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RDF method application to phase analysis of X-ray amorphous products of gibbsite thermal activation

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Abstract. The phase compositions of finely dispersed initial and rehydrated products of gibbsite thermal activation prepared by different technological methods – thermochemical activation (TCA) and centrifugal thermal activation (CTA) were studied using radial distribution function (RDF) method. The initial phase composition was shown to depend on the preparation method and determine the composition of the rehydrated products. Nuclei of different hydroxide phases are formed in addition to χ-alumina – pseudoboehmite in the case of the TCA process and bayerite for the CTA process. This leads to different phase compositions of rehydrated products. For TCA, pseudoboehmite is the primary rehydration product, whereas bayerite is formed for CTA.

Introduction

Due to their unique properties, alumina materials are widely used as ceramics, adsorbents, catalyst components and catalyst supports. Usually alumina materials are prepared by thermal decomposition of the corresponding hydroxides. Pulse thermal decomposition of gibbsite is one of the methods used for synthesis of active alumina. During this process crystalline gibbsite is transformed from a chemically inert state into a different metastable state with high surface area, high chemical activity and highly disordered structure [1]. Depending on the conditions, rehydration of the prepared product results in the formation of different hydroxides – pseudoboehmite AlOOH and bayerite $Al(OH)_3$. Thermal activation of these hydroxides leads to synthesis of γ- and η-Al_2O_3, which are very important catalyst supports. One of the methods used for gibbsite thermal activation is its thermochemical activation (TCA) in the counterflow of combustion gases [1]. Lately a new method for alumina synthesis has been developed at Boreskov Institute of Catalysis. A new hardware has been suggested for this process – TSEFLAR^{TM} installation (centrifugal flash reactor) [2, 3]. It secures ecological cleanliness and high reproducibility of the obtained centrifugal thermal activation (CTA) product.

Current publication is devoted to investigation of the phase composition of gibbsite thermal activation products prepared by different methods and products of their rehydration.

Methods

The phase composition of finely dispersed initial CTA and TCA products was studied using the RDF (radial distribution function) method commonly used for investigation of such materials. Calculated pair functions were presented as radial distribution of electron density curves. The experimental X-ray scattering curves were processed using the original computer program developed at Boreskov Institute of Catalysis [6].

Model curves used in this study were calculated using a previously described method [7, 8] and Mathcad 2001i Professional © computer software. Reference structural data [9] for pseudoboehmite and bayerite were used.

Quantitative phase analysis of the crystallized rehydration products was carried out using calibrating graphs constructed in $I_1/I_2 = f(C_1)$ coordinates, where I_1 and I_2 are the intensities of selected diffraction peaks of different phases, C_1 is the weight concentration of one of these phases.

Experimental

Finely dispersed initial gibbsite CTA and TCA products and materials prepared by their rehydration in alkaline medium at room temperature for 1 and 7 days were used in the study. Diffraction patterns of the initial products in the Bragg angle range 3-140°, wavelength 0.7 Å were obtained using high resolution diffractometer in the Siberian Synchrotron and Terahertz Radiation Centre (Budker Institute of Nuclear Physics, Novosibirsk, Russia). The rehydrated products were studied using HZG-4 diffractometer with monochromated copper irradiation.

Results

Figure 1 presents the diffraction patterns of the CTA and TCA products recorded using synchrotron irradiation. The diffraction patterns of the samples are very similar. They mostly consist of one diffuse peak at d/n=1.397Å belonging to χ-Al_2O_3. Also the patterns show the presence of small amounts of crystalline hydroxide phases: the initial gibbsite and crystallized boehmite.

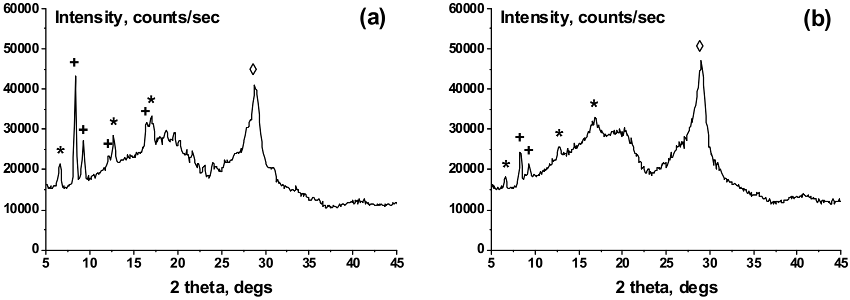

*Figure 1. Diffraction patterns of the TCA (a) and CTA (b) products, ◊ –amorphous χ-phase, * – boehmite, + – gibbsite.*

Figure 2 schematically shows the changes in the phase composition of the CTA and TCA products occurring during rehydration according to the data of quantitative XRD analysis. The initial products mostly consist of the amorphous χ-like phase. After rehydration for 24 h the CTA product is converted to bayerite whereas the TCA product is converted to boehmite. After 150 h the transformation of the CTA product to bayerite continues, whereas boehmite formed from the TCA product is converted to bayerite. We tried to find the reasons for the differences observed in this process in the phase composition of the initial products because the rehydration conditions were identical.

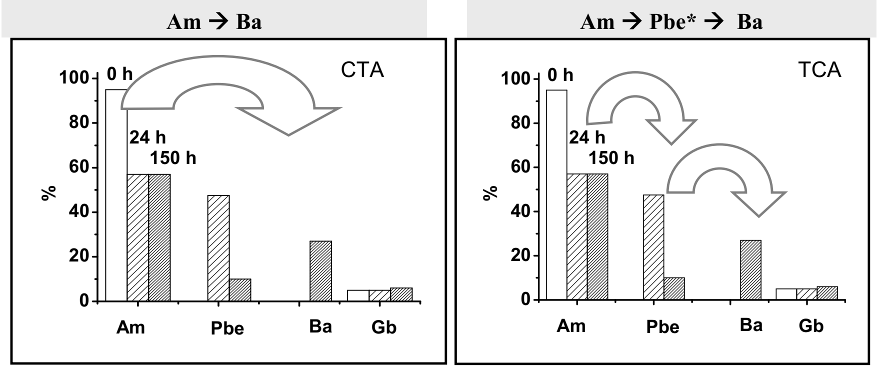

Figure 2. Diffraction patterns observed after rehydration of the TCA and CTA products in alkaline medium at 20°C. Am –amorphous χ-phase, Pbe – pseudoboehmite, Ba – bayerite, Gb – gibbsite, h - hours.

More detailed information on the phase composition of the initial TCA and CTA products was obtained using the RDF method. Figures 3 and 4 show RDF curves observed for these products in comparison with those calculated for the hydroxides. A strong peak is observed ca. 5 Å in the model RDF curve of bayerite. It is observed for the CTA product as well whereas it is absent in curve calculated for the boehmite structure. Meanwhile, interatomic distances typical for pseudoboehmite are observed for the TCA product. These observations led us to the conclusion that finely dispersed bayerite phase is the present in the CTA product whereas the TCA product contains pseudoboehmite. These phases are not observed in the diffraction patterns due to small coherent scattering area dimensions. These nanoparticles appear to act as nuclei for the formation of the bayerite and pseudoboehmite phases during rehydration. The presence of the bayerite nuclei in the CTA product after the gibbsite thermal decomposition may be caused by higher vapor pressure used in the CEFLAR process compared to the TCA process.

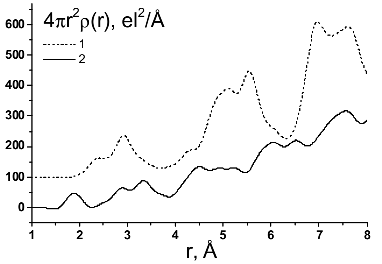

Figure 3. Model RDF curve calculated for the bayerite (1) phase and RDF curve of the CTA (2) product.

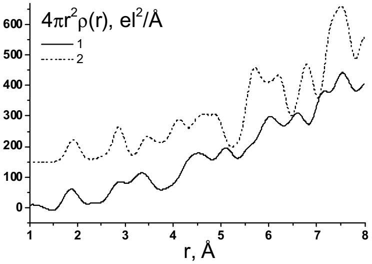

Figure 4. Model RDF curve calculated for the boehmite (1) phase and RDF curve of the TCA (2) product.

Conclusion

The phase composition of the initial finely dispersed products of the gibbsite thermal decomposition obtained using different methods has been determined using the RDF method. Finely dispersed phases of different hydroxides have been found for the thermal activation products in addition to phases observed by conventional XRD analysis.

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