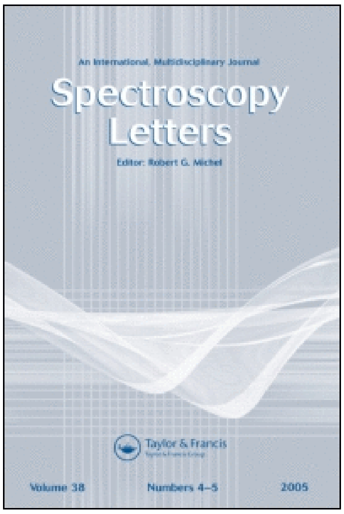

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The Role of Infrared Spectroscopy and X-Ray Diffraction Analysis in the Investigation of the Influence of Fluorides on the Process of Calcination of Aluminium Hydroxide

Stojan R. Stojković[a]; Živan D. Živkovid[a]; Nada D. Štrbac[a]; Ivana S. G. StojkoviĆ[a]
[a] Technical Faculty at Bor, University in Belgrade, Bor, Yugoslavia

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THE ROLE OF INFRARED SPECTROSCOPY AND X-RAY DIFFRACTION ANALYSIS IN THE INVESTIGATION OF THE INFLUENCE OF FLUORIDES ON THE PROCESS OF CALCINATION OF ALUMINIUM HYDROXIDE

KEY WORDS: Ir spectrophotometry, X-ray diffraction, aluminium fluorides, calcination, aluminium hydroxide, alumina.

Stojan R. Stojković, Živan D.Živković, Nada D.Štrbac
and Ivana S.G. Stojković

University in Belgrade
Technical Faculty at Bor, Bor
Yugoslavia

ABSTRACT

The aim of this work was to check the possibility that by use of infrared spectroscopy the influence of fluorides on the calcination process of aluminium hydroxide can be followed. The DTA method shows it clearly. It was, namely,found that the added fluoride influences the process of polymorphous transformation of the formation of α-Al_2O_3 from $Al(OH)_3$. According to DTA, IR, and X-ray analyses, it was found that the added fluoride lowers the temperature of the mentioned transformation for some 300 degrees.

For this purpose recorded were IR spectra and X-ray difractograms of pure $Al(OH)_3$ as well as of such samples with added fluoride, in this case of AlF_3, in the range of 0.1 to 10 per cent. The samples were examined in the temperature range of 298 to 1673 K in different time intervals.

INTRODUCTION

In the work of Bulgakov et al. [1] , using infrared spectra, data on skeletal vibrations of aluminium fluoride compounds are given. Absorption band appearing at 660 and 540 sompounds are given. Absorption bands appearing at 660 and 540 cm^{-1} correspond to the sekelton of waterless aluminium fluoride. Bands at 645 and 585 cm^{-1} are assigned as sekeletal vibrations of the lattice of aluminium hydroxo-fluoride. The valence and deformation vibration of the structural OH groups appear at 3680 and 1108 cm^{-1} respectively. Another work of the same authors [2] is based on the possibility of interaction of the structural vibration of OH groups from aluminium hydroxo fluoride at 3680 cm^{-1} with molecules being adsorbed, as well as with their substitution at contact with D_2O vapour.

In the present work, by X-ray diffraction and IR spectroscopy the changes were followed which result from the process of calcination of aluminium hydroxide. This process comprises dehydration and structural transformations of dehydrated aluminium oxide [3,4,5] . Schematically, the observed process may be envisaged as

$$Al(OH)_3 \xrightarrow{473\text{-}523\ K} AlOOH \xrightarrow{723\text{-}773\ K} Al_2O_3 \xrightarrow{1023\text{-}1223\ K} \alpha\text{-}Al_2O_3$$

According to the opinion of the author of Ref. 5, the interaction of AlF_3 and water at 723-773 K produces first HF. It is being adsorbed on the surface of γ-Al_2O_3. Increase of temperature leads to a weakening of the bonds in the crystal lattice, leading at 1173 K to an energy of activation enabling the transformation of γ-into α-Al_2O_3. According to Belitskii [6] , fluorine has no catalytic influence on the transformation. It is being incorporated into the lattice of aluminium oxide and forms solid solutions.

EXPERIMENTAL

For the present investigations aluminium hydroxide produced by KAP (Aluminium Combine, Podgorica, Yugoslavia) was applied.

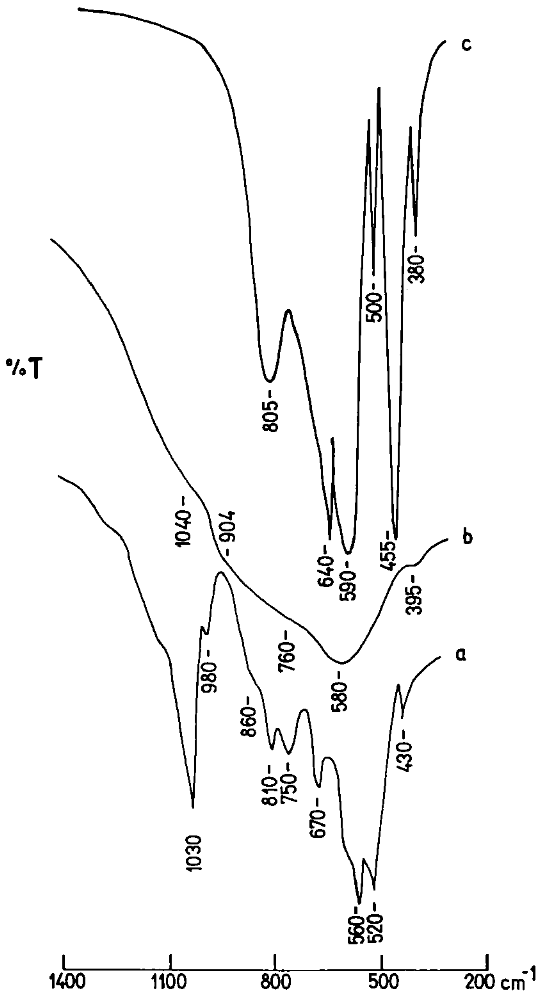

Fig.1. Infrared spectra of Al(OH)3 with various added amounts of AlF3: a-0.3%, b-1% and c-3%,

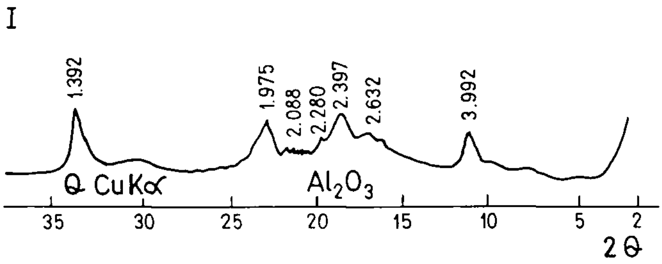

Fig. 2.X-ray diffractogram of $Al(OH)_3$ with 1% AlF_3 heated to 1193 K.

The X-ray difraction analyses, with the purpose of mineralogical characterization of the samples, were done with a Siemens diffractometer. Recordings were made with a Cu anticathode, the radiation being filtered with nickel filters. The current was 20 mA with a voltage of 40 kV.

The IR spectra were recorded with a Perkin-Elmer 983 G spectrophotometer, using the pellet method. The pellets were prepared by mixing of 0.3 mg of the sample with 150 mg of KBr.

RESULTS AND DISCUSSION

In order to determine the optimum amount of the fluoride added to the $Al(OH)_3$ sample during crystallization, a series of IR spectra were recorded with samples containing from 0.3 to 10 per cent of AlF_3.

According to the cpectra, shown in Fig.1, it may be concluded that the samples with 0.3 and 1% of AlF_3 are incopmletely crystallized. The samples with 3% or more show a complete crystalline form of α-Al_2O_3 at 1573 K. According to the band assignments the following can be concluded. The band at 380 cm^{-1} corresponds to the vibrations of the pore openings of the outer rings. In the spectra a and b of Fig.1 it may be seen that bands at 430 and 460 cm^{-1} in the spectrum c (3% AlF_3) are transformed into a band with a maximum at 450 cm^{-1}; the band at 590 cm^{-1} is getting a weak shoulder which practically does not influence the position of the maximum when the concentration of AlF_3 is changed. These bands correspond to the isolated AlO_6 octahedra of α-Al_2O_3 and belong to the normal vibrations ν_{4a} (E) and ν_2 (A1) 7 . The band at 640 cm^{-1} , according to the calculated coordination number by the Dehill-Roy relation, is in full

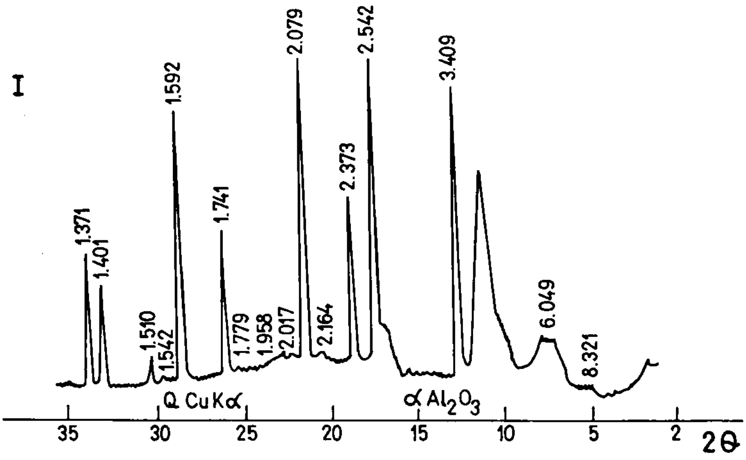

Fig.3.X-ray diffractogram of Al(OH)3 with 1% AlF_3 heated to 1523 K.

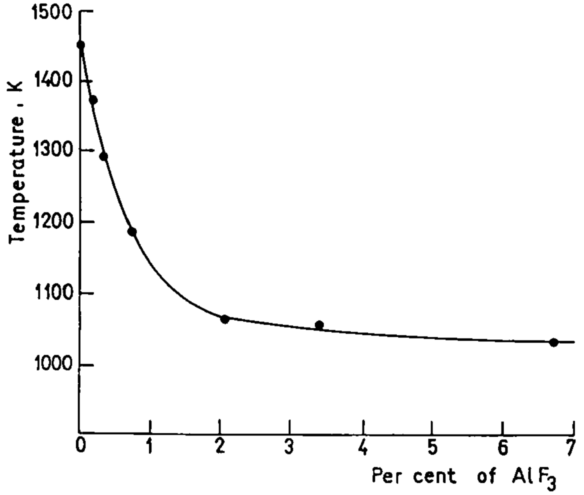

Fig.4.The influence of the amount of added fluoride on the temperature of crystalization of α-Al_2O_3.

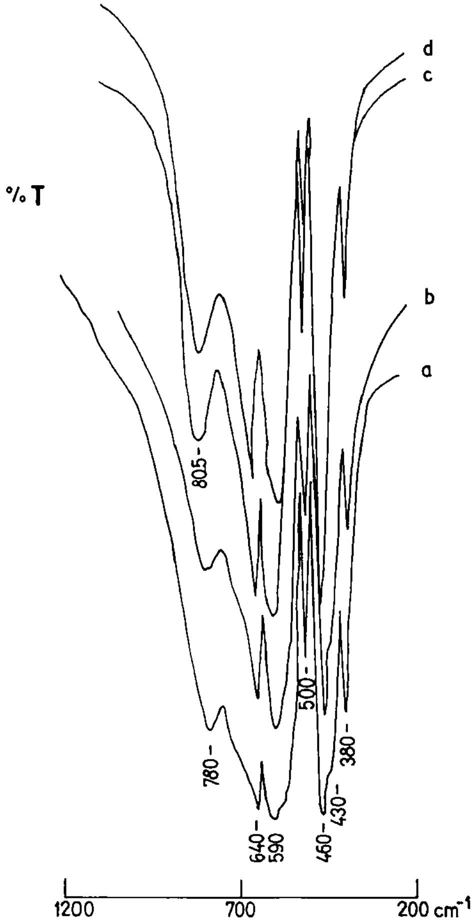

Fig.5.Infrared spectra of samples: α-$Al(OH)_3$; b-Al_2O_3, 673 K; c-Al_2O_3, 1073 K; d-Al_2O_3, 1300 K.

agreement with the data of X-ray analysis, which is a proof of the presence of AlO_6 octahedra in α-Al_2O_3. The band at 780 cm^{-1}, which is present at concentration of 0.3%, with the increase of AlF_3 concentration shifts to higher wave numbers, up to 805 cm^{-1}. It is assigned to valence vibrations of isolated AlO_4 tetrahedra.

For the samples of $Al(OH)_3$ with 1% of AlF_3, heated to temperatures 1193 and 1523 K, X-ray analyses were done. The diffractogram shown in Fig. [2] does not contain expressed α-Al_2O_3 phases, but reflections due to x-Al_2O_3, meaning that the process of crystallization is not terminated. After heating of the same sample to 1523 K, the α-phase appears, as seen in Fig.3.

According to the applied techniques for the following of the changes occurring during the calcination of $Al(OH)_3$, it may be concluded that infrared spectra yield more accurate results. This is confirmed also by the curve of the influence of the added amount of fluoride at the temperature of α-Al_2O_3 crystallization, shown in Fig.4, which is obtained from DTA data. It shows that only at concentrations of AlF_3 above 3% a constant experimental temperature of the peak maximum is attained.

The temperature changes in infrared spectra of Al_2O_3 with added fluoride are shown in Fig.5. As it may be seen, the temperature increase changes the shapes of the spectra.

Spectrum a, corresponding to $Al(OH)_3$ heated to 373 K, shows in the 400 to 500 cm^{-1} range the deformation vibrations of AlO_4 tetrahedra. The 500 to 680 cm^{-1} range contains vibrations of bonded AlO_6 octahedra. The interval of 750 to 900 cm^{-1} displays the bands of asymmetric valence vibrations of bonded $AlO4$ tetrahedra. The band 1030 cm^{-1} corresponds to the vibration of the -O-Al-O group. Spectrum c, which corresponds to a temperature of 1070 K, shows the presence of crystalline phase g-alumina. The bands at about 620 and 770 cm^{-1} are due to valence vibrations of AlO_6 octahedra and to valence vibrations of isolated AlO_4 tetrahedra respectively. The appearance of the spectrum with broad an ill defined bands points to the fact that crystalline γ-alumina has a lesser ordering compared with a-alumina, shown in spectrum d. This result is the consequence of deformations of its crystal lattice, leading to a decrease of the bonding strength in it. This in turn produces a decrease of activation energy enabling a complete transition of γ-Al_2O_3 into α-Al_2O_3.

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