

THE DEHYDROXYLATION OF ALUMINIUM HYDROXIDES AND THE KINETICS OF α -Al₂O₃ FORMATION

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Studies were made of the dehydroxylation of several aluminium hydroxide modifications and the kinetics of α -Al₂O₃ formation. The investigated samples differed in both mineral composition and the level of alkali admixtures. It was found that the rate of formation and the quantity of α -Al₂O₃ depend mainly on the purity of the aluminium hydroxides, while the transition forms of alumina depend on the initial type of the aluminium hydroxide.

Alumina is currently a valuable construction material in the various branches of industry. Its wide-ranging applications demand that alumina fulfils very high requirements as concerns chemical purity, hardness, crystallographic structure, degree of comminution and many other physicochemical features.

Alumina is chiefly obtained by the dehydroxylation of aluminium hydroxides. The final aim is most often the manufacture of the most stable form of Al₂O₃ i.e. α -Al₂O₃, corundum. Corundum has excellent properties, such as high hardness, thermal resistance and high melting temperature. The final physicochemical properties of the produced ceramic material and the economy of the technological process of its manufacture depend on the rate of formation and the quantity of α -Al₂O₃.

The dehydroxylation of aluminium hydroxides is a very complicated process. Numerous research works [1-9], have demonstrated this, though the conclusions are sometimes discrepant. The transformations of the structure of aluminium hydroxides during heating up to the formation of new crystalline products depend on many factors, such as the type and origin of the aluminium hydroxide, grain size, chemical purity, heating rate, calcination time, atmosphere, mineralizer additives and others. Irrespective of these factors, greater or smaller amounts of α -Al₂O₃ are always obtained if the calcination temperature is adequately high. The proposed schemes of dehydroxylation differ because of the various methods of manufacturing of

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aluminium hydroxide, i.e. carbonization or chemical precipitation of $\text{Al}(\text{OH})_3$ from an aqueous solution of an aluminium salt with a base. The different and controversial conclusions can be explained on this basis. A detailed study of this process and the recognition of the formation of transition stages would give the chance to produce new kinds of alumina with valuable properties, such as the capability of gas absorption, higher reactivity, etc. It has been suggested [10] that the transition forms of alumina should be considered not as polymorphic modifications of alumina, but as nonstable stages between the unordered network structure of dehydrated $\text{Al}(\text{OH})_3$ and the ordered network structure of corundum. A recent study [11] reports the following, simplified and obligatory scheme of dehydroxylation of $\text{Al}(\text{OH})_3$:

200-400°C		500-600°C		900-1000°C		1100-1200°C
hydrargillite	→	χ	→	κ	→	α
bayerite	→	ϵ	→	θ	→	α
boehmite	→	γ	→	δ	→	α

Experimental procedure

The aim was to investigate the process of dehydroxylation of various modifications of $\text{Al}(\text{OH})_3$ and to describe the rate of $\alpha\text{-Al}_2\text{O}_3$ formation in terms of the calcination temperature. Samples of $\text{Al}(\text{OH})_3$ obtained in the treatment of aqueous sodium aluminate solution with CO_2 were used. Data on the samples are given in Table 1.

Table 1 Physicochemical properties of investigated samples of $\text{Al}(\text{OH})_3$

Chemical analysis, %	A	B	C	D
$\text{K}_2\text{O}, \text{Na}_2\text{O}$	0.494	0.360	0.052	0.180
$\text{CaO}, \text{Fe}_2\text{O}_3, \text{SiO}_2$	0.180	0.033	0.097	0.120
Al_2O_3	99.326	99.607	99.851	99.700
Mineral composition, %				
Hydrargillite	95	58	7	
Bayerite	5	42	93	
Boehmite				100
Density, g/cm^3	3.26	3.48	3.88	

Chemical analysis, differential thermal analysis with a G-24 Setaram thermoanalyzer, X-ray diffraction studies with a Philips diffractometer and

a SEM technique and other examinations were performed. Qualitative-quantitative examinations of the formation of transition forms of alumina and α - Al_2O_3 were carried out using samples A, B, C and D initially calcined at 650° . After cooling to 20° , samples were introduced into the furnace at $1000, 1100, 1200, 1300, 1400$ and 1450° and were heated at a given temperature for 1 hour. Next, these samples were rapidly cooled and then prepared for further examinations.

The differential thermal analyses (DTA, DTG, TG and T) were carried out with the following parameters:

heating rate – 10 deg/min, atmosphere – argon, reference material – α - Al_2O_3 , crucible – Pt.

Results and discussion

The DTA curves (Fig. 1) clearly exhibit the differences between hydrargillite and bayerite as concerns the number of peaks and the range of

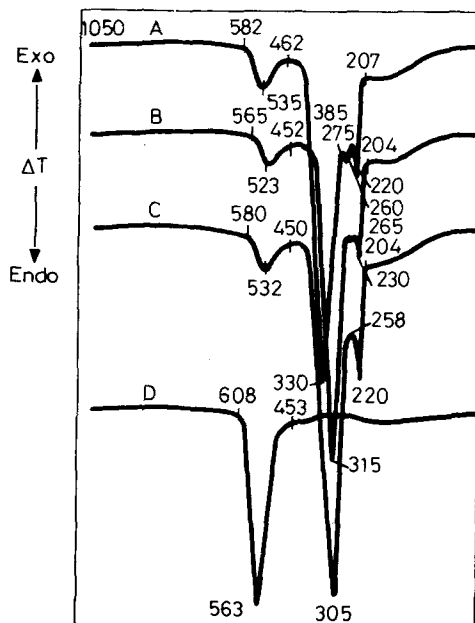


Fig. 1 DTA curves of investigated samples A, B, C and D

temperature of occurrence. The dehydroxylation of hydrargillite at 205-270° proceeds in two steps, and that of pure bayerite in one step. The dehydroxylation of a mixture of hydrargillite and bayerite has an intermediate character. For the samples A, B and C, the DTA curves show the chief endothermic peak between 260 and 460°. The last peak is to be seen between 460 and 580°, which is related with the dehydroxylation of the boehmite phase. The fourth DTA curves (sample D) for boehmite shows one chief endothermic peak between 450 and 610°.

Thus, the DTA analysis results gave the essential information that there is no Al(OH)₃ at higher temperatures than 610°. The transition forms of alumina begin to occur above that temperature. X-ray diffraction analysis (Tables 2 and 3) shows the occurrence of various transition forms of alumina, while α -Al₂O₃ appears by 1100°. Sample A with the highest content of harmful alkali additives exhibits the following transition forms of alumina: γ , K, and near α -Al₂O₃, β -Al₂O₃ also occurs, starting from 1200°. Sample B contains the θ and K phases, but α and β -Al₂O₃ also exist, starting from 1300°. Samples A and B have high alkali contents, i.e. from 0.5 to 0.35%.

Table 2 Transition forms of alumina in the investigated samples

T, °C	A	B	C	D
1000	γ , K, θ	θ , K	θ , η	θ
1100	K, θ , α	θ , α , K	α , θ	α , θ
1200	α , θ , β	α , β	α	α
1300	α , β	α , β	α	α
1400	α , β	α , β	α	α
1450	α , β	α , β	α	α

$\beta = \text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$

Table 3 Contents of α -Al₂O₃ in the investigated samples, %

	Calcination temperature, °C				
	1100	1200	1300	1400	1450
Sample A	8	51	63	65	66
Sample B	12	66	88	94	95
Sample C	66	86	92	95	99
Sample D	34	84	91	98	98

Thus, at the expense of α -Al₂O₃, a large amount of β -Al₂O₃ is formed in these samples. The θ and η transition forms of alumina and (starting from 1100°) α -Al₂O₃ are observed in sample C, which contains the smallest amounts of alkalis (0.052%). The θ and δ phases of alumina occur in sample

D, which contains 0.18% of alkalis, but α -Al₂O₃ is also seen, starting from 1100°.

The largest differences in the kinetic process of α -Al₂O₃ formation were observed between samples A and C. At 1100° only 8% of α -Al₂O₃ occurs for sample A, containing most alkali whereas 66% of α -Al₂O₃ was found for sample C containing the smallest amount of alkalis. The process of α -Al₂O₃ formation runs most dynamically between 1100 and 1350°, as is seen in Table 3.

Conclusions

1. The rate and quantity of α -Al₂O₃ formation depend not so much on the initial crystallographic form of Al(OH)₃, as on the content of harmful additives of alkalis.

2. The most dynamic process of α -Al₂O₃ formation occurs between 1100 and 1350°.

3. The process of α -Al₂O₃ formation begins below 1100°, rapidly for the samples with the smallest contents of alkali (samples C and D).

4. The nature and the range of formation of the transition forms of alumina depend on the initial type of Al(OH)₃.

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Zusammenfassung — Es wurde die Dehydroxylierung verschiedener Aluminiumhydroxid-modifizierungen sowie die kinetische Untersuchung der Bildung von α -Al₂O₃ durchgeführt. Die untersuchten Proben unterschieden sich sowohl in ihrer Mineralienzusammensetzung als auch im Grad der Verschmutzung mit Alkalien. Man stellte fest, daß sowohl Geschwindigkeit als auch Menge von α -Al₂O₃ hauptsächlich von der Reinheit des Aluminiumhydroxides abhängen und daß die Übergangsformen von Aluminiumoxid von ihrem ursprünglichen Typ von Aluminiumhydroxid abhängen.