

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

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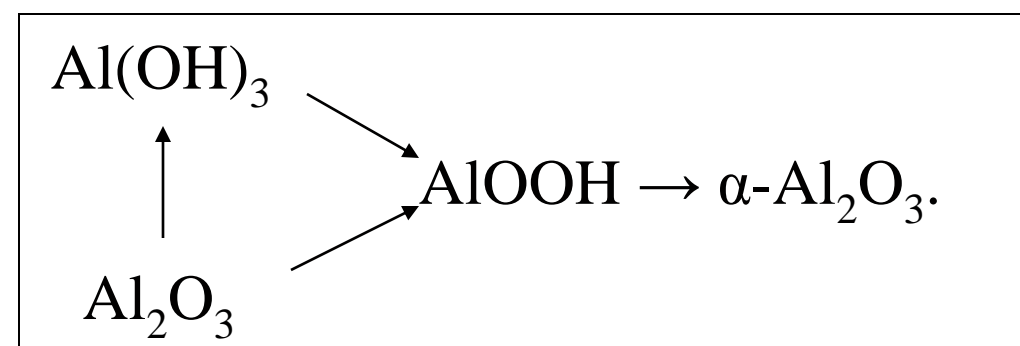
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INTRODUCTION

Earlier [1, 2] it was shown, that the process of aluminum hydroxide (hydrargillite) transformation into corundum in supercritical water fluid ($T=400^{\circ}\text{C}$, $P=20\text{--}26\text{ MPa}$) occurs due to the quasi-equilibrium processes of hydroxylation - dehydroxylation of structure of hydrargillite or boehmite with gradation in direction of theirs dehydration:



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.

In this report the results of studies of processes, taking place in fluids of primary alcohols, and in solid phase, aluminum hydroxide, in autoclave in the same conditions ($T=400^{\circ}\text{C}$, $P=20\text{ MPa}$) are represented.

MATERIALS AND METHODS

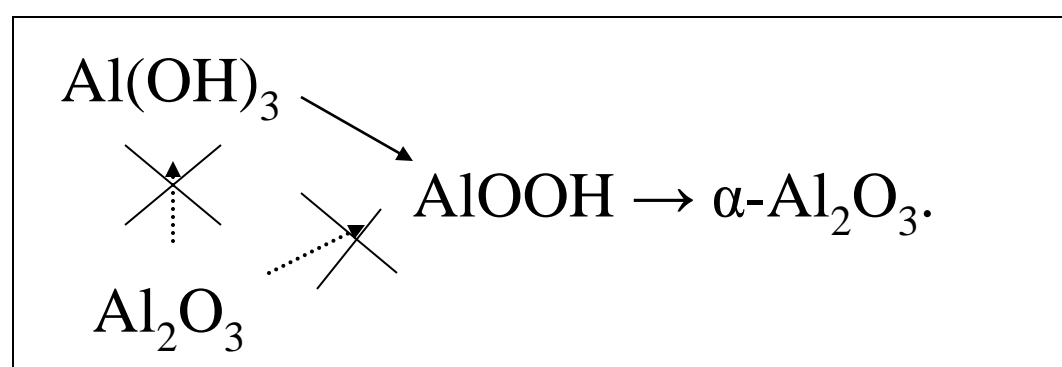
For study of transformation hydrargillite into corundum in supercritical fluids of alcohols the methanol and ethanol of the mark “for chromatography”, methanol “chemically pure”, ethanol “A” and “high pure” were utilized. As raw material was used industrial hydrargillite of the mark “GD-00”.

The products of alcohols transformation in supercritical conditions in contact with $\text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ 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.

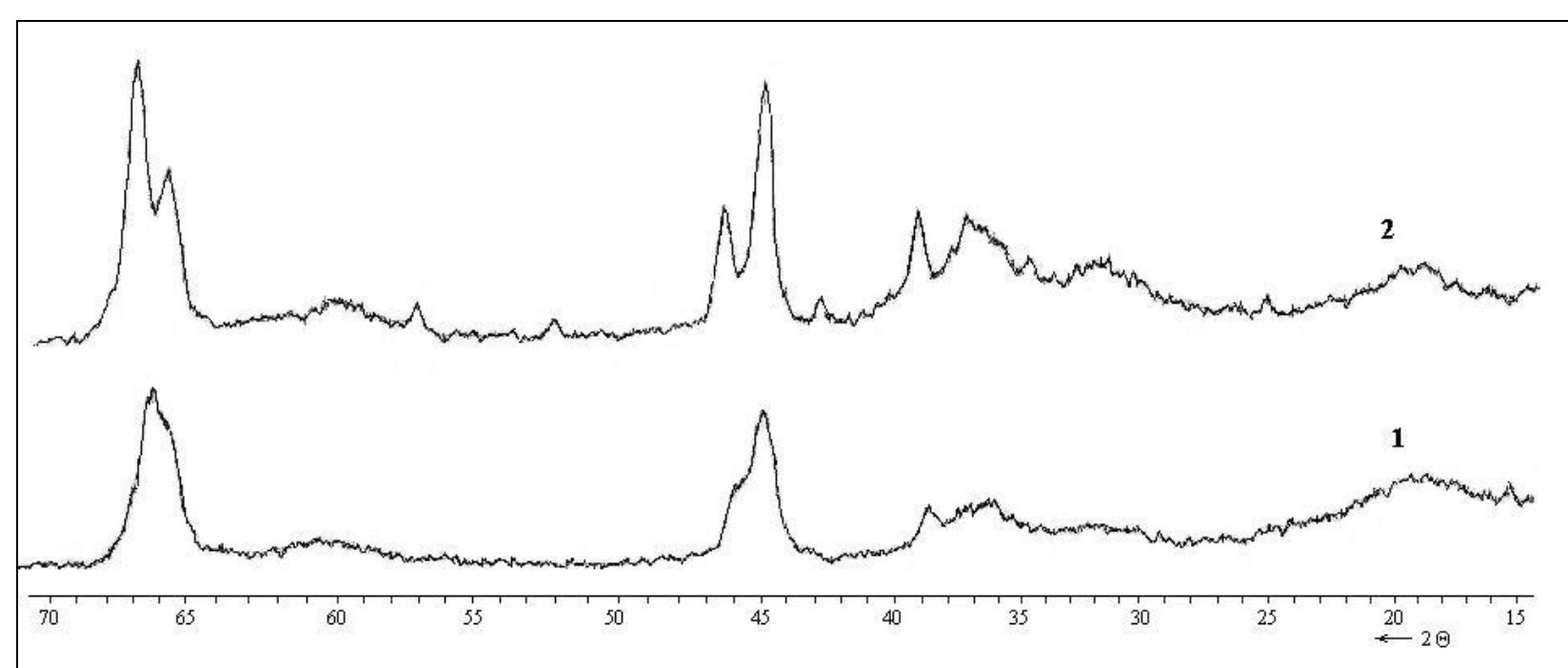
The heat treatment of $\text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ in supercritical fluid of alcohols was carried out in laboratory autoclaves (18 cm^3). The container with raw material in autoclave is located. The alcohol was filled between walls of autoclave and container. The temperature of realization of the process was 400°C . The pressure of alcohol was 20 MPa .

RESULTS AND DISCUSSION

The process of hydrargillite transformation in supercritical fluid of alcohols 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.



However, hydroxylation of aluminum oxide in medium of alcohol does not happen.



The interaction of alcohol with Al_2O_3 does not result in formation of a boehmite and corundum, but ordering structure of aluminum oxide is observed.

The reflexes in the diffractogram of aluminum oxide become more acute and more intensive (Figure 3).

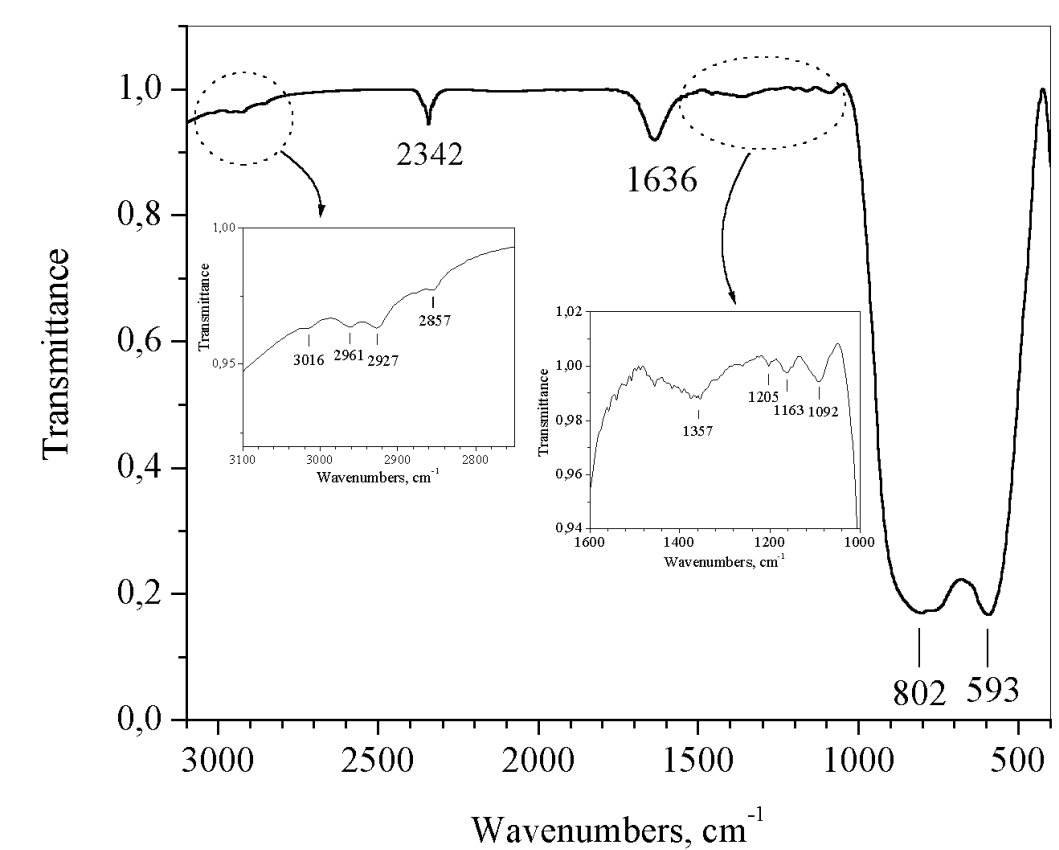


Figure 6. IR-specter of aluminum oxide in methanol after treatment by methanol fluid at 400 C .

It is interesting to mark, that in supercritical methanol fluid without water vapor also takes place the grafting of alkoxy - groups to aluminum-oxygen frame of aluminum oxide. The bands in IR-spectrum in the range of $1000\text{--}1500\text{ cm}^{-1}$ and $2800\text{--}3000\text{ cm}^{-1}$ testify to it (Figure 6). 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.

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).

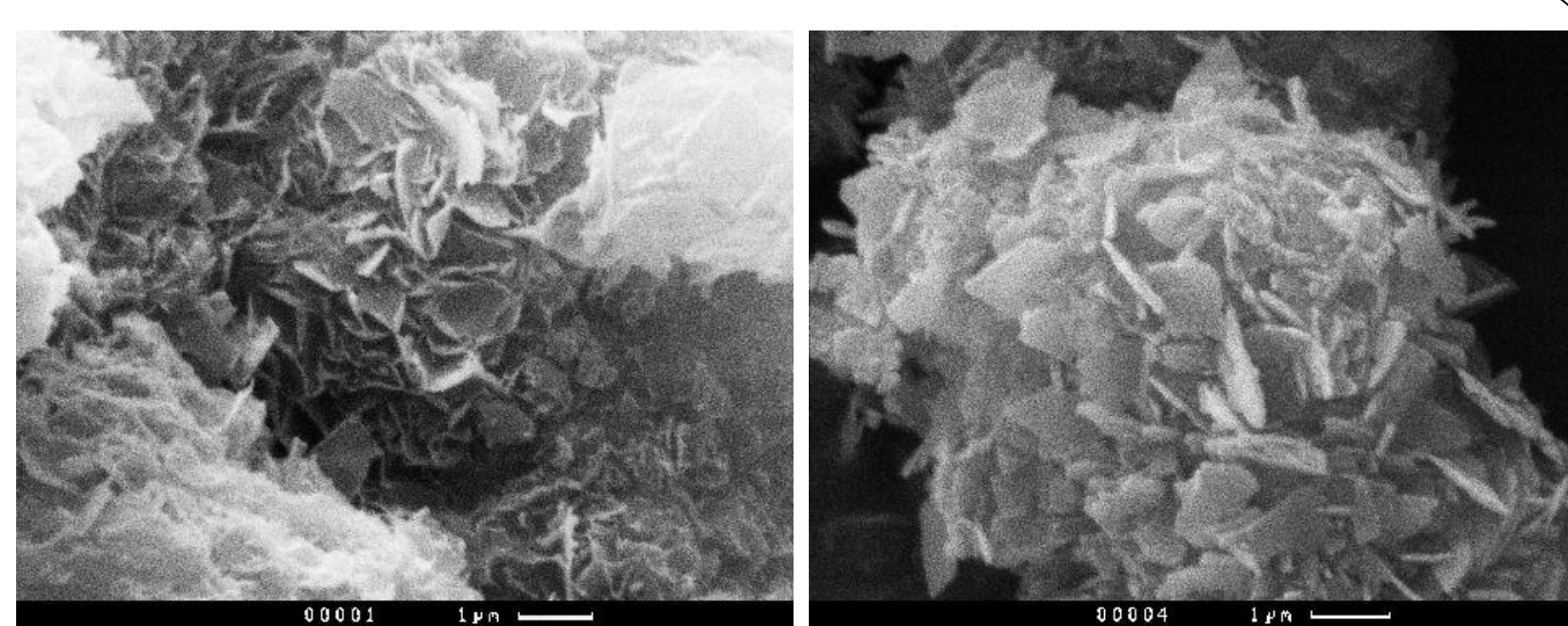
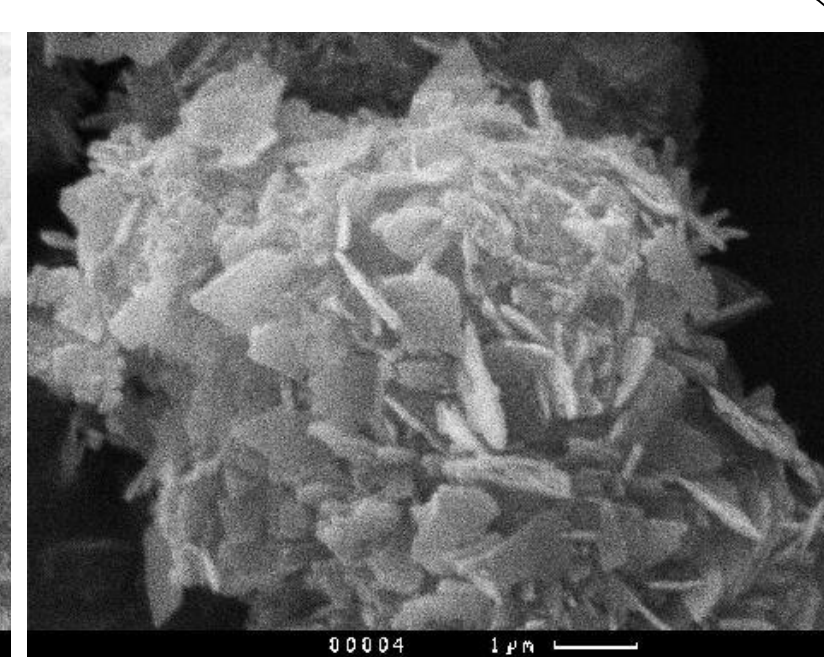


Figure 1. The boehmite obtained in methanol, 200 C



The boehmite obtained in ethanol, 200 C

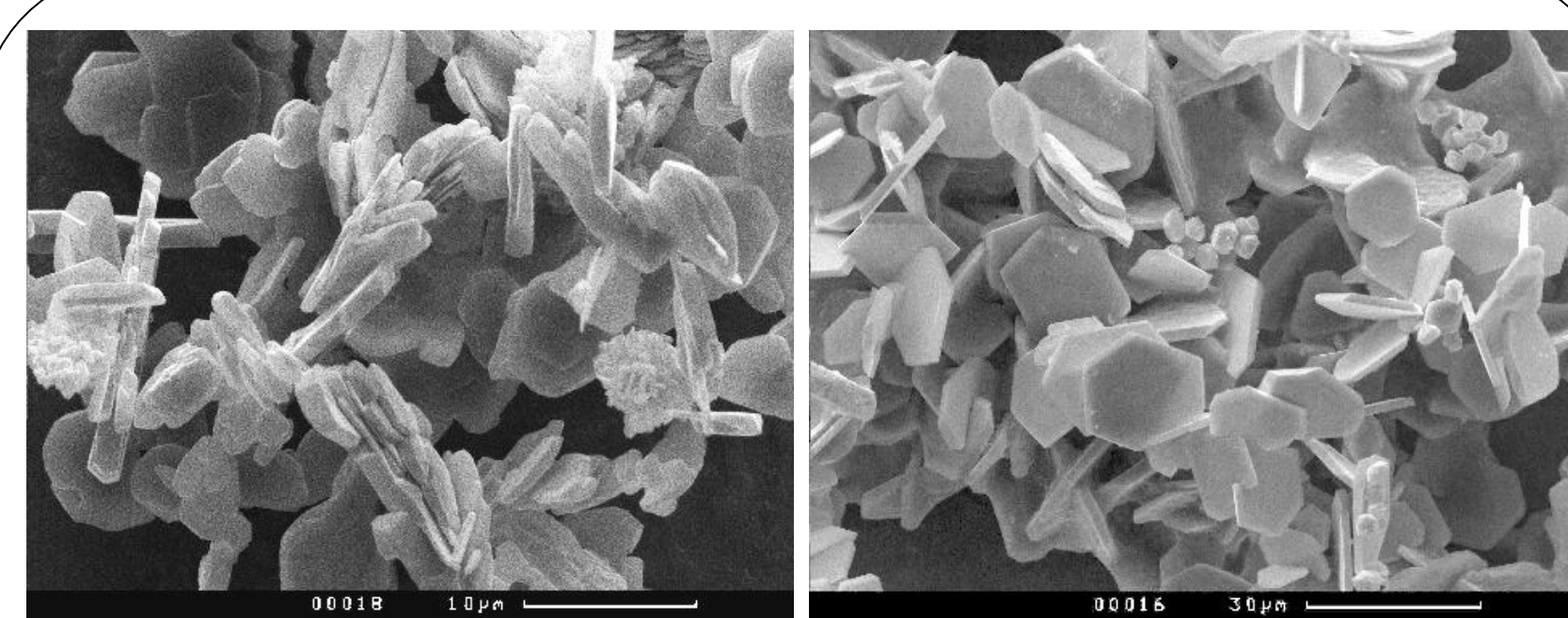


Figure 2. Corundum obtained in ethanol, 400 C

Corundum obtained in methanol, 400 C

The IR-spectrums of boehmite, obtained in methanol fluid, except the bands typical for boehmite, obtained in water fluid, contain absorption bands of small intensity in the region of $2850\text{--}2960\text{ cm}^{-1}$ and $1000\text{--}1500\text{ cm}^{-1}$ (Figure 4). These bands are referred to alkoxy - 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 aluminum-oxygen oscillatory 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 alkoxy - groups on some aluminum-oxygen oscillations. These grafted alkoxy - groups are partially saved in corundum obtained from it boehmite (Figure 5). The variation of the corundum habitus can be connected with such influencing of alkoxy - groups.

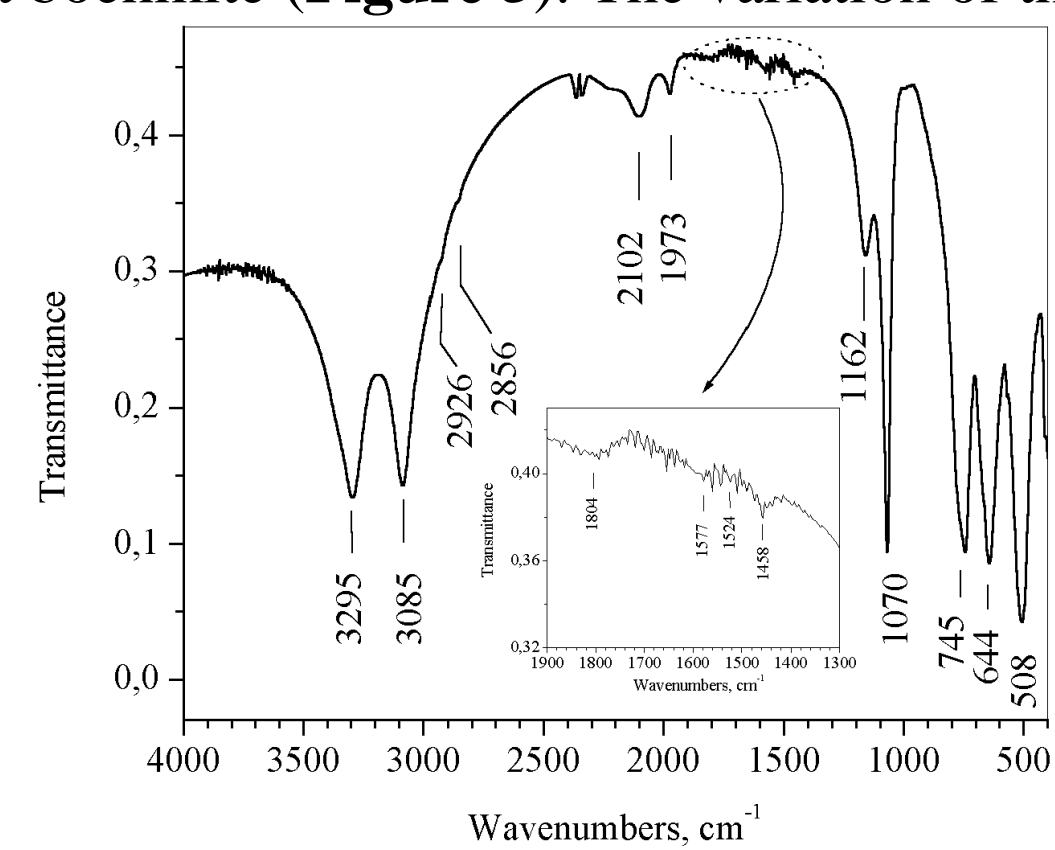


Figure 4. IR-specter of boehmite, obtained in methanol, 400 C , 1 h .

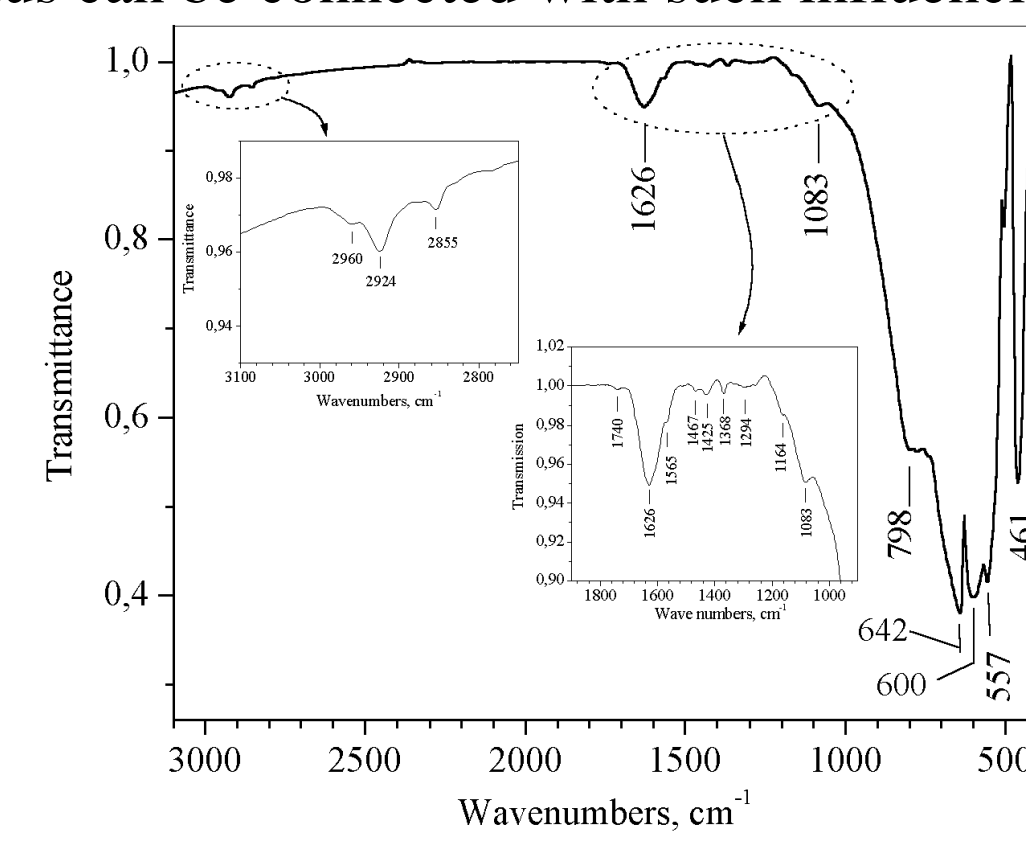
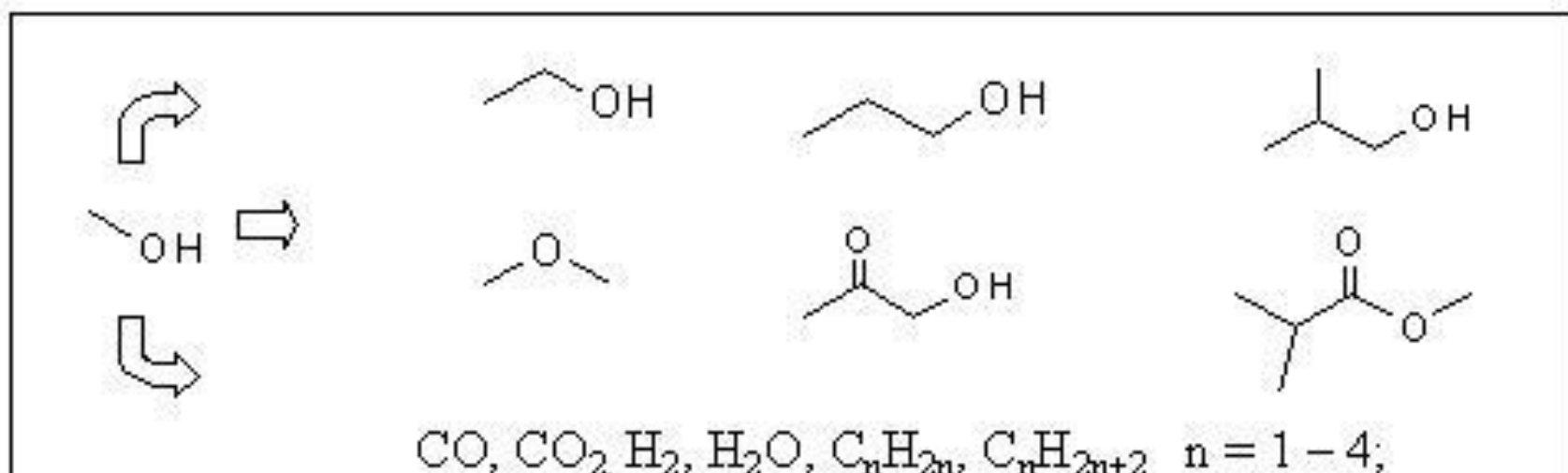
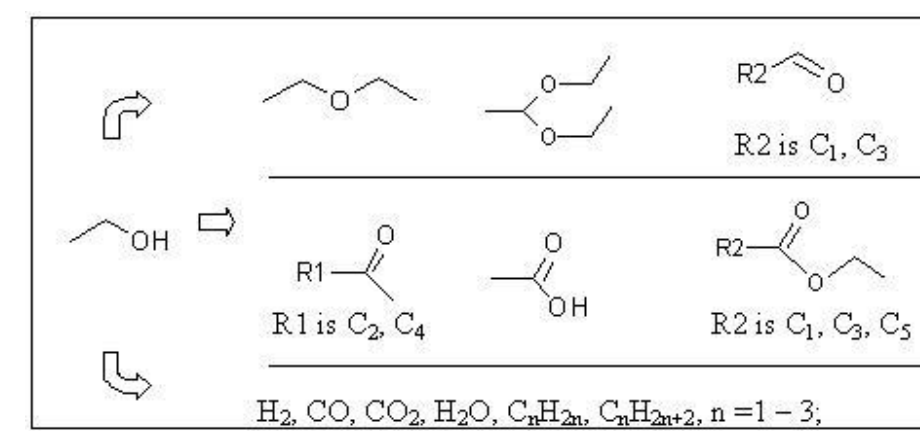


Figure 5. IR-specter of corundum, obtained in methanol, 400 C , 21 h .

Simultaneously with solid-phase transformations in alcohol fluid the diversiform reactions proceed. The range of generated products are very wide. The water removes from structure of hydrargillite and boehmite during their transformation and interacts with alcohol. At terminating of process the relation of alcohol moles to moles of water decreases up to 3. Simultaneously there is a catalytic pyrolysis of alcohol. The products of transformation of alcohol fluid at ambient temperature represent gas and liquid phases. For short time (1.5 hours) of the treatment of hydrargillite in fluid of methanol at 400°C in the gas phase CO , H_2 , methane, ethane, propane are derived. In a condensate except for methanol the traces of dimethoxy methane are detected. After 60 hours of treatment of boehmite in methanol the composition of products is dilated. Their total does not exceed 5% :

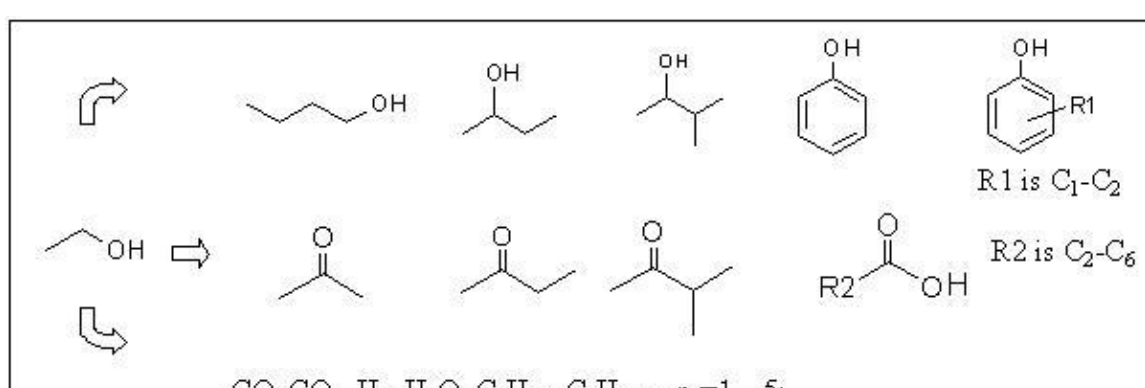


The composition of products in ethanol fluid after corundum synthesis depends also on purity of starting alcohol. At usage of ethanol of the grade “High pure” the following products are detected:



Main products are: acetaldehyde, ethoxyethane, ethyl acetate. Their amounts do not exceed 5% . Other products are present at amounts less than 1% .

In products of transformation of ethanol of the grade “A” are detected:



$\text{CO}, \text{CO}_2, \text{H}_2, \text{H}_2\text{O}, \text{C}_n\text{H}_{2n}, \text{C}_n\text{H}_{2n+2}, n=1-5.$

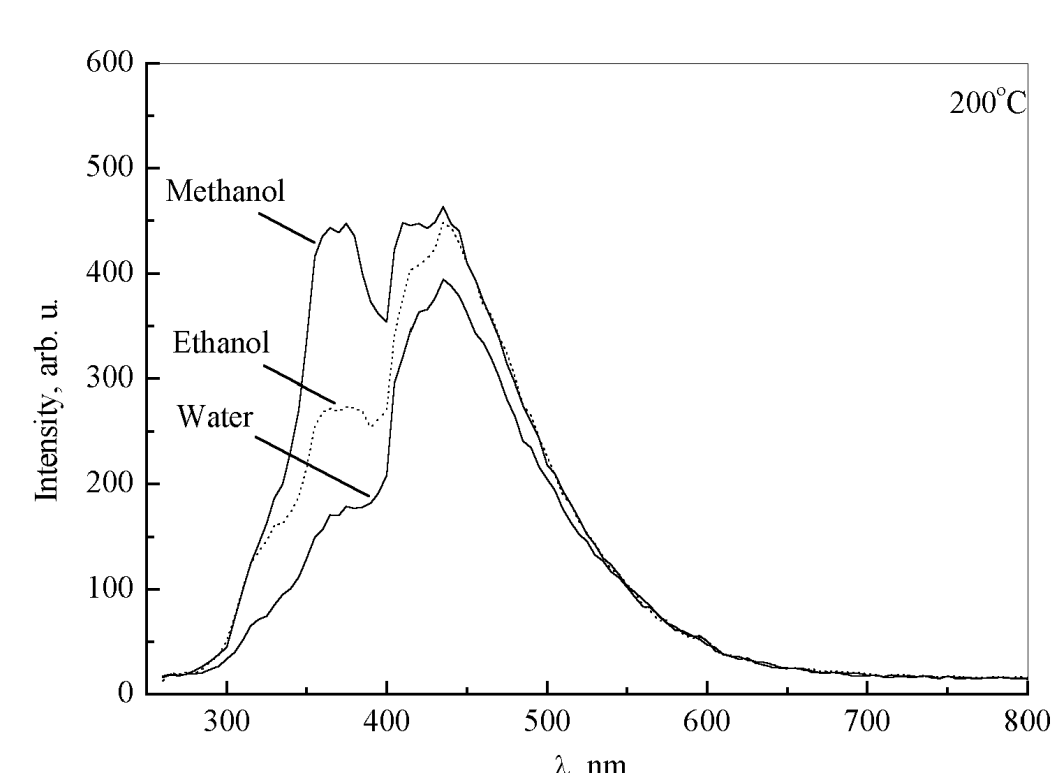
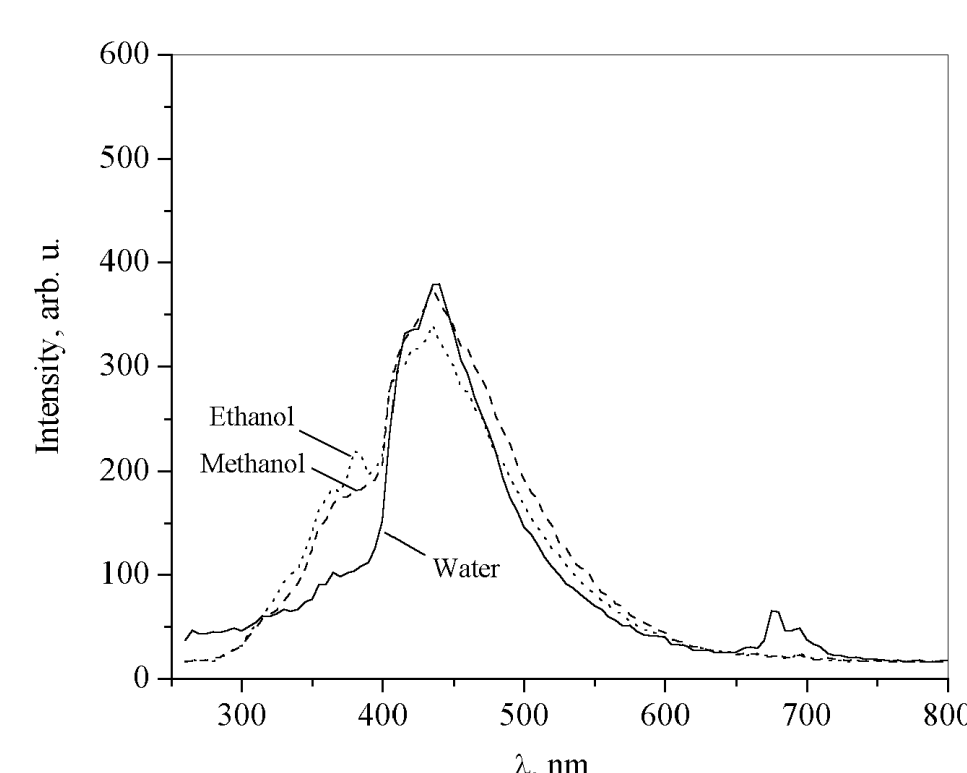


Figure 7. The luminescence specter of boehmite.



The luminescence specter of corundum.

At formation of boehmite in reduction medium the heightened amount of oxygen vacancies in generated boehmite are produced. It is exhibited in magnification of intensity of the luminescence bands in the region of $300\text{--}500\text{ nm}$ (near 370 nm). These bands are related to F - centers, which have arisen on basis of anionic vacant centers (Figure 7). The Figure 7 demonstrates, that the boehmite and corundum, synthesized in fluid of methanol, contains the greatest amount of F-centers.

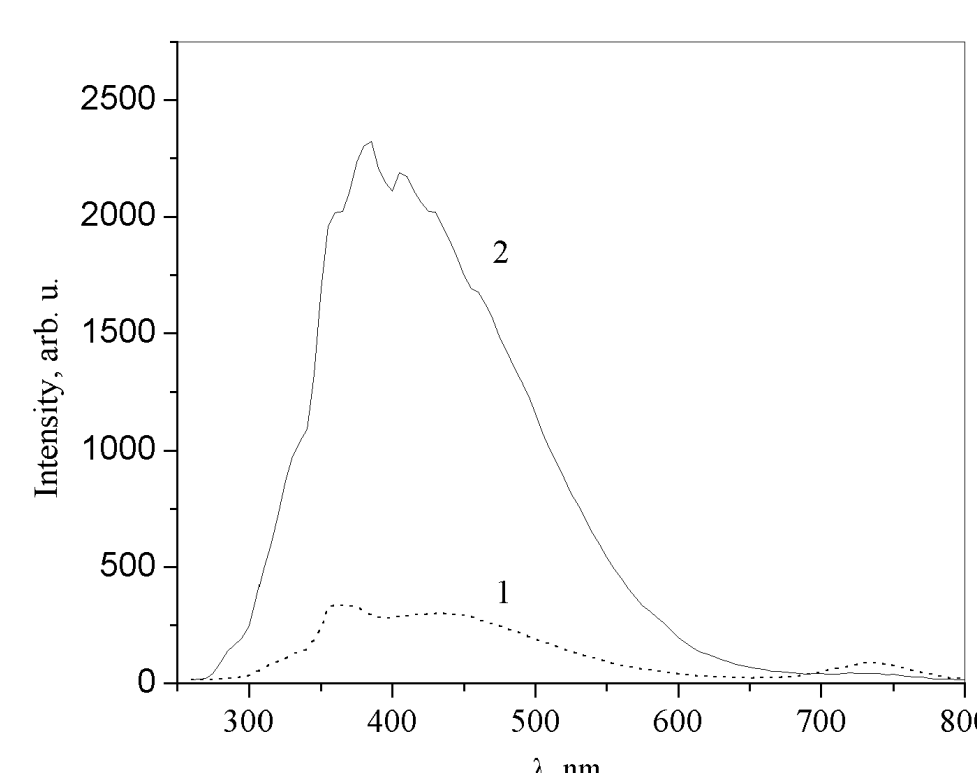


Figure 8. The luminescence specter of aluminum oxide before (1) and after (2) treatment by methanol fluid at 400 C .

Figure 8 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.

CONCLUSION

The study of processes, which are proceeded in the system: “supercritical fluid of primary alcohols - the hydroxide of aluminum ($T=400^{\circ}\text{C}$, $P=20\text{ MPa}$)”, 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.

References:

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