

THE REACTION OF THERMAL DECOMPOSITION OF AMMONIUM ANALCIME

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To investigate the mechanism of thermal decomposition of natural ammonium-bearing aluminosilicates the ammonium-exchanged form of natural analcime $\text{Na}_{1.83}[\text{Al}_{1.88}\text{Si}_{4.12}\text{O}_{12}]\times 1.97\text{H}_2\text{O}$ (r.Nidym, Siberian platform) was used as a model object. Thermal decomposition of NH_4 -analcime was studied by DTG, gas chromatography and IR spectroscopy at 25-700°C.

The DTG curve of NH_4 -analcime contains one peak between 400° and 700° with maximum at 600° of 12.2% weight loss. According to gas chromatography, in this temperature interval NH_4 -analcime loses 12.3 wt.% of water and 1.5 wt.% of nitrogen. At room conditions the NH_4 -analcime is waterless. Thus we can suppose that at rising temperature the water is formed by reaction between the ammonium hydrogen and the framework oxygen - dehydroxylation. This process evidently leads to significant destruction of the framework, due to a large amount of water removed from the sample. The nitrogen formed at the decomposition of ammonium is fixed in the sample and only partially removed at 700°.

IR spectrum of NH_4 -analcime contains at room temperature in the region of 2500-4000 cm^{-1} only absorption bands of NH_4^+ -ion (cm^{-1}): 1430, 3060, 3250 and overtone 2850. The deviation from selection rule for tetrahedral molecule - appearance in the IR spectrum of band 3060 cm^{-1} (ν_1) and splitting of band 1430 cm^{-1} (ν_4) observed at -160° - evidences for the distortion of the NH_4^+ -ion configuration [1] influenced by hydrogen bonds with the framework oxygen.

The decomposition of NH_4^+ -ions starts at 400° and reaches its half-way at 500°, according to the gradual decreasing of corresponding bands in the IR spectrum (Fig.1). The narrowing of the band 1430 cm^{-1} of bending vibrations of the NH_4^+ -ion at 550° evidences for its geometry to approach to the ideal tetrahedron. This is probably related to the changing of its hydrogen bonds with the framework due to the deformation of structural channels.

At $t=550$ -650° the bands 1330, 1625 cm^{-1} of ammonia bonded to Lewis acid sites $\equiv\text{Al}:\text{NH}_3$ [2] are observed in the IR spectrum. These bands increase in intensity with temperature in parallel with decreasing of the NH_4^+ -ion bands intensity, and practically disappear at 700°. The formation of complexes $\equiv\text{Al}:\text{NH}_3$, most probably located in the framework, is caused by several factors. Narrow channels of the analcime structure prevent fast diffusion of ammonia formed at the decomposition of NH_4^+ -ions. At $t > 550^\circ$ the dehydroxylation of the framework proceeds intensively giving rise to Lewis centres - coordinately unsaturated aluminum species. These centres

are known to adsorb easily the ammonia molecules to form stable complexes $\equiv\text{Al}:\text{NH}_3$ [3].

A sharp changes of the spectrum in the region of the framework overtone vibrations 1500-2000 cm^{-1} at 550° are probably related to the transformation and starting destruction of the analcime framework, caused by dehydroxylation.

Start from 550° a shoulder of O-H stretching vibrations in hydroxyl groups appears in the region of 3600 cm^{-1} (fig.1). As it was suggested, these groups are localized in the framework. As temperature increases, this shoulder is shifted to high frequencies and decreases in intensity. The band 3660 cm^{-1} observed at 650° seems to correspond to mixed absorption of OH-groups and molecular water.

The decomposition of ammonium and complexes $\equiv\text{Al}:\text{NH}_3$, as well as the removal of water from the sample are almost completed at 700°, according to IR spectroscopy and gas chromatography. The calculation of weight loss in NH_4 -analcime shows that the formation of 12.3 wt.% of water requires a complete decomposition of ammonia on nitrogen and hydrogen. Evidently this is the case, as ammonia is unstable at high temperatures. Moreover, the framework "activated" by dehydroxylation seems to catalyze the decomposition of ammonia.

The kinetic diameter of the nitrogen molecule exceeds the diameter of structural channels in the analcime framework by about 1 Å [4]. This is one of the reasons for fixing of nitrogen in our sample. We also have to suppose that a part of nitrogen forms chemical bonds with the framework atoms to restore the charges balance disturbed at dehydroxylation when the analcime framework loses one fifth part of the total amount of oxygen.

Thus we can divide the process of thermal decomposition of NH_4 -analcime into several steps:

400° - beginning of decomposition of ammonium on ammonia and protons, formation of the framework hydroxyl groups;

550° - beginning of dehydroxylation, further decomposition of ammonium, formation of complexes $\equiv\text{Al}:\text{NH}_3$, strong deformation of the framework;

600-650° - decomposition of complexes $\equiv\text{Al}:\text{NH}_3$ and ammonia, dehydroxylation with mass removal of water;

700° - completion of decomposition of ammonium and ammonia, destruction of complexes $\equiv\text{Al}:\text{NH}_3$ and dehydroxylation, partial removal of nitrogen.

The peculiarity of the analcime structure - the presence of narrow channels in its framework - causes active interaction of the ammonium decomposition products with the framework leading to its destruction at 700°.

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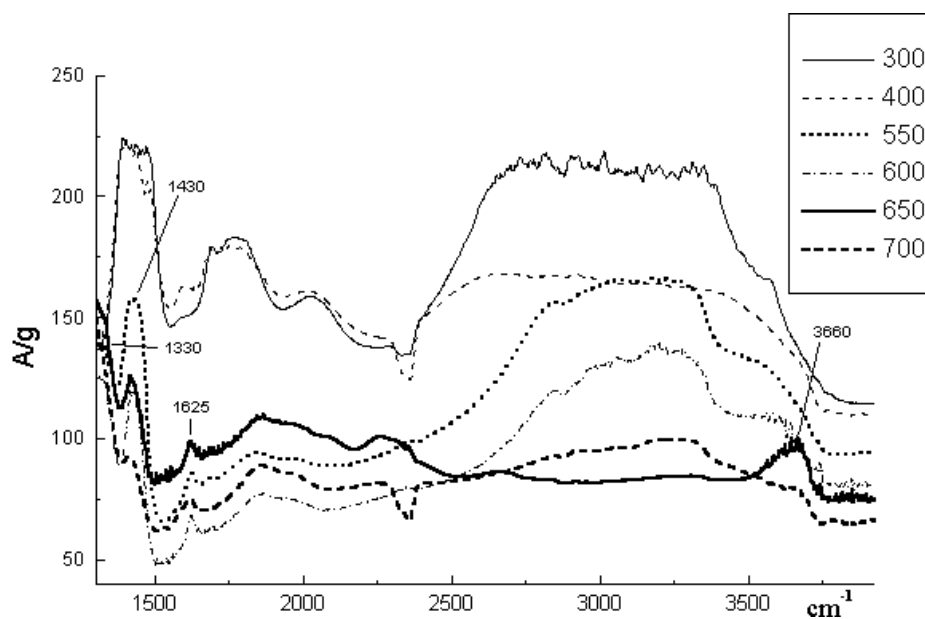


Fig. 1. IR spectra of NH_4 -analcime at 300-700°C (A/g - normalized optical density)