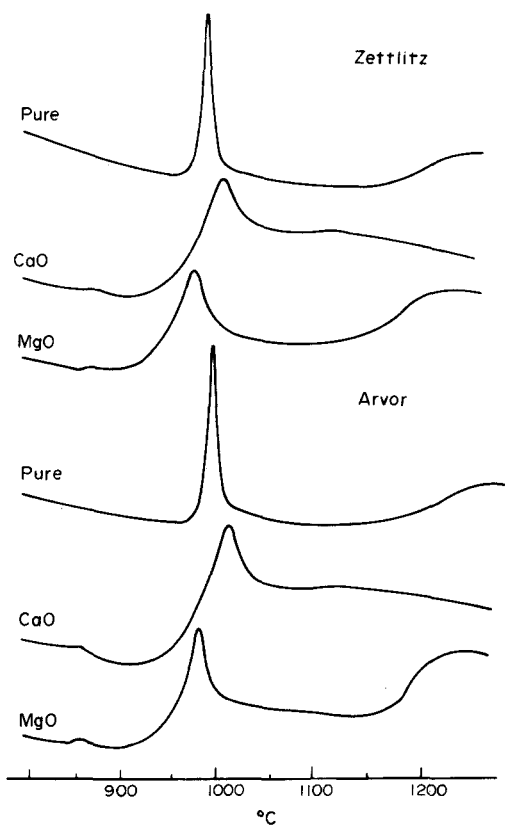


Figure 2. DTA curves of well-ordered kaolinites Arvor and Zettlitz, mineralized with Ca and Mg ($r = 0.063$).

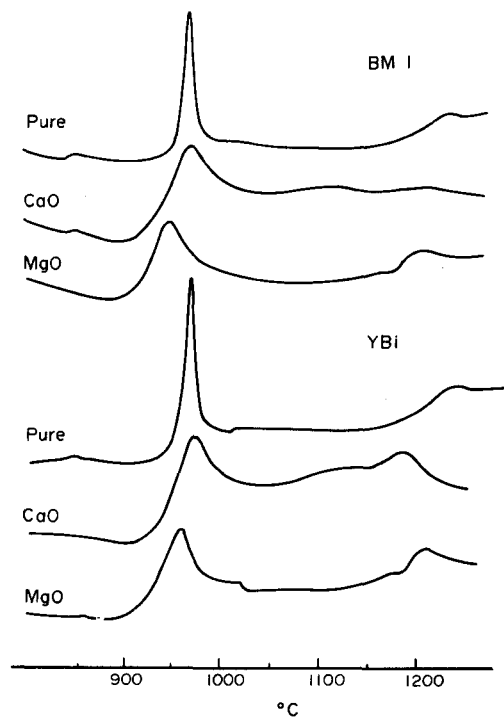


Figure 3. DTA curves of poorly ordered kaolinites BM I and YBi mineralized with Ca and Mg ($r = 0.063$).

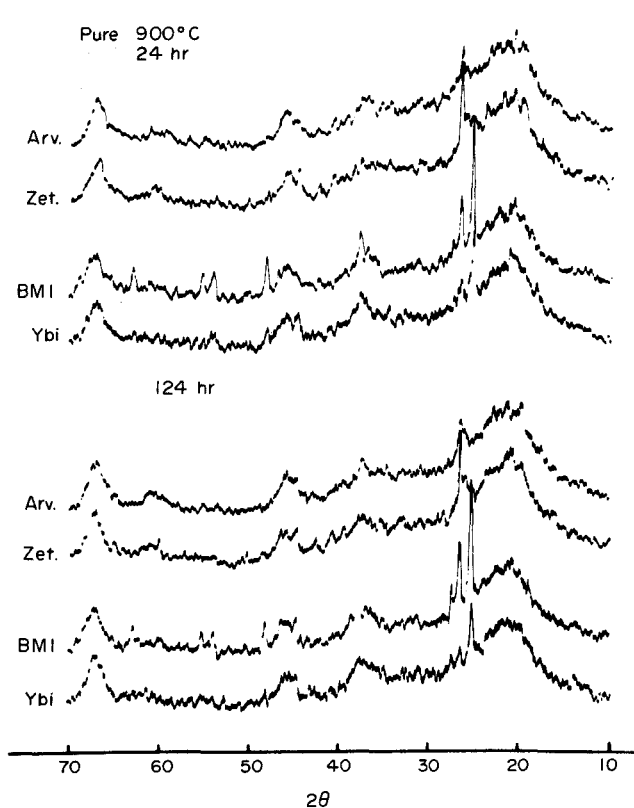


Figure 4. X-ray powder diffraction diagrams of pure kaolinite samples of different crystallinity fired for 24 and 124 hr (900°C).

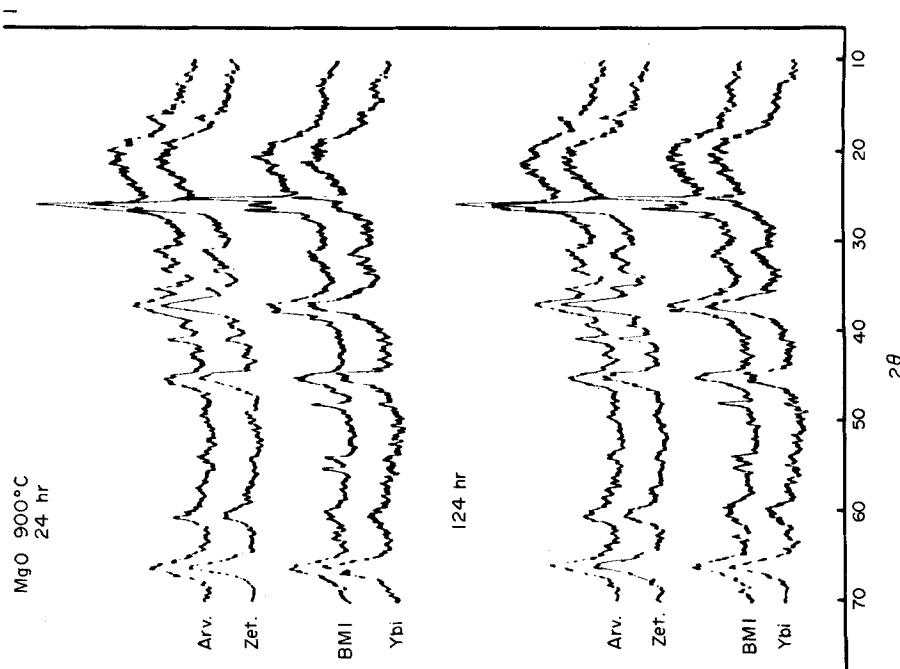


Figure 6. X-ray powder diffraction diagrams of kaolinite samples of different crystallinity, mineralized with MgO ($r = 0.063$), fired for 24 and 124 hr (900°C).

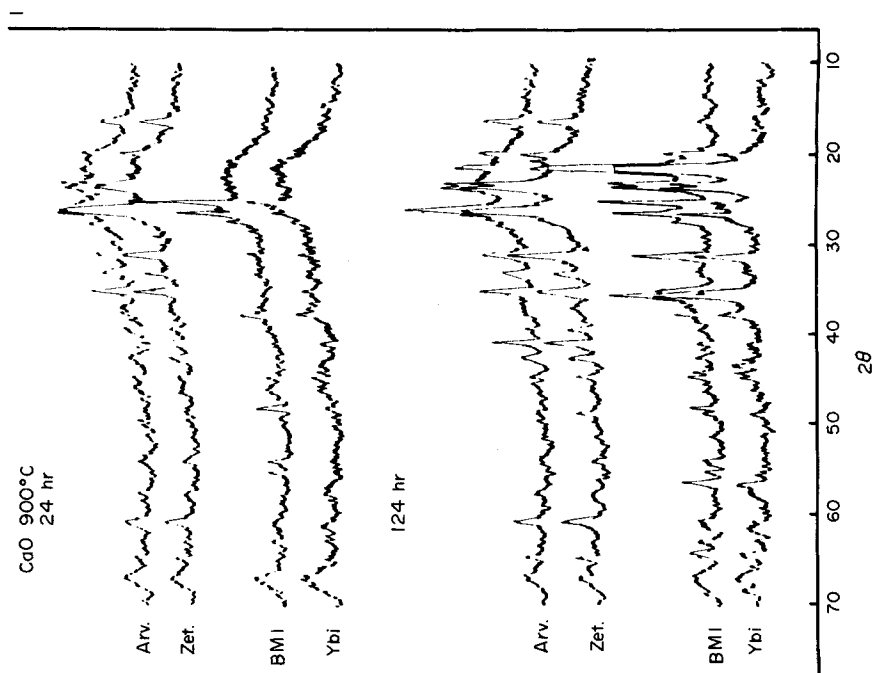


Figure 5. X-ray powder diffraction diagrams of kaolinite samples of different crystallinity, mineralized with CaO ($r = 0.063$), fired for 24 and 124 hr (900°C).

6 (samples mineralized with MgO). Pure samples exhibit three broad reflections characteristic of a cubic type phase. Quartz is detected in Arvor and Zettlitz ($d = 3.34 \text{ \AA}$), and TiO_2 (anatase) is visible in BM1 and YBi samples ($d = 3.51 \text{ \AA}$). MgO mineralized samples present essentially the same pattern but the spinel reflections are more sharply defined (Figure 6). CaO mineralized samples present mullite reflections especially in Arvor and Zettlitz near ($d = 3.38, 2.88, 2.69, 2.54, 2.41 \text{ \AA}$). BM1 and YBi samples exhibit very intense reflections of cristobalite after heating for 124 hr ($d = 4.11 \text{ \AA}$).

DISCUSSION

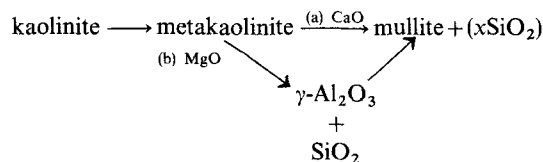
A comparison of the X-ray powder diffraction patterns indicates that the degree of crystallinity of the kaolinite material is a determining factor which influences the formation of new phases in the 900°C region. When using CaO as a mineralizer (which is known to promote mullite), one observes that well-crystallized kaolinites (Arvor and Zettlitz) fired 24 hr at 900°C exhibit distinct mullite reflections and also quartz. After prolonged firing, the mullite reflections increase in intensity. This observation agrees with previous results (Lemaitre *et al.*, 1975) on a kaolinite of medium crystallinity (c.i. = 0.56). On the other hand, poorly ordered kaolinites (BM1 and YBi) have a very different behavior when fired in the presence of CaO (Figure 5). In this case, no mullite is formed even after firing for 124 hr; but one observes the formation of a TiO_2 peak which increases with time, and a very intense reflection of cristobalite after prolonged heating.

With MgO as a mineralizer (Figure 6), the behavior of all of the kaolinites (poorly and well-ordered) does not exhibit such striking differences. In both cases, very intense reflections of a cubic-type phase are observed. A small amount of mullite is formed in well-ordered kaolinites. When the samples are pure (no mineralizer), the X-ray diagrams are similar to the ones with MgO, but the peaks are less developed.

The results of the differential thermal analysis show that, both with CaO and MgO, the amount of heat liberated during the exothermic effect increases considerably in all samples studied (Table 3). The exothermic effect also broadens over a wider temperature range. However, in the case of well-ordered samples, one observes that MgO decreases the exothermic temperature maximum by about 20°C , whereas CaO increases this temperature by approximately 10°C . In the poorly ordered samples, one observes that only MgO lowers the temperature, whereas CaO has no effect.

These observations show that, in the case of well-crystallized kaolinites at least, the two-path reaction hypothesis proposed earlier (Lemaitre *et al.*, 1975), a hypothesis which rests on the factual possibility of directing the reaction either way, is valid. The thermal transformation of metakaolinite into mullite can

occur according to the following scheme:



Path (a) can be enhanced by a mullite promoter, e.g. CaO; path (b) occurs in the presence of a spinel promoter, e.g. MgO. In the case of poorly crystallized kaolinites, path (a) is diminished, if not completely impeded at 900°C . CaO evidently does not have the same effect as in well-ordered samples, since it does not affect the maximum temperature of the exothermic peak. A number of recrystallizations do occur, however, but these are not of a reconstructive nature. One observes, for example, after prolonged heating, intense reflections of anatase (TiO_2), and cristobalite (SiO_2).

The sharp exothermic reaction accompanying the structural breakdown of the metakaolinite structure is usually thought to be accompanied by a shift in bonding from face-sharing octahedral units present in kaolinite to more stable edge-sharing units which normally exist in high-temperature structures such as mullite. This transformation occurs more readily in well-ordered kaolinites. In poorly ordered samples, by firing at 900°C , segregation of alumina and silica is greater than in the former, to such an extent that a 'direct' mullite construction reaction (promoted by CaO) cannot be attained. Only separated crystallizations of segregated phases occur, e.g. SiO_2 to cristobalite.

It should be noted that DTA results for pure samples and MgO samples exhibit a second very diffuse exothermic reaction in the $1100\text{--}1200^\circ\text{C}$ region (Figures 2 and 3). This effect could possibly be attributed to a recombination reaction of segregated phases e.g. $\gamma\text{-Al}_2\text{O}_3$ and SiO_2 to form what other authors have called 'secondary mullite' (Wahl and Grim, 1964). Note that this effect does not occur with well-crystallized samples mineralized with CaO, suggesting that path (a) is very much predominant and leaves little if no phases to recombine at higher temperature. However, in very poorly crystallized kaolinites, such as YBi (c.i. = 0.02), this effect is observed even with CaO, suggesting that path (b) is the most probable reaction mechanism in very disordered kaolinites.

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