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Physico-chemical properties of Tseflar^{TM}-treated gibbsite and its reactivity in the rehydration process under mild conditions

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Abstract

Physical and chemical properties of TSEFLAR^{TM}-treated gibbsite/hydrargillite (centrifugal thermal activation) CTA HG were studied with X-ray analysis, TA, EM, BET and IRS. CTA HG product obtained at the temperature range of 330–580 °C and contact time ~1 s is the one with a transitional non-equilibrated layered hydroxide structure with partly lost hydroxide groups. The CTA HG structure does not correspond to the produced chemical composition $Al_2O_3{\cdot}(0.4–2)H_2O$ and, therefore, the products reveal a higher reactivity. Such products are already readily hydrated at room temperature in water and aqueous ammonia to form eventually the stable bayerite-like hydroxide structure.

Keywords: Gibbsite; Thermal activation; Reactivity; Hydration

1. Introduction

The thermal activation of hydrargillite/gibbsite (HG) is known to be a method for the production of a highly reactive state of $Al_2O_3{\cdot}nH_2O$ ($n = 0.4–2$). Rehydration of this product is a basis of a number of wasteless/low-waste technological lines used for manufacturing the pseudoboehmite-structured hydroxide with the skipped reprecipitation stage, which requiring a large consumption of feedstocks and producing wastewater in a large amount [1–3].

The properties of the products of the thermal decomposition and their reactivity will depend considerably both on properties of the initial hydrargillite (including the particle size) and on conditions of the thermal decomposition process, viz. the decomposition temperature, heating rate, HG bed thickness, residence time in the hot zone, quenching rate, water partial pressure etc., which determine the defect structure of an oxide phase formed and, hence, its physical and chemical properties.

Few methods for the implementation of the thermal decomposition process were developed. These are:

1. thermal decomposition in the flue gas backflow at high temperatures [1];
2. thermal decomposition in the flue gas backflow at moderate temperatures and certain steam pressure—TCA [2];
3. thermal decomposition in the fluidized bed of a catalyst or solid heat carrier—TDP [3];
4. thermal decomposition in a thin bed in flowing flue gases [4].

The thermal decomposition of hydrargillite using a TSEFLAR^{TM} installation ([5,6], also see a paper in this issue by Pinakov et al.) is a new way to implement the thermal decomposition process, which allows a combination of a fixed decomposition temperature, thin bed, fast heating and cooling, short contact times and variation of the steam pressure. In addition, a more pure product, so called (centrifugal thermal activation) CTA HG, is obtaining without contamination by incomplete burning products or by the heat carrier.

Specific features of the TSEFLAR^{TM} process of the HG thermal decomposition necessitated investigation of the conditions of formation of the active product (CTA HG), its

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nature, and its physico-chemical properties, including its reactivity to the rehydration reactions.

2. Experimental

2.1. Sample preparation

HG from the Pikalev Silica Complex was the starting material. Its initial moisture content was 2–9 wt.%; Na_2O (impurity) content was 0.22%; the particle size distribution: 8% was lower than 38 μm, 10% was 38–53 μm, 55% was 63–106 μm, 27% was larger than the 106 μm. Specific surface area measured at 100 °C (S_{sp}) was 0.5 m^2/g.

The product was subjected to the thermal decomposition at the varied process parameters: the initial HG wetness, rotation speed of the heat carrier (plate): 100–200 rpm, contact time (0.5–1.4 s), initial power temperature: 20–200 °C, decomposition temperature (350–600 °C), feeding rate (5–40 kg/h), particles size: 0–150 μm (with and without sifting) and steam pressure (up to 1 atm).

TSEFLAR^{TM}-treated gibbsite was subjected to mechanical treatment in different mills, such as the planetary bell mill and dezintegrater DEZI.

2.2. Sample characterization

The samples were characterized using such techniques as XRD (including the mode with the synchrotron radiation-SR), DTA, BET, IRS, SEM, and TEM.

XRD patterns were obtained with a URD-6 diffractometer (Germany) using Cu Kα radiation in the 2θ range 10°–75°. The quantitative phase analysis was carried out using data on mechanical mixtures according to the procedure described in [7]. Typical particle sizes were estimated from the broadening of 2 0 2 (for bayerite), 0 2 0, 0 3 1, 1 2 0 (pseudoboehmite) and 0 0 2, 0 2 4, 3 1 4 (gibbsite) diffraction peaks. High-resolution XRD patterns were obtained on Beamline no. 2 of VEPP-3 storage ring in Siberian Synchrotron Radiation Center, Novosibirsk, Russia. The wavelength in the experiment was 0.07 nm. The scanning (within 2θ) region was equal to 5°–135°.

The textural features of the CTA HG products were studied by SEM with a BS-350 machine (resolution limit is about 5–10 nm). Electron microscopy data were obtained with a JEM-2010 microscope. The resolution limit of the machine is about 0.14 nm, the accelerating voltage 200 kV. Specimens were deposited onto a holey-carbon film supported on a copper grid from ethanol slurry.

The thermal analysis was carried out on a DQ-1500 device. The samples (200 mg) were heated with the rate of 10 °/min from 20 °C up to 900 °C on the air. The degree of certainty of phase analysis was 1%.

IR-spectra were obtained using Fourier spectrometers IFS-113v Bruker and BOMEM MB-102; samples were prepared by pressing in alkali metals halides or by dusting on KBr and CsJ supports. IR spectra were recorded in the 500–4000 cm^{-1} range in transmission or diffuse scattering mode, respectively.

The specific surface area (S_{sp}, m^2/g) was determined by the BET method using Ar thermal desorption data.

The particle size distribution was determined by Coulter method [8] using Coulter counter TA-2 by registration and counting of variable pulses of voltage drop in capillary (200 μm in diameter), through that a suspension of power (under investigation) in electrolyte (0.9% NaCl) was going.

Solubility of the samples was determined in acidic and basic media. Samples were dissolved in the sulfuric acid solution (1:1), while the temperature was increased from 20 to 100 °C and in the ammonia solution with pH ∼ 10 at 22 °C. The solution analysis was carried out with the help of the atomic absorption spectroscopy (a BAIRD spectrometer).

3. Results and discussion

3.1. The CTA HG product phase composition

According to X-ray analysis, the phase composition of the CTA HG products is considerably affected mainly by the TSEFLAR^{TM} plate temperature, pre-drying temperature, the contact time and the feeding rate. For example, the XRD data show that the rise of the plate temperature from 330 to 600 °C results in the decrease in the HG [JCPDS 33–0018] proportion in the CTA product while the content of the X-ray amorphous component increases and boehmite [JCPDS 17–0940] is detected. Almost the whole product formed upon the treatment at 530–580 °C is X-ray amorphous. Table 1 shows the preparation conditions and the characteristics of some CTA HG products.

The DTA data demonstrate a non-uniformity of even the high-temperature (fully X-ray amorphous) CTA HG product; it seems to comprise both "oxide" and "hydroxide" constituents. The broadened endoeffect below 800 °C accompanied by a monotonic weight decrease and an exoeffect at 810 °C at no weight change, seen in DTA curves of CTA HG samples, indicate the presence of not only a disordered oxide phase and chemisorbed water but also disordered hydroxide phases (Fig. 1).

From the IRS data, the CTA HG products also comprise χ-like alumina along with weakly bonded/molecular water (removed on heating at 100 °C) and structurally disordered hydroxides [9–11] (Figs. 2 and 3). That is seen from a poorly resoluted IR absorption data at the region of stretching vibrations of bound hydroxides. Therefore, the X-ray amorphous CTA HG product seems to contain a considerable quantity of structurally disordered hydroxides in its "hydroxide" constituent and chemisorbed water in its "oxide" constituent. The IRS data show also the presence of carbonate species in the CTA products, which may form due to an interaction of the active oxide species produced during the thermal

Table 1
Some properties of the CTA Gibbsite products

Sample	Chemical composition	Dispergation	Phases (%) (X-ray)	TA					Solubility (%)		
				Humidity (%)	Am. (%)	$Al(OH)_3$ gibbsite (%)	AlOOH boemite (%)	AlOOH, pseudoboemite (%)	NH_4OH, pH 10, 20 °C, 60 min	H_2SO_4[a] 40 °C, 1 min	H_2O[b] 25 °C, 120 min
Gibbsite	$Al_2O_3{\cdot}3.5H_2O$	No	Gib-92 Boe-8	38	No	77	23	0	No	–	No
CTA-380	$Al_2O_3{\cdot}1.7H_2O$	No	Am-65 Boe-15 Gib-20	23	44	39	17	0	1.9	1.2	0.02
CTA-380	$Al_2O_3{\cdot}1.9H_2O$	DEZI	Am82 Boe-3 Gib-15	25	37	45	18	0	1.0	11.5	0.03
CTA-580	$Al_2O_3{\cdot}0.8H_2O$	No	Am-98 Gib-2	12	81	6	8	5	2.2	2.0	0.02
CTA-580	$Al_2O_3{\cdot}H_2O$	DEZI	Am-95 Boe-3 Gib-2	17	84	5	12	0	1.4	3.9	0.03
TCA (for comparison)	$Al_2O_3{\cdot}0.8H_2O$	DEZI	Am-95 Gib-5	12	76	11	13	0	3.0	2.0	0.01

[a] Samples solubility in sulfur acid (1:1) during heating, up to 80 °C (full solubility).
[b] Water pH rises up to 10–11.

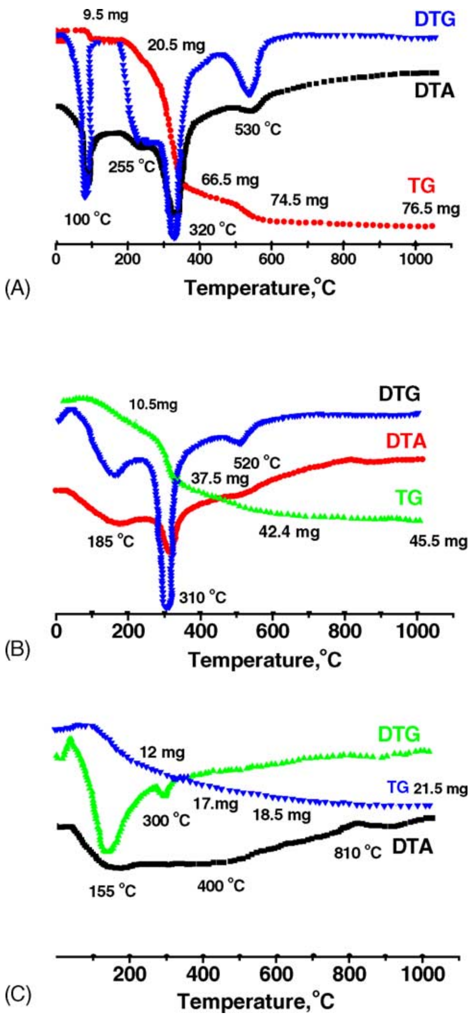

Fig. 1. Thermogram of gibbsite (A), and gibbsite treated with TSEFLAR^{TM} at 380 °C (B) and at 580 °C (C).

decomposition with carbon dioxide, which is present in the ambient (Fig. 3).

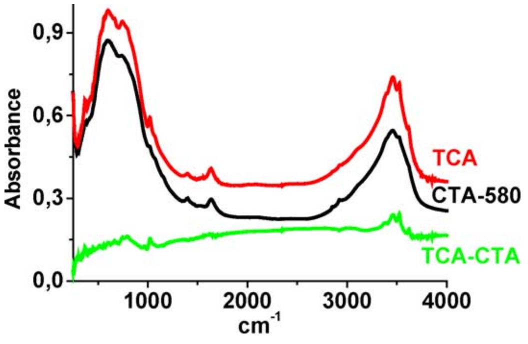

Fig. 2. IRS data on gibbsite treated with TSEFLAR^{TM} at 580 °C (CTA-580), on TCA product and on their differed spectra (THA–CTA).

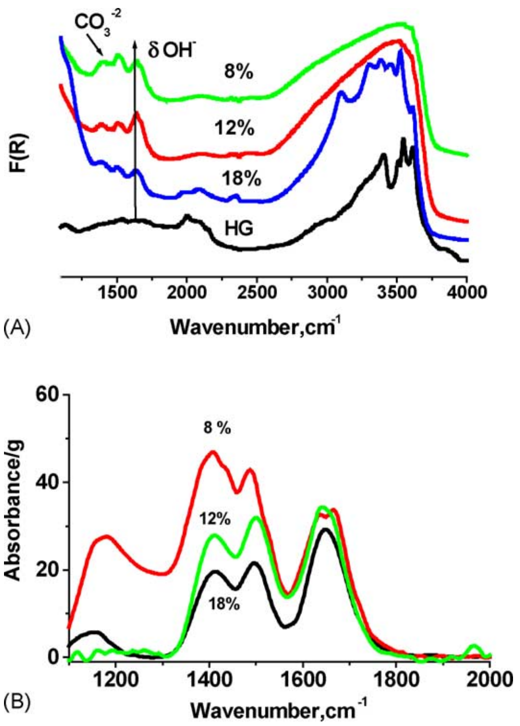

Fig. 3. IRS data on gibbsite (HG) and gibbsite treated with TSEFLAR^{TM} vs. product humidity (%) (A); IRS differed (20–100 °C) spectra TSEFLAR^{TM}-treated HG products with different humidity.

The IRS data argue in favor with the SR-data on the phase composition which allow, due to a higher sensitivity, a χ-like phase of alumina [JCPDS 13–373], admixture of hydrargillite [JCPDS 33–0018] and boehmite [JCPDS 17–0940] to be detected in the CTA-580 HG sample (Fig. 4).

The increase in the content of the amorphous oxide component in the products also is favored at longer contact times (lower rates of the HG consumption by TSEFLAR^{TM}), while a pre-drying of the samples at 180 °C results naturally in a higher content of boehmite in the product.

Therefore, respectively, low temperatures of CTA treatment (below 400 °C), high consumption rates (15–20 kg/h), pre-heating of HG at the temperature not higher than 100 °C will cause an increase in the content of an “amorphous hydroxide” component in the CTA products, and vice versa, high temperatures (above 600 °C), the small particle size and low consumption rates (lower than 10 kg/h) will allow a fully X-ray amorphous “hydroxide”-free products to be obtained, in which aluminum atoms form a kind of the χ-oxide phase in its close proximity (from the IRS data).

Hence, X-ray amorphous CTA product seems to be as in high-dispersed χ-like phase of alumina, as in a non-equilibrium metastable (hydroxide) state of oxide phase. Preservation of the layered HG structure in the products of the TSEFLAR^{TM} thermodecomposition indicates feasibility of the dehydration stage without a concomitant rearrangement of the oxygen sub-lattice. Such layered structure of the CTA is not proper for the formed product with the composition close to $Al_2O_3\cdot 0.8H_2O$ (the oxide product). For this reason, such “hydroxide” product will possess a higher energy capacity and a higher reactivity. Both product states are possible as well. When the temperature of the HG treatment

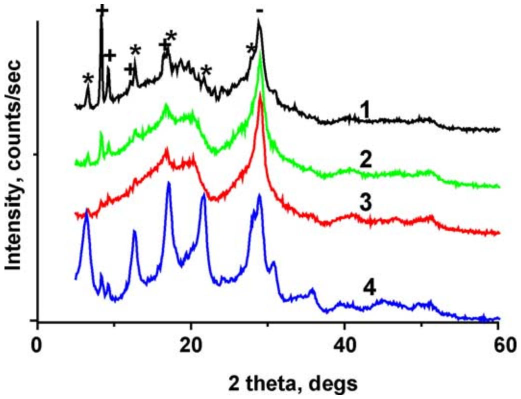

Fig. 4. The samples' phase composition according to the Synhrotron XRD vs. the preparation conditions: (1) TCA+DEZI; (2) CTA-580; (3) CTA-580+DEZI; (4) 3+hydration in an ammonia solution at pH 10 during 2 h. ((*) Boehmite, (+) gibbsite, (-) χ-like alumina).

is elevated to above 600 °C, the formation of only oxide well crystalline phase is not excluded in the CTA product. Hence, some temperature range may be identified for the formation of the active CTA product most likely with the transitional non-equilibrium layered structure of the hydroxide type, which is dehydrated in more or less extent; this is the range between 330 and 600 °C.

3.2. The surface area of the CTA HG products

TSEFLAR™ treatment of HG results in a considerable increase in surface area depending on the conditions of thermal decomposition. The surface area increases upon the elevation of the decomposition temperature but decreases upon the elevation of the pre-drying temperature. For example, if the CTA HG temperature is in the range of 470–545 °C, specific surface area increases up to 180 m^2/g in the sample pre-heated to 140 °C but up to 250 m^2/g in the sample not subjected to pre-heating. It is interesting that the surface area is considerably lower, when being determined at 100 °C than that after the pretreatment at 300 °C. This is evidence of inaccessibility of some art of the adsorbate surface due to the presence of chemisorbed water and/or specific morphological arrangement of the particles.

3.3. Morphology of CTA HG products

The particle aggregates are practically not varied in size after treating HG with TSEFLAR™ (from the SEM data and the data obtained by Coulter) (Fig. 5). The electron microscopic studies reveal that the particles formed during HG treating with TSEFLAR™ at 470 and 575 °C are a pseudomorphose to the initial HG (Fig. 6). These are almost regularly shaped (truncated hexagon or distorted rectangular in projection) coarse (1–1.5 μm) particles with the slightly broken surface. Sometimes, fine acicular particles of ca. 70–100 Å in size are seen at the particle edges. Elongated spots—slit-like pores—can be observed in some individual particles. There

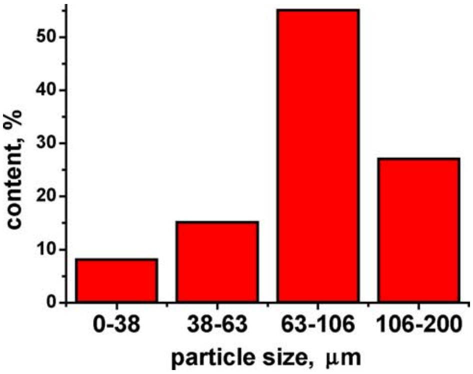

Fig. 5. Particle's size distribution of TSEFLAR™-treated gibbsite (Coulter data).

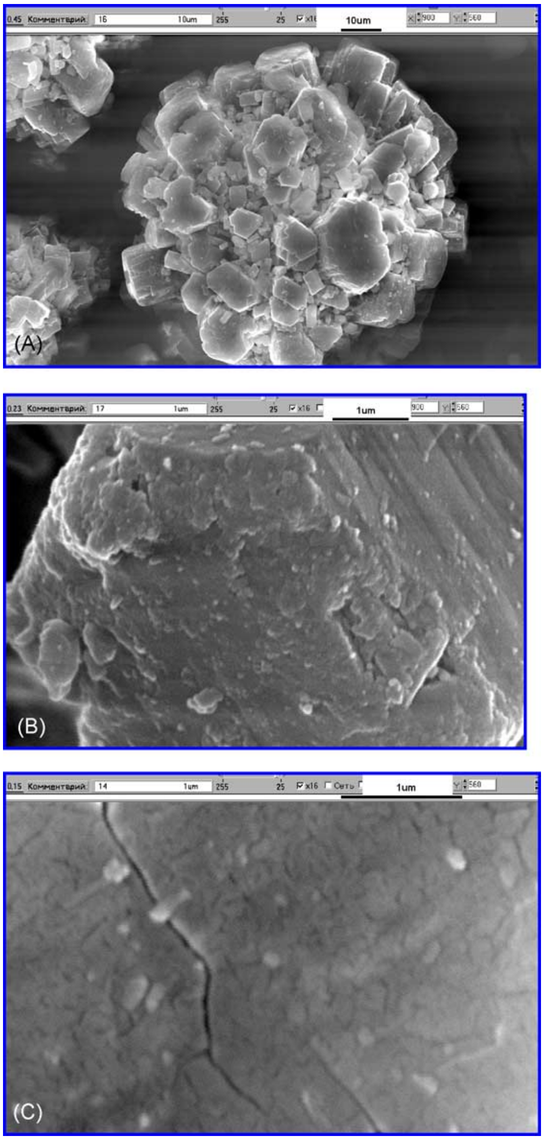

Fig. 6. Photomicrography of gibbsite treated with TSWFLAR™ at 580 °C (different magnifications).

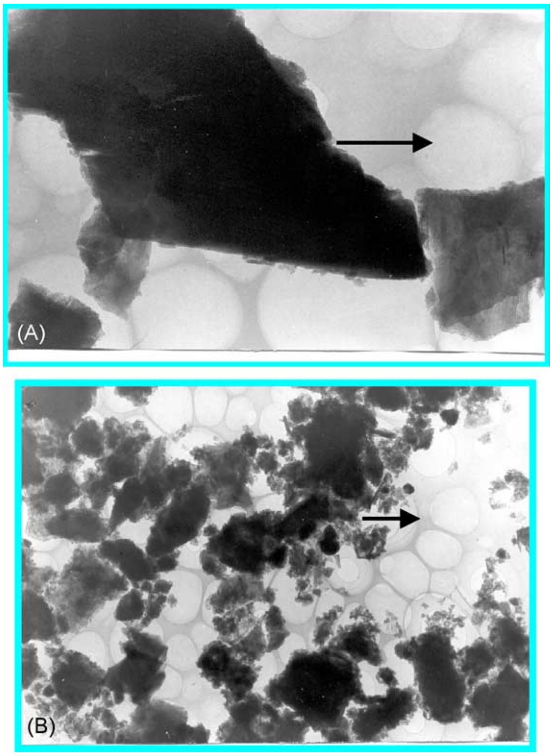

Fig. 7. Photomicrography of gibbsite treated with TSWFLAR^{TM} at 580 °C before (A) and after mechanical treatment in DEZI (B) (0.4 μm eroute).

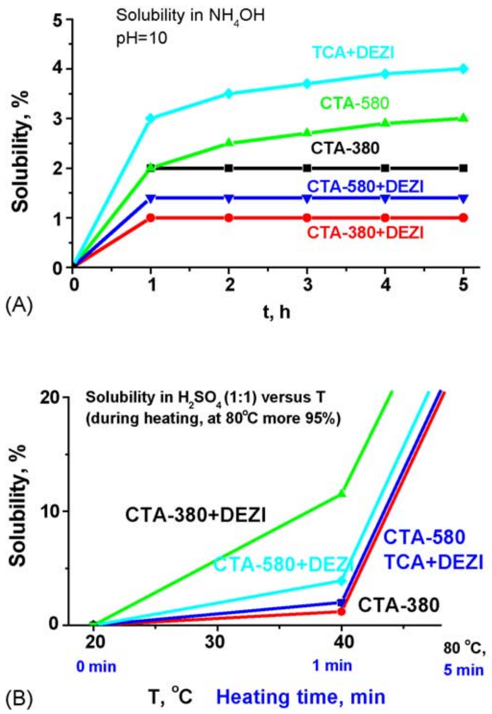

Fig. 8. CTA products solubility in an alkali (A) and an acid (B) media.

are also shapeless aggregates of lamellar microporous particles of 0.5–2 μm in size in the samples. Hence, the formed particles differ from the initial one since all are laminar, split and porous.

CTA product particles are easily grinding to 0.1–0.5 μm size in DEZI, the planetary ball mill and others mills (Fig. 7).

3.4. Reactivity of the CTA HG products

Depending on the preparation conditions, different solubilities are characteristic of the CTA HG samples (Table 1, Fig. 8). For example, the solubility in alkaline ammonia solution at 20 °C increases with the elevation of the decomposition temperature and, vice versa, decreases if the samples are disintegrated (Fig. 8). The solubility in acid solutions varies opposite to that in the alkaline solutions (Fig. 8). The water solubility is rather low for all the samples; the solution formed showing an alkali reaction (pH 10–11). It is interesting that the TCA HG sample is the one of the most soluble in the ammonia solution and lest soluble in water that indicates its acidic properties (that may be accounted for by higher temperatures of the sample preparation or by a lower steam partial pressure), while the CTA HG product is more alkaline.

Hydration of the samples in an alkaline medium and water produces, at first, pseudoboehmite (Fig. 4, curve 4) and then, at even longer exposure, bayerite (Fig. 9). The hydration during a week results in formation of almost one-phase bayerite from both TCA HG and CTA HG (Fig. 9). However, there is a considerable difference in the maximal quantity of the formed pseudoboehmite. For example, the bayerite phase is detected as early as 5 h of hydration of the CTA HG product in water (when the pseudoboehmite content reaches ca.

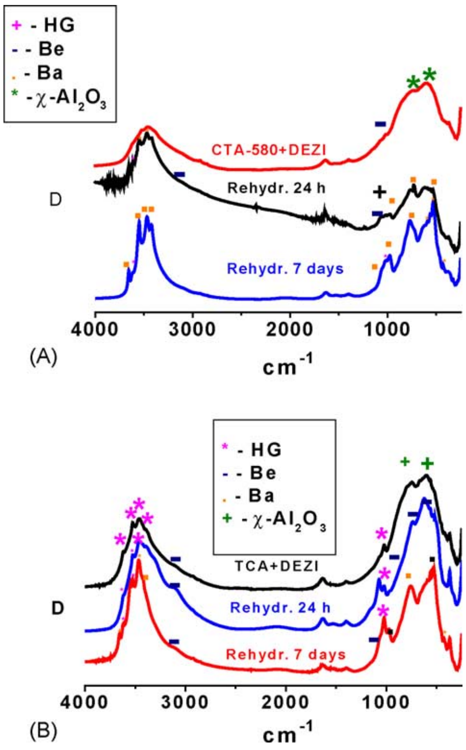

Fig. 9. IRS data on CTA (A) and TCA (B) products after DEZI treatment before and after rehydration in ammonia solution during 24 h and a week.

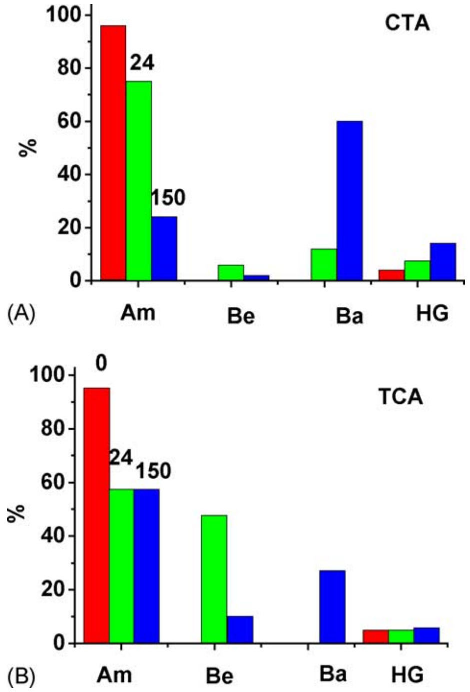

Fig. 10. Phase composition (amorphous, pseudo boehmite, bayerite and gibbsite) of CTA (A) and TCA (B) products after their rehydration in ammonia solutions during 24 and 150 h (a week).

10%) but in 24 h (when the pseudoboehmite content reaches ca. 50%) of hydration of the TCA HG (Fig. 10).

It is not excluded that rehydration of the CTA HG products skips the stage of their redissolution but by the reaction solid + liquid. This process may be favored due to the layered structure of the products, because rehydratation of CTA HG in “oxide state” practically does not leads to formation of hydroxides. One can also notice that according to X-ray data, no formation of hydroxide phases is detected during 24 h in an acidic medium (at otherwise identical conditions) and, again, exposure of HG or pseudoboehmite (reprecipitation) in acid or alkali aqueous solutions does not cause any changes in the phase composition of the samples.

4. Conclusion

CTA HG products at the temperature range of 330–580 °C are the ones with a transitional non-equilibrated layered hydroxide structure with partly lost hydroxide groups. The structure does not correspond to the produced chemical composition and, therefore, reveals a higher reactivity. Such a system is already readily hydrated at room temperature in aqueous ammonia to form eventually the stable bayerite-like hydroxide structure.

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