ON THE QUESTION OF THE EXISTENCE OF METAKAOLINITE AND THE NATURE OF THE EXOTHERMIC EFFECTS OF ALUMINA

![Fig. 1](figure)

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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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ON THE QUESTION OF THE EXISTENCE OF METAKAOLINITE AND THE NATURE OF THE EXOTHERMIC EFFECTS OF ALUMINA

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As is known (⌢1), kaolin in the uncalcined state exists in the form of crystals $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$. On heating, dehydration occurs, accompanied by an endothermic effect in the temperature range 450–600°, with kaolin passing into the amorphous state. A number of investigators (2,3) believe that in this process kaolin decomposes into free oxides of aluminum and silicon; others (4,5) believe that dehydration produces an amorphous compound (metakaolinite). The first exothermic effect (970°) is likewise explained in different ways: by crystallization of amorphous alumina into the γ-modification (⌢6); by decomposition of metakaolinite into free alumina and silica with subsequent crystallization of γ-Al_2O_3 (⌢4); by formation of mullite $3Al_2O_3 \cdot 2SiO_2$ (⌢7) or, finally, by formation of sillimanite $Al_2O_3 \cdot SiO_2$ (⌢8).

Fig. 1

Attempts to shed light on these contradictory data by investigating the behavior of alumina on heating to 950–1050° have likewise not been successful (5,7), which is apparently explained by the dependence of this behavior on the nature of the initial specimens and on the experimental conditions (⌢9). In general, the number of alumina modifications discovered ranges from four ($\alpha, \beta, \gamma, \varphi$) (⌢10) to ten ($\alpha, \chi, \eta, \delta, \theta, \kappa$, and 4 modifications of γ) (11,12).

The aim of the present work was to elucidate, by means of thermographic and X-ray investigations, the nature of the thermal effects of alumina and to obtain additional experimental material for resolving the question of the existence of metakaolinite as a definite chemical compound. For this purpose alumina obtained from hydrargillite and from the nitric-acid and sulfuric-acid salts of aluminum was studied. Investigation of hydrargillite $Al(OH)_3$ (or $Al_2O_3 \cdot 3H_2O$), which has structural elements in common with kaolin (layers composed of alumino-oxygen and alumohydroxyl-oxygen octahedra) (⌢13), was

Fig. 2

Figure 2: Fig. 2

of additional interest.

The X-ray investigation was carried out both on an ionization apparatus with a proportional amplifier and a high-temperature (up to 1400°) heater (CuK$_\alpha$ radiation, nickel filter), and using Debye chambers 65.1 mm in diameter (CoK$_\alpha$ radiation, monochromatized by reflection from a calcite crystal).

Figure 1 gives the heating curves of two specimens of hydrargillite, white and pink (the latter contained 0.014% Fe_2O_3)* . In addition to the three previously known endothermic effects ($\frown$14), two exothermic effects were found on the curves—thermal effects: in the region of 940-1050° (maximum 970°) for both samples, in the region of 1060-1150° (maximum 1100°) for the pink sample, and in the region of 1180-1280° (maximum 1230°) for the white sample.

Figure 2 shows X-ray ionization curves obtained at the temperatures indicated on the right. At 200° (the temperature region of the first endothermic effect, in which partial removal of water occurs (^{14}): $Al_2O_3 \cdot 3H_2O \rightarrow Al_2O_3 \cdot 2.5H_2O + 0.5H_2O$), the appearance of lines of a new phase is noticeable (the nature of which remained unexplained, and whose lines are marked with crosses), as well as weakening and somewhat broadening of the lines of hydrargillite, indicating partial destruction of its lattice. At 300° (the region of the second endothermic effect, where further removal of water occurs: $Al_2O_3 \cdot 2.5H_2O \rightarrow Al_2O_3 \cdot H_2O + 1.5H_2O$), the structure of hydrargillite is completely destroyed and the monohydrate $Al_2O_3 \cdot H_2O$ —boehmite—is formed, as well as amorphous alumina, the existence of a small amount of which may be judged from the broadening of the maxima in the region of angles 31-35°*. The latter is confirmed by the curve obtained at 500° (the third endothermic effect), when the lines of boehmite and of the unknown phase completely disappear and the entire sample passes into an amorphous or highly dispersed state (two very broad maxima, the position of the second of them being very close to the position of the brightest line (440) of the low-temperature modification of alumina). The formation of the fine-crystalline cubic (spinel-structure, defect type) γ-low-temperature modification of alumina (γ_H) occurs at a temperature of 600°, corresponding to the rise on the heating curves of hydrargillite (Fig. 1). The γ_H modification of alumina is stable in the temperature range 600-950°. At the temperature of the first exothermic effect (maximum 1000°), formation of the χ-modification of alumina occurs; it is stable

Fig. 2

* The chemical analysis was performed in the analytical laboratory of the Institute of Silicate Chemistry, Academy of Sciences of the USSR.

Fig. 3

Figure 3: Fig. 3

over a small temperature interval; at the temperature of the second exothermic effect the χ-modification transforms into the α-modification (corundum). The onset of its transformation into corundum depends on the presence of impurities in the samples: in the pink

* The most intense platinum lines are superimposed on some maxima (the sample during recording was in a platinum holder), which is denoted by the symbol +Pt.

in a sample of hydrargillite containing 0.014% Fe_2O_3, crystallization of corundum begins at 1050°, while in a white sample it begins only at 1200°.

The scheme of the thermal transformations of hydrargillite may be represented as follows:

$$\mathrm{Al(OH)_3}\ \text{hydrargillite} \xrightarrow{190^\circ} \left\{\begin{matrix}\text{Hydrargillite, } x\text{-phase}\\ 200^\circ\end{matrix}\right\} \xrightarrow{260^\circ} \left\{\begin{matrix}\text{Boehmite,}\\ x\text{-phase,}\\ \text{alumina}\\ \text{amorphous}\\ 375^\circ\end{matrix}\right\} \xrightarrow{435^\circ} \left\{\begin{matrix}\text{Amorphous}\\ \text{or finely}\\ \text{dispersed}\\ \text{alumina}\\ 500^\circ\end{matrix}\right\} \xrightarrow{600^\circ}$$

$$\xrightarrow{600^\circ} \underset{600\text{–}950^\circ}{\gamma_{\mathrm{H}} - \mathrm{Al_2O_3}} \xrightarrow{950^\circ} \underset{1000^\circ}{\chi - \mathrm{Al_2O_3}} \xrightarrow{1050\text{–}1200^\circ} \underset{1100\text{–}1230^\circ}{\alpha - \mathrm{Al_2O_3}}$$

A different course of thermal transformations was observed in alumina obtained from nitrate and sulfate salts of aluminum (Fig. 3). On the heating curve of $Al(NO_3)_3 \cdot 9H_2O$ there are three endothermic effects (two weak ones with maxima at 180 and 250°, and a third large one with a maximum at 380°) and two exothermic effects (a clearly expressed one with a maximum at 850° and a strongly broadened one with a maximum at 1050°). On the heating curve of $Al_2(SO_4)_3 \cdot 18H_2O$ there are only endothermic effects with maxima at 100, 350, and 900°. Exothermic effects up to a temperature of 1100° were not observed.

Fig. 3

The first two endothermic effects on the curves of both samples are caused by the removal of adsorbed and crystallization water.

At a temperature of 380° (heating curve of $Al(NO_3)_3 \cdot 9H_2O$), decomposition of $Al(NO_3)_3$ occurs, accompanied by amorphization of the substance (as evidenced by two broadened maxima on ionization curves obtained at temperatures of 600–800° (Fig. 4, *a*)). The maximum at 850° (exothermic) corresponds to crystallization of amorphous (or highly dispersed) alumina into the γ_H-modification

Fig. 4

Figure 4: Fig. 4

of alumina (Fig. 4, *b*). This fact refutes the view that crystallization of the γ_{H}-modification of alumina must be accompanied by absorption of energy [15].

γ_{H}-alumina, obtained from aluminum nitrate salt, remains stable up to the beginning of crystallization of corundum at the temperature of the second exothermic effect, 1050°.

The scheme of the thermal transformations of alumina obtained from aluminum nitrate salt should be represented as follows:

$$\mathrm{Al(NO_3)_3} \xrightarrow{380^\circ} \left\{ \begin{array}{c} \text{Alumina} \\ \text{amorphous or} \\ \text{highly dispersed} \end{array} \right\} \xrightarrow{825^\circ} \gamma_{\mathrm{H}} - \mathrm{Al_2O_3} \xrightarrow{1000^\circ} \alpha - \mathrm{Al_2O_3}$$

850° 1050°

Decomposition of aluminum sulfate salt occurs at temperatures lying considerably above the stability region of amorphous alumina. Therefore, simultaneously with decomposition (900°), crystallization of γ_{H}-alumina is observed (Fig. 4, *c*). The transition into α-alumina begins at a temperature of 1200° (Fig. 4, *d*), i.e., considerably higher than in the case of alumina obtained from $\mathrm{Al(NO_3)_3}$. The scheme of the thermal transformations of alumina obtained from aluminum sulfate salt has the form

$$\mathrm{Al_2(SO_4)_3} \xrightarrow{900^\circ} \gamma_{\mathrm{H}} - \mathrm{Al_2O_3} \xrightarrow{1200^\circ} \alpha - \mathrm{Al_2O_3}$$

Thus, a clearly pronounced exothermic effect at 950-1050° is found only in alumina obtained from hydrargillite. However, the energy release in this case is due to crystallization of the χ-modification, whereas in kaolin, in this temperature region, the formation of γ -alumina is observed ([3],[6]).

As shown above, crystallization of γ -alumina occurs either after dehydration of hydrargillite and decomposition of the nitrate salt, accompanied by amorphization of the substance, or simultaneously with decomposition,

Fig. 4

as was observed for the sulfate salt, but in all cases at a temperature considerably lower than that of the first exothermic effect of kaolin. The absence of crystallization of alumina into the γ -modification in kaolin after dehydration (400-600°) indicates the presence of a close bond between the oxides, since free alumina would have had to crystallize into the γ -modification at temperatures of 600–850°. X-ray diffraction patterns of Prosyanovka kaolin (not purified by elutriation), obtained by us in the temperature range 600–1400°, showed that, along with mullitization, the principal process responsible for the first exothermic effect of kaolin (970°) is the formation of γ -alumina, whose crystallization can occur only after destruction of the (possibly partial) complex $Al_2O_3 \cdot 2SiO_2$.

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