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INVESTIGATION OF THERMAL TRANSFORMATIONS IN ALUMINIUM HYDROXIDES SUBJECTED TO MECHANICAL TREATMENT

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Abstract

The influence of the mechanical activation of hydrargillite $Al(OH)_3$ on the mechanism of its thermal dehydration and crystallization in response to treatment with steam was studied. The effects of grinding on the texture, structure and thermal behavior were examined by means of XRD, DTA, TG, DSC, IR spectroscopy and SEM. The mechanical activation of hydrargillite leads to formation of the amorphous state, and also results in a change in the thermal dehydration mechanism in the dynamic mode in the air, with a decrease in the ΔH value of dehydration. The transition of hydrargillite into corundum on treatment with steam is facilitated after mechanical activation. The activated state of hydrargillite was found to be unstable and its reactivity decreases as time elapses.

Keywords: aluminium hydroxides, thermal transformations

Introduction

Mechanical treatment, which leads to an increase of redundant energy, can be regarded as an unconventional form of influence upon the reactivity of solids. Redundant energy results in decreased potential barriers to phase transitions, decomposition processes, with other substances and in changed physical properties such as density, porosity and concentrations of various defects [1–3]. One of the most important manifestations of mechanical activation is the change in intermediate stage sequence in processes where activated substances are involved.

In the present work, a study was made of the influence of the mechanical activation of hydrargillite $Al(OH)_3$ on the mechanism and thermochemical parameters of its dehydration and crystallization during heating in air in the dynamic mode and during treatment with steam, which yields α-Al_2O_3.

Experimental

The industrial hydrargillite used in this work was prepared from bauxite by Bayer's process. It contained 34.6% of water and had a specific surface area of $0.2\ m^2\ g^{-1}$; the particle size was measured to be 20–80 μm.

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Mechanical treatment of the initial hydrargillite was performed in a vibration ball mill. The effects of treatment on the sample structure during different times of grinding were estimated by measurements of particle size, intensities of X-ray diffraction peaks, zones of Bragg scattering (D) and IR spectra. Powder X-ray diffraction patterns were obtained with a DRON-3M diffractometer, using Ni-filtered CuK$_\alpha$ radiation.

Hydrargillite dehydration was investigated by means of thermal analysis with Q-1500D derivatograph in the temperature range 20–1000°C at a heating rate of 5 K min^{-1} in platinum crucibles in air. At the same time, thermal effects of hydrargillite dehydration were measured with a DCM-2M differential scanning microcalorimeter at a scanning rate of 8 K min^{-1}. IR spectra were obtained with a Specord 75 IR spectrometer in the range 400–4000 cm^{-1}. Samples were prepared by mixing with KBr (3 wt.% sample).

The structural morphological features of the crystalline modifications were studied by using a BS-301 scanning electron microscope.

Structural transformation studies of the activated hydrargillite during heating in steam were carried out in a stainless steel autoclave (internal volume 18 cm^3) at 260 atm and 400°C. The compositions of the products were determined by X-ray phase analysis.

Results and discussion

Mechanical activation of hydrargillite

Mechanical treatment of hydrargillite leads to its destruction with formation of a completely amorphous phase. Figure 1 shows the changes in the basic characteristic features of hydrargillite as a function of the grinding time. Even after a short duration of treatment (10 min), breaches in the hydrargillite structure lead to a decrease in the /002/ X-ray diffraction peak intensity and in the value of the Bragg scattering zones (D_{nm}). Loss of the fine structure of the IR spectra in the range of Al–O stretching vibrations at 700–800 cm^{-1} and in the region of O–H stretching vibrations at 3300–3700 cm^{-1} occurs [4, 5]; 1640 cm^{-1} band corresponding to the bending vibrations of molecular water appears. The formation of molecular water is controlled by the dehydration that accompanies formation of the amorphous phase during the mechanical treatment of hydrargillite [4]. The band at 2000 cm^{-1} corresponds to two O–H stretching vibrations [6]. The more considerable changes in the nature of the bonding in hydrargillite after further mechanical activation lead to effects in all regions of the IR spectrum. The shift in the bending vibration bands of the water molecules to the low frequency range, down to 1620 cm^{-1}, indicates a change in the bonding the water formed with the framework (Fig. 2).

In the range of grinding times from 30 to 60 min, there is an abrupt decrease in the /002/ peak intensity in the X-ray diffraction pattern and also a decrease in the Bragg scattering zones (D_{nm}), which indicate a considerable destruction of the lattice. Microdistortions of the crystal lattice $<\varepsilon>^{1/2}$ increase from

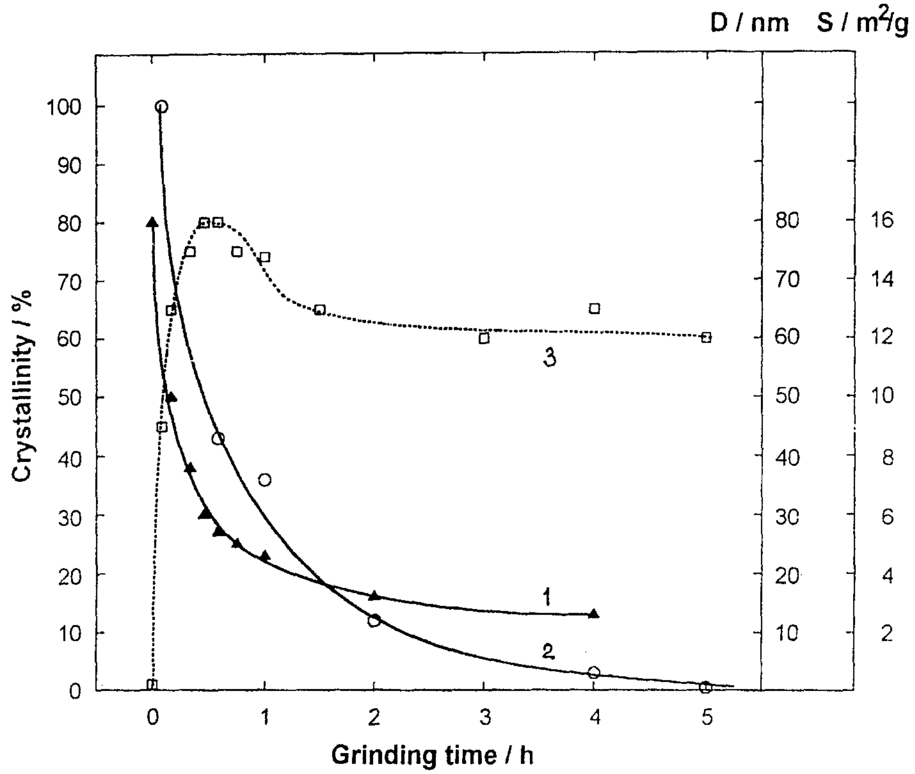

Fig. 1 Variations of the Bragg scattering zones D_{nm} (1), crystallinity (2) and specific surface area S (3) with grinding time

1×10^{-3} to 5×10^{-3} after 1 h of mechanical treatment. By this time, formation of the amorphous state reaches 80% (Fig. 1), i.e. only fragments of its initial structure remains.

The data obtained by electron microscopy revealed that initial hydrargillite consisted of aggregates 20–80 μm in size, formed from prismatic crystals with a size of 5–20 μm. After a short duration of grinding (less than 10 min), the initial aggregates crack, this process resulting in the formation of cracks and cavities with no change in granule size. Increase of the mechanical treatment time to 10 min leads to destruction of the granules and results in the formation of separate crystals 2–10 μm in size. Treatment for 20 min yield particles 0.5–0.7 μm in size, which do not change on longer grinding.

Thermal decomposition of hydrargillite

The influence of mechanical activation on the thermal transformation was investigated by means of thermal analysis with simultaneous investigation of the phases formed by X-ray phase analysis.

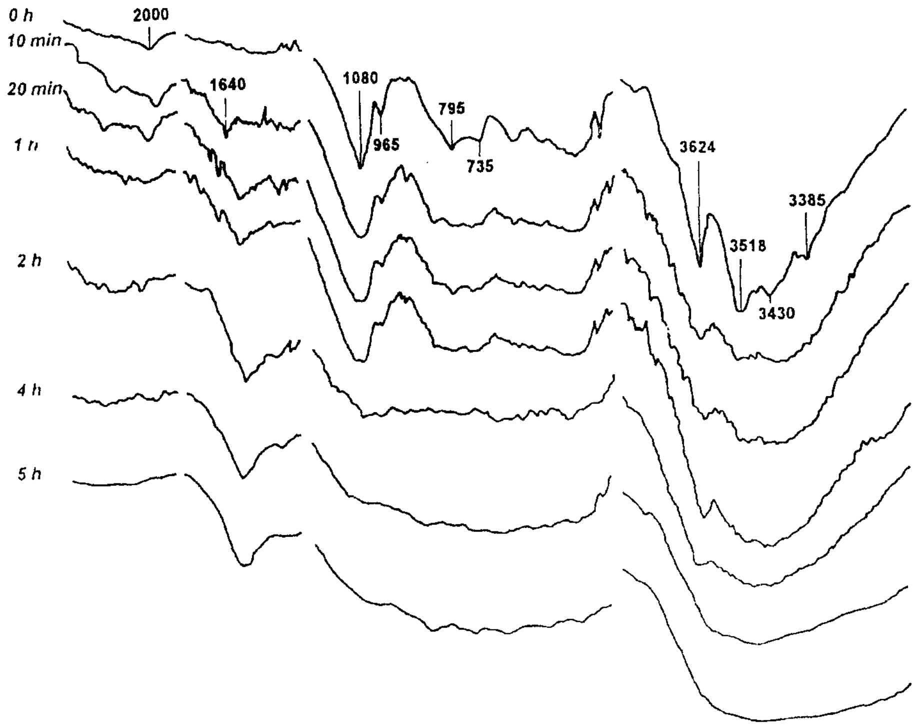

Fig. 2 Variation of IR spectra of hydrargillite in dependence on the grinding time

Table 1 lists the phase contents of the products of thermal decomposition of the initial and ground (for from 10 min to 5 h) hydrargillite heated to the indicated temperatures. It can be seen from Fig. 1 that after treatment for 5 h, complete destruction of the hydrargillite lattice has occurred. This sample retains its

Table 1 X-ray diffraction results of alumina phases obtained by the calcination of hydrargillite ground for various lengths of time

Grinding	Calcination temperature/°C					
time	20–200	200–250	250–500	500–800	800–900	900–1000
0 h	H	H+Bo	Bo+ρ_χ	ρ_γ+ρ_χ	ρ_γ	ρ_α
10 min	H*	H*+Bo^a	ρ_χ+Bo^a	ρ_χ	ρ_χ	ρ_χ
20 min	H*	H*+Bo^a	ρ_χ+Bo^a	ρ_χ	ρ_χ	ρ_χ
1 h	H*	ρ_χ	ρ	ρ	ρ	α+ρ
2 h	H*	ρ	ρ	ρ	ρ	α+ρ
4 h	amor.+(H*)^a	amor.	amor.	amor.	ρ_η	α+ρ_η
5 h	amor.	amor.	amor.	amor.	ρ_η	α+ρ_η

^{a}: Trace, H: hydrargillite, H*: mechanical activated hydrargillite, Bo: boehmite, amor.: amorphous, ρ: weakly ordered phase of aluminas.

amorphous state after heating to temperatures higher than 800°C. At 838°C, weak-intensity peaks corresponding to η-Al_2O_3 appear. After heating to 1000°C, sharp peaks of α-Al_2O_3, with an intensity of about 40% of that of single-crystalline corundum, can be found in the pattern. The shorter the time of mechanical treatment, and consequently the smaller the extent of amorphous phase formation, the less α-Al_2O_3 forms after heating to 1000°C. As for untreated hydrargillite, in the temperature range 20–1000°C the intermediate phases boehmite, γ-Al_2O_3 and small amounts of æ-Al_2O_3 are successively observed, but α-Al_2O_3 does not appear. Mechanical treatment, at first, leads to an abrupt decrease in boehmite formation and to the appearance of χ-Al_2O_3 as an intermediate of the thermal decomposition, which is then replaced by the amorphous state (Table 1).

Figure 3 shows DTA curves for starting material and hydrargillite subjected to grinding for different times. When heated from 20 to 1000°C, unground hydrargillite (curve 1) exhibits three endothermic effects (at T_{max}=235; 320 and 535°C), accompanied by a loss in mass because of water removal. The total loss in mass between 20 and 1000°C is 34.6%, which fits the stoichiometry $2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$ and shows that no adsorbed water could be detected

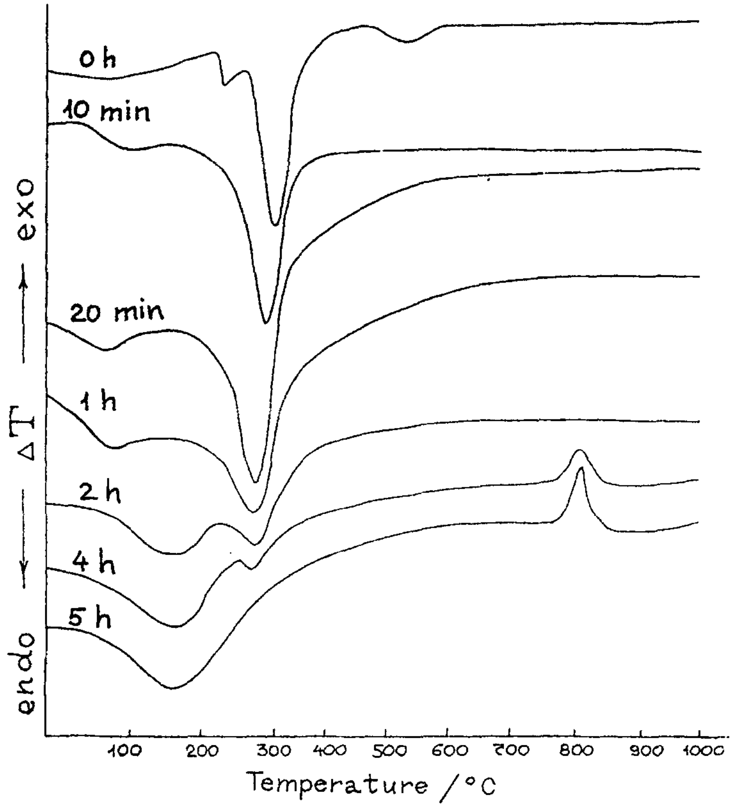

Fig. 3 DTA curves of hydrargillite ground for various lengths of time

in the range of thermobalance sensitivity. For the first and second peaks, $\Delta H_1=44.0\pm0.4$ kJ mol^{-1} H_2O ($T_{max}=235$°C) and $\Delta H_2=89.6\pm0.4$ kJ mol^{-1} H_2O ($T_{max}=320$°C). The first peak corresponds to the dehydration of hydrargillite with the formation of boehmite, while partially crystallized alumina also forms in the process at 320°C. The total quantity of water removed in the temperature interval from 20 to 320°C indicates that hydrargillite yields 54% of boehmite and 46% of aluminium oxide. ΔH_1 relates to the evaporation enthalpy of weakly bound water [7], while ΔH_2 is typical for the removal of a single hydroxide from the MeO framework [4]. The third peak in the DTA curve ($T_{max}=535$°C) corresponds to the reaction $AlOOH\rightarrow Al_2O_3$ and, according to the mass loss, 54% of the hydrargillite is transformed into boehmite. The constant rate of water evaporation in the temperature range form 600 to 1000°C conforms to the removal of a single hydroxide group from the product of decomposition.

A short duration of mechanical activation of hydrargillite (10 min) changes the shape of the DTA curves considerably, along with an insignificant decrease in mass loss. As can be seen in Fig. 3, the peak at $T_{max}=235$°C disappears and another peak arises at $T_{max}=97$°C, which corresponds to the evaporation of adsorbed water. The third peak shifts to lower temperature ($T_{max}=310$°C). The X-ray diffraction pattern suggests that the product of hydrargillite dehydration contains aluminium oxide with weak reflections of χ-Al_2O_3 and traces of boehmite (≈5%) (Table 1). In the range 800–1000°C, weak peaks of η-Al_2O_3 appear.

As the crystallinity of hydrargillite decreases during mechanical treatment, the main peak of thermal decomposition at $T_{max}=282$–310°C also decreases, and it finally disappears after formation of the completely amorphous phase. At the same time, the magnitude of the peak at 150°C with $\Delta H=13.0$ kJ mol^{-1} H_2O increases. It can be inferred from Table 2 that the enthalpy of water evaporation becomes less as hydrargillite becomes more amorphous. The water removed

Table 2 The enthalpy of water evaporation from hydragillite in dependence on grinding time

Grinding time/h	T_{max}/°C	Weight loss/%*	$\Delta H^{**}\pm0.4$/kJ mol^{-1} H_2O
0	235	5.7	44.0
	320	22.7	89.6
1	90	10.7	
	282	23.7	39.0
2	150	19.9	
	283	14.4	31.0
5	150	34.4	13.0

* In temperature range of peak

** Evaporation enthalpy in temperature range of peak.

with low enthalpy from completely amorphous hydrargillite at 150°C could be considered to be coordination-linked molecular water in the bulk and on the surface of the amorphous oxide.

The exothermic effect at T_{max}=838°C for strongly amorphous hydrargillite relates to the phase transition amorphous phase→η-Al_2O_3. The enthalpy of the transition increases as the quantity of the amorphous phase increases. As shown in [8], the crystallization enthalpy of calcination products of hydrargillite varies from −2.5 to −17.5 kJ mol^{-1} as a function of the grinding time (temperature range: 750–880°C).

When heated to 1000°C, weakly-ordered η-Al_2O_3 is transformed into α-Al_2O_3, with traces of amorphous Al_2O_3 (Table 1). The content of α-Al_2O_3 in the product increases as the quantity of the amorphous phase increases.

Transformation of hydrargillite under conditions of steam treatment

When heated at 400°C in water vapour at 2.6·10^7 Pa with the addition of activators, hydrargillite undergoes thermal dehydration in two steps: boehmite formation and then the formation of small single-crystals (1–100 μm) of α-

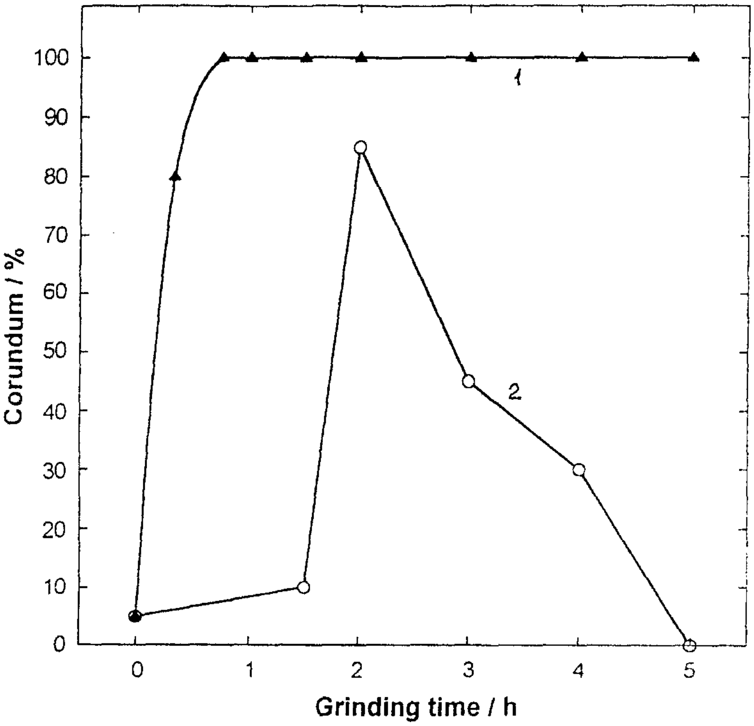

Fig. 4 The dependence transformation of hydrargillite into corundum under hot steam treatment (for 7 h at 400°C, P_{H_2O}=260·10^5 Pa) with grinding time, 1 – after 10 days since mechanical activation; 2 – after 6 months since mechanical activation

Al_2O_3 with well-mounted faces [9]. During the increase of temperature to 400°C, hydrargillite is completely transformed into boehmite. The formation of corundum from boehmite starts after a 6 h delay period. The complete transformation of hydrargillite into corundum occurs in 17 h. After mechanical activation, the delay period before corundum formation decreases. Figure 4 presents the content of corundum formed after thermovapour treatment for 7 h, as a function of the duration preliminary mechanical activation of the hydrargillite. In the case of unactivated hydrargillite, only 5% of α-Al_2O_3 was formed after 7 h of thermovapour treatment; after mechanical activation for 20 min, 80% α-Al_2O_3 was obtained under the same conditions (Fig. 4). Mechanical treatment for 40 min lead to the complete transformation of hydrargillite to corundum in 7 h.

It is worthy of mention that the activated state of hydrargillite is unstable: its reactivity falls as time elapses. Curve 1 in Fig. 4 illustrates hydrargillite dehydration in water vapour 10 days after mechanical activation. Six months following activation, the function of the α-Al_2O_3 yield (under thermovapour treatment for 7 h) on the duration of mechanical treatment displays a maximum at approximately 2 h (curve 2 in Fig. 4). X-ray phase analysis (Fig. 1) reveals that, on activation for more than 2 h, hydrargillite becomes 80% amorphous. In this case, the water state in the structure changes. It follows from the IR spectra (Fig. 2), the DTA curves (Fig. 3) and the dehydration enthalpies of these samples (Table 2) that the water molecules formed from the hydroxyl groups during the decomposition of hydrargillite are activated in the field of the disordered aluminium oxygen framework. These molecules of water, with extremely low evaporation enthalpies, are coordinately linked aluminium ions, and form an unstable aqua complex, which helps the aluminium to change its coordination [10]. The amorphous oxide resulting from the mechanical treatment, which contains only coordinately linked water, has a high reactivity and is able to undergo relaxation.

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