PROCESSES OCCURRING IN FLUID OF PRIMARY ALCOHOLS AT HIGH PRESSURE DURING SYNTHESIS OF CORUNDUM

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In this report the results of studies of processes, taking place in fluids of primary alcohols, and in solid phase, aluminum hydroxide, in autoclave were represented. The processes were carried out at contact of alcohol to aluminum hydroxide in supercritical conditions (T=400°C, P=20 MPa). The products of alcohols transformation in supercritical conditions in contact with $Al_2O_3 \cdot nH_2O$ by the chromatographic and mass-spectrometry were studied. The solid-phase transformation products of aluminum hydroxide by methods X-Ray diffraction, IR-spectroscopy, photoluminescence and scanning electron microscopy were investigated. In alcohols fluid (methanol and ethanol at 400°C) at the presence of water vapor and $Al_2O_3 \cdot nH_2O$ reactions catalytic pyrolysis, destruction, the increase of the number of the carbon chain, oxidation-reduction reactions, etherification and others proceed. At heating aluminum hydroxide in supercritical fluid of methanol and ethanol at 400°C the boehmite and then the corundum will be formed. The generated boehmite has the shape of spherical aggregates from thin plates, which then transform into plate corundum.

INTRODUCTION

Earlier [1, 2] it was shown, that the process of aluminum hydroxide (hydrargillite) transformation in corundum in supercritical water fluid (T=400°C, P=20-26 MPa) proceeds due to quasi-equilibrium processes of hydroxylation - dehydroxylation of hydrargillite structure with gradation in direction of its dehydration: $Al(OH)_3$? AlOOH ? a-Al_2O_3.

With pressure decrease of water vapor the generation rate of corundum is slow down. With small rate this process can flow past and without the addition of water in autoclave due to the water selected during dehydration of hydrargillite. It is known [3], that in supercritical conditions ?H of water fluid about 10. It leads to the supposition of the participation of hydroxyl ions in transformation of hydrargillite. Really, the addition of alkalis speed up this process.

It was interesting to investigate the process of forming of corundum from hydrargillite in the same conditions (? =400°? , ? =20-26 MPa), but not in water fluid, but in fluid of primary alcohols. The processes, which are flowing past in supercritical fluids of alcohols, can influence on solid-phase processes of transformation hydrargillite.

MATERIALS AND METHODS

For study of transformation hydrargillite in corundum in supercritical fluids of alcohols methanol and ethanol of the mark “for chromatography” and industrial hydrargillite of the mark”GD-00” were utilized. The solid-phase transformation products of hydrargillite by methods

X-Ray, IR-spectroscopy, the photoluminescence and scanning electron microscopy were investigated. The electron-microscopic photography is carried out on the device “Cam Scan Series 2”.

The spectrums of photoluminescence were registered on the device SDL 2M at ambient temperature in the interval 260-800 nm at exciting irradiating corundum by light with wavelength 254 nm.

The IR-absorption spectrums were measured on the device an IR Fourier-spectrometer EQUINOX 55/S in range of 4000-400 cm^{-1}.

The products of alcohols transformation in supercritical conditions in contact with $Al_2O_3 \cdot nH_2O$ by the chromatographic and mass-spectrometry were studied. The chromato-mass-spectrometer - Finnigan INCOS 50. The mass-spectrometer - MI 1311.

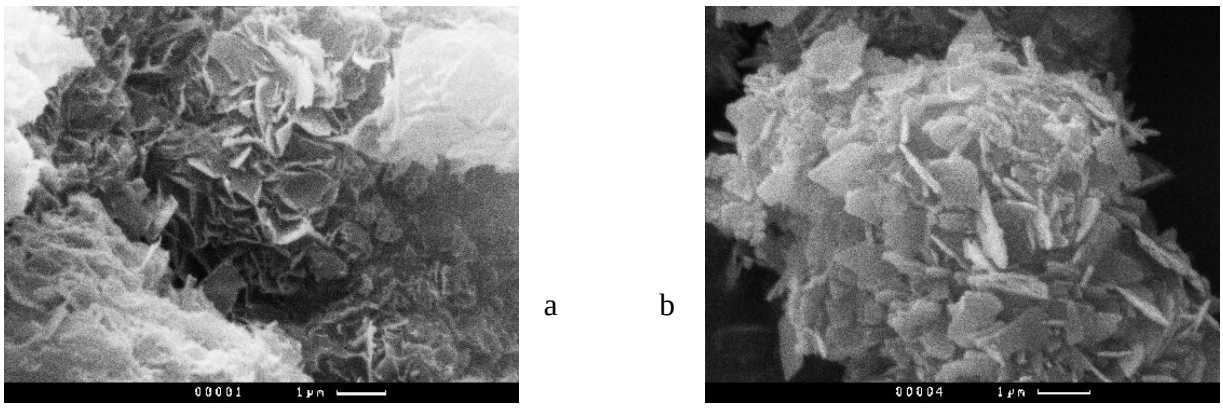
The X-ray analysis was carried out with diffractometer DRON - 3M in filtered Cu-K_a radiation.

The heat treatment of hydrargillite in supercritical fluid of alcohols was carried out in laboratory autoclaves (18 cm^3). The container with hydrargillite in autoclave is located. The alcohol was filled between walls of autoclave and container. The temperature of realization of the process was 400°C. The pressure of alcohol was 23 MPa.

RESULTS AND DISCUSSION

The XRD analysis of transformation products of hydrargillite in supercritical fluid of alcohols has shown, that the process proceeds through the same stages, as well as in water fluid: at heating of autoclave up to 400°C will be formed boehmite and then the corundum. The rate of boehmite transformation into corundum slow down in a series of fluids: methanol - water - ethanol.

In supercritical fluid of methanol and ethanol the generated boehmite has the shape of spherical aggregates from thin plates (**Figure 1**), which then transform to plate corundum (**Figure 2**).



a b

Figure 1.
a) The boehmite obtained in methanol, 200°C; b) The boehmite obtained in ethanol, 200°C

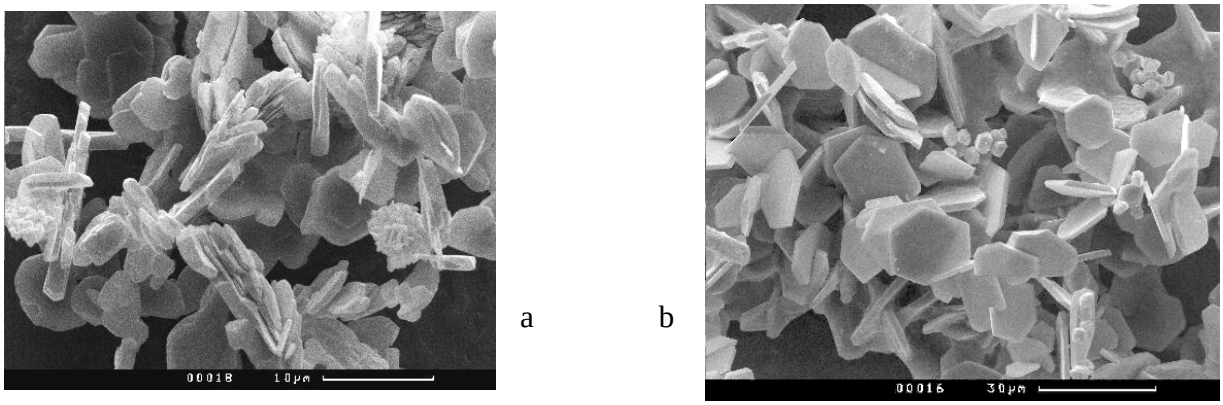


Figure 2. a) Corundum obtained in ethanol, 400°C; b) Corundum obtained in methanol, 400°C.

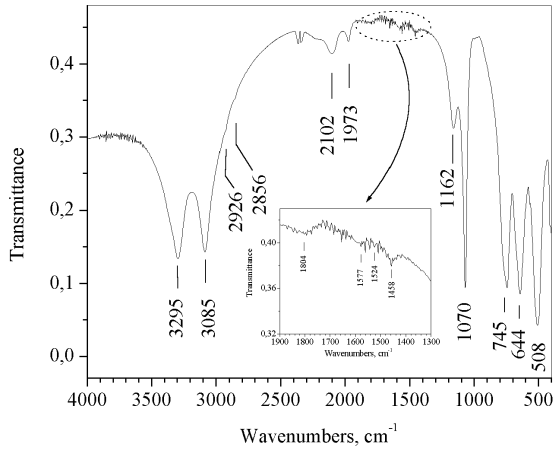


Figure 3. IR-specter of boehmite, obtained in methanol, 400°C, 1 h.

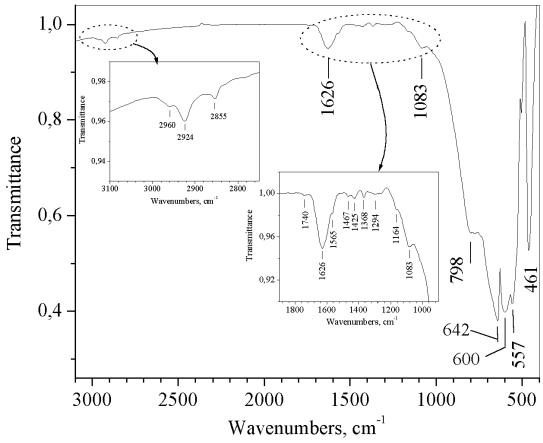


Figure 4. IR-specter of corundum, obtained in methanol, 400°C, 21 h.

The IR-spectrums of boehmite, obtained in methanol fluid, except the bands characteristic for boehmite, obtained in water fluid, contain absorption bands of small intensity in the region of 2850 – 2960 cm^{-1} and 1000 - 1500 cm^{-1} (**Figure 3**). These bands are referred to alkyls – and acetate - groups, grafted into aluminum-oxygen frame of boehmite or aluminum oxide. The spectrum of aluminum methoxide shows such similar bands [4, 5]. In the region of the oscillating aluminum-oxygen bands the increase of intensity of boehmite band at 508 cm^{-1} (and 557 cm^{-1} of corundum) is visible. It is evidenced of the influencing alkyls - groups on some aluminum-oxygen bands. These grafted alkyls - groups are partially saved in corundum obtained from it boehmite (**Figure 4**). The variation of the corundum habitus can be connected with such influencing of alkyls - groups.

At formation of boehmite in reduction medium the heightened amount lattice vacancies in generated boehmite produce. It is exhibited in magnification of intensity of the luminescence bands in the region of 300 - 500 nm (near 370 nm). These bands are related to F – centers, which have arisen on basis of anionic vacant centers (**Figure 5**). The Figure 5 demonstrates, that the

boehmite and corundum, synthesized in fluid of methanol, contain the greatest amount of F-centers.

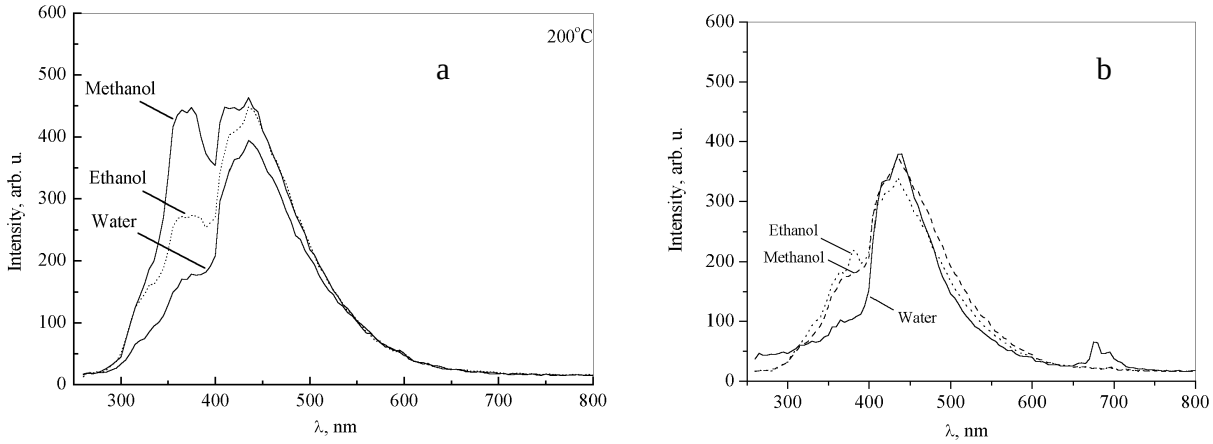
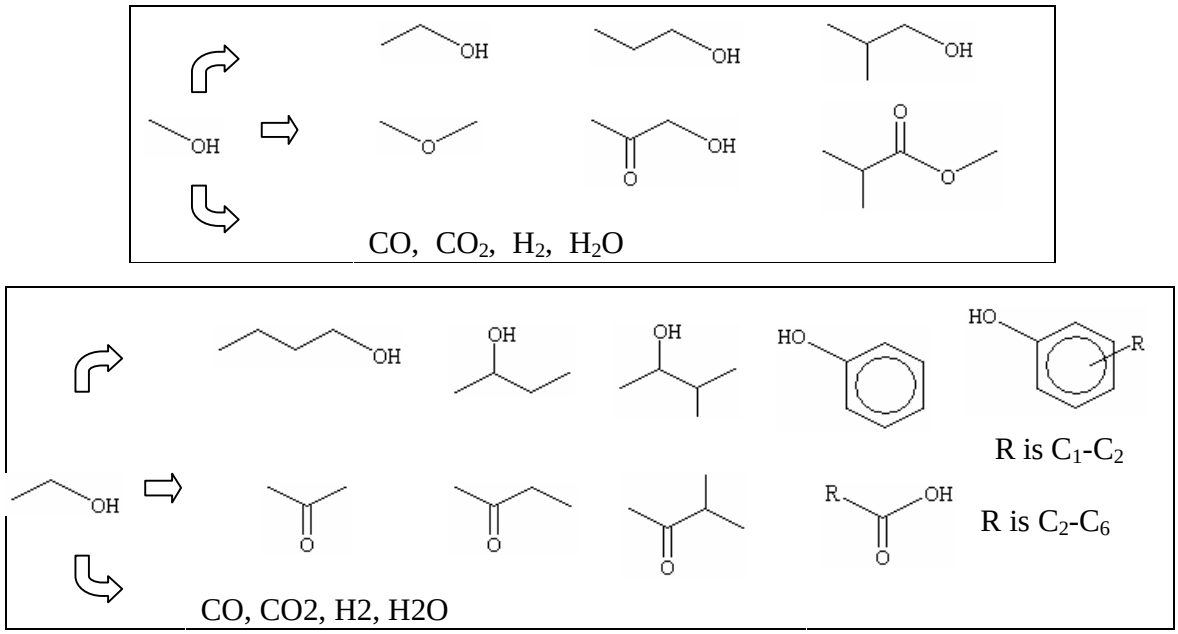


Figure 5. a) The luminescence specter of boehmite. b) The luminescence specter of corundum.

Simultaneously with transformations hydrargillite in alcohol fluid the diversiform reactions proceed. As have shown the chromatographic and mass-spectrometer studies of transformation products of alcohols in supercritical conditions in contact with $Al_2O_3 \cdot nH_2O$, the range of generated products is very wide:

Schema



In alcohols fluid at 400°C at the presence of water vapor and $Al_2O_3 \cdot nH_2O$ reactions catalytic pyrolysis, destruction, the increase of the number of the carbon chain, oxidation-reduction reactions, etherification and others proceed. At decomposition of methanol will be produce CO, CO_2 and H_2, which carry out reduction medium. It explains heightened contents of anionic vacant centers in corundum, which is generated in this medium. The increase of the number of the carbon chain of reactions products in methanol fluid takes place up to C_4 with formation of alcohols and ethers. In a case ethanol the increase of hydrocarbon chain takes place up to C_5 predominantly with formation of hydrocarbons, ketones and acids. In the same conditions in absence of water vapor and at substitution of aluminum hydroxide by the waterless Al_2O_3 in main takes place catalytic decomposition of methanol. In this case the formation of corundum from Al_2O_3 does not take place, but the ordering pattern of source aluminum oxide is watched.

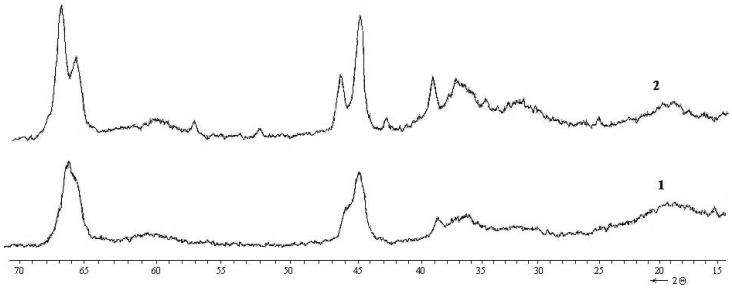


Figure 6. The diffractogram of aluminum oxide before (1) and after (2) treatment by methanol fluide at 400°C.

The reflexes in the diffractogram of aluminum oxide become more acute and more intensive (**Figure 6**).

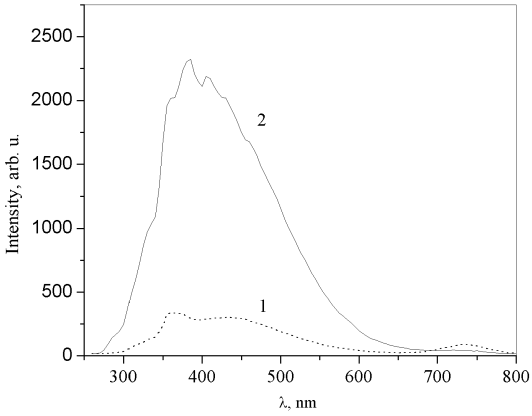


Figure 7. The luminescence specter of aluminum oxide before (1) and after (2) treatment by methanol fluid at 400°C.

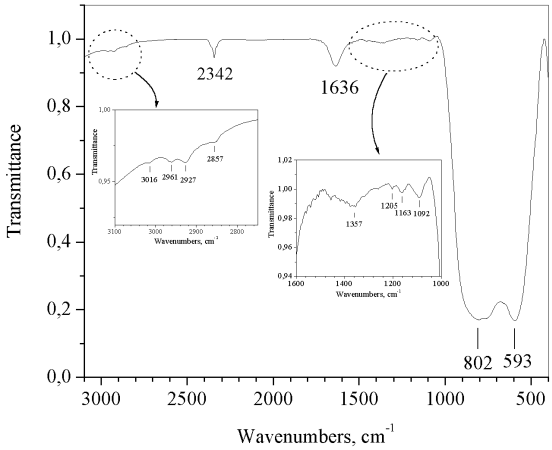


Figure 8. IR-specter of aluminum oxide in methanol after treatment by methanol fluid at 400°C.

Figure 7 shows the increase of the amount of vacancies in structure of aluminum oxide after treatment by methanol fluid at 400°C due to reduction medium, since the intensity of bands of F-centers increases.

It is interesting to mark, that in supercritical methanol fluid without water vapor also takes place the grafting of alkyls - groups to aluminum-oxygen frame of aluminum oxide. The bands in IR-spectrum in the range of 1000 - 1500 cm^{-1} and 2800 – 3000 cm^{-1} testify to it (**Figure 8**). However, it is not enough for restructuring of aluminum oxide in corundum, for this purpose the presence of water is necessary condition. At addition of water in alcohol fluid the aluminum oxide pass trough stages: hydroxylations, then dehydroxylations with restructuring and formation of boehmite and then of corundum.

CONCLUSION

The study of processes, which are proceeded in the system: "supercritical fluid of primary alcohols - the hydroxide of aluminum (? = 400°C, ?=20-26 MPa)", has shown, that the processes in fluid and in solid phase are interdependent. The water removed from aluminum hydroxide during its transformation in corundum, promotes the oxidation reactions of alcohols and products of their catalytic pyrolysis (catalyst – aluminum hydroxide and then boehmite and corundum). On the other hand the grafting of alkyls - groups to aluminum-oxygen frame changes the process of the forming of crystals of corundum and intermediate phase, boehmite, slowing down the growth of some faces, for example, in case of formation of corundum of a face C. It results in the formation of the plate crystals of corundum and boehmite.

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