HYDROTHERMAL SYNTHESIS OF ALUMINA MICRORODS

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A facile hydrothermal and thermal decomposition route was used to synthesize the alumina microrods with mesoporous structure. The as-synthesized products were characterized with use of Raman spectroscopy, XRD, SEM, thermal analysis and N_2 adsorption-desorption measurement. Formation of the ammonium aluminium carbonate hydroxide phase was ascertained to be an indispensable condition for formation of alumina microrods. Thermal decomposition of ammonium aluminium carbonate hydroxide was shown to afford formation of amorphous alumina microrods. These microrods are microporous-structured and crystallize as γ-Al_2O_3 at temperatures over 800˚C. With gases burning out, mesopores are formed with the amorphous alumina framework.

Introduction

Alumina is commercially widely usable as adsorbents, catalysts, and catalyst support due to their unique properties. The conventional chemical method for synthesis of alumina is dehydration of boehmite, but the morphology of alumina remains the same [1]. For specific applications, the mesoporous properties of the support have a large impact on the catalytic effect. Therefore, various methods describing preparation of mesoporous alumina with such adjustable parameters as surface area, pore volume and pore size with use of structure directing agents, such as different surfactants, were reported. However, alumina synthesized using this approach has relatively low thermal stability over time that limits its usefulness at high temperature. Therefore, preventing extensive shrinkage is the most important method to retain the morphology of mesoporous alumina.

The recent literature sources report a new strategy to synthesize mesoporous materials in a controllable thermal decomposition process [2, 3], where in the mesopores are generated via thermal decomposition of the salt precursors. During this process, generation of gases is accompanied by a marked shrinkage in the materials' framework.

Mesoporous alumina featured by morphologically retained adjustable surface area and pore volume was readily obtained from ammonium aluminium carbonate hydroxide thermally decomposed in presence of non-ionic surfactant as templating agent. This procedure afforded formation of the 1D alumina microstructure [4].

Herein, we described a facile hydrothermal route to synthesize ammonium aluminium carbonate hydroxide microrods without any surfactants and using alcohol as a structure directing agent. Moreover, we investigated the growth process of microrod structures and discussed the possible formation mechanism.

Experimental part

Alumina was prepared by baking products of homogeneous precipitation from nitrate or chloride solution under HT-conditions. Homogeneity of the process was attained by using carbamide as a precipitator. Molar ratios of the synthesis components were as follows: $1Al(NO_3)_3 \cdot 9H_2O$ $(AlCl_3 \cdot 6H_2O)$ // $5i$-PrOH// $85H_2O$// $2CO(NH_2)_2$. Synthesis temperature was varied in the 90-130° range. Duration of the synthesis was 65 h. Products were calcined in air atmosphere at 650 °C, whereupon they were isothermally kept for 5 h.

Low-temperature nitrogen adsorption isotherms were registered at -196 °C by means of the ASAP 2020 device (Micrometrics, USA), after degassing the material under vacuum at 350 °C for 3 h. Specific surface area (S) of specimens was calculated as per the BET method in 0.05-0.25 p/p_0 interval of relative pressure values. Total pore volume (V_{tot}) was calculated from the quantity of nitrogen adsorbed at relative pressure $p/p_0 \approx 0.99$. Pore size distribution and average pore diameter values were determined from desorption isotherms using the BJH method.

Diffractograms were registered by means of the automatic XRD-7000 diffractometer (Shimadzu, Japan) using the CuK_a-radiations in the angle interval $2\Theta=10-80°$.

Microphotographs of specimens were taken using an electron scanning microscope, model XR-3000 (Evex, USA).

Registration of Raman spectra was made using the multifunctional Senterra spectrometer (Bruker, Germany) in 400-1200 cm^{-1} diapason. Preparatory to registration, specimens were dried under vacuum at 105 °C.

Thermogravimetric analysis (TGA) and different scanning calorimetry (DSC) were carried out in a TGA/DSC 1 METTLER-TOLEDO analyzer ramped the temperature from 25 to 100 °C with an air flow at a heating rate 10 $K \cdot min^{-1}$.

Results and discussions

During hydrolysis of carbamide taken in excess to Al^{3+} ions, gradual isolation of hydroxyl ions throughout total volume of liquid phase takes place, this process not leading to local super-saturations of a solution. Under these conditions, a great deal of highly dispersive

primary particles as products of incomplete hydrolysis (basic salts) is formed. At a low coagulation rate and large super-saturation values, these particles, being amorphous, firstly coagulate into indefinitely formed aggregations. On the ageing, hydrolysis, dehydration, and crystallization processes continue within particles, thus, in the end, leading to formation of a regular crystalline structure of the material. Intensiveness of these secondary processes is determined by synthesis temperature [5].

With the use of Raman spectroscopy (Fig. 1), phase composition of the inorganic gel-precursor obtained from the nitrate or chloride solution under HT-conditions has been ascertained to occur – with treatment temperature increasing from 90 to 130 °C – via the following route: amorphous hydrated alumina → ammonium aluminum carbonate hydroxide → boehmite.

Thermal decomposition of the inorganic gel-precursor – while heated in the air up to 650 °C – proceeds pseudomorphically; at this point, alumina aggregates under formation become shaped as gel-precursor crystals [4], that is, the porous structure parameters of alumina become dependent on the inorganic gel-precursor structure that, in turn, is determined by its phase composition.

In accord with findings of the SEM micrographs formation of aggregates comprised of plane-oblong shaped particles organized
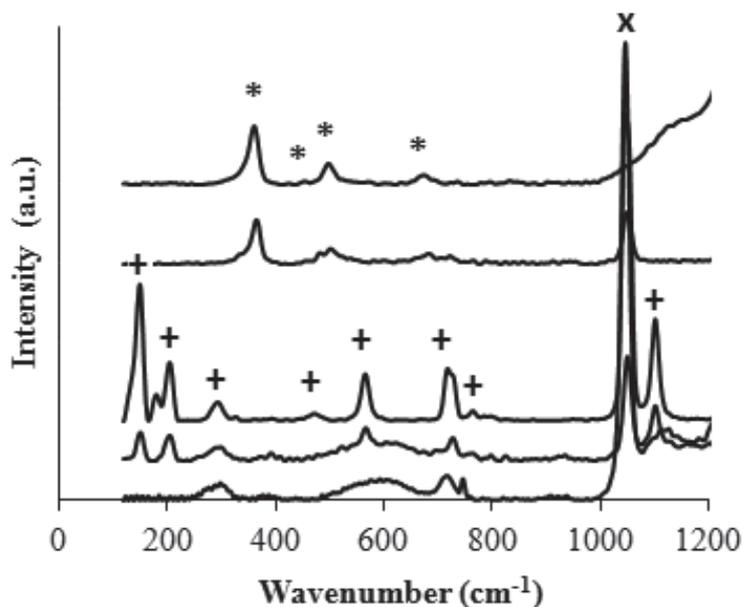

Fig. 1. Raman spectra of alumina gel-precursors; * γ-AlOOH; + $NH_4Al(OH)_2CO_3$; x NO_3

as microrods observed for the samples synthesized at 110 °C (Fig. 2a). Further increase of the hydrothermal synthesis temperature ($\geq$120 °C) is accompanied by re-aggregation alumina particles as somatoide structures (Fig. 2b, c). This phenomenon is caused by directed growth of primary $NH_4Al(OH)_2CO_3$ particles along the main crystallographic axis and the phase transfer of $NH_4Al(OH)_2CO_3$ to boehmite (γ-AlOOH) with increasing the HT synthesis temperature.

The XRD patterns of microrods' gel-precursor shown in Fig. 3a may be assigned to crystalline ammonium aluminum carbonate hydroxide with a composition of $NH_4Al(OH)_2CO_3$ (JCPDS card 42-0250). The high intensity of the (110) crystal face gives evidence that the ammonium aluminum carbonate hydroxide crystals preferably grow along the crystallographic c axis under the synthesis conditions. No other diffraction peaks detected indicate the absence of any impurities in the ammonium aluminum carbonate hydroxide gel-precursor.
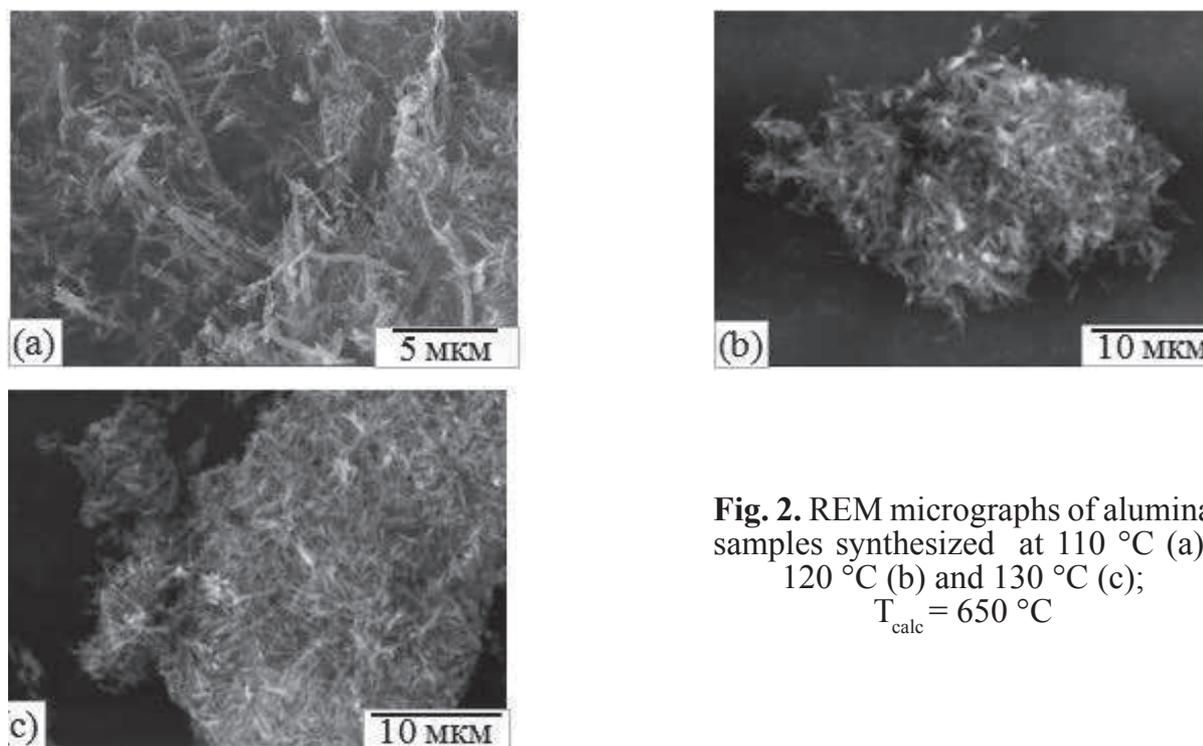

Fig. 2. REM micrographs of alumina samples synthesized at 110 °C (a), 120 °C (b) and 130 °C (c); T_{calc} = 650 °C

The XRD patterns (Fig. 3b) and the results of thermal analysis (Fig. 4) indicate that, with increasing calcination temperature, the ammonium aluminum carbonate hydroxide gel-precursor thermally decomposes and transforms to amorphous and polycrystalline γ-Al_2O_3 at 200 °C and 800 °C, respectively. The low intensity of the XRD peaks indicates that the alumina specimens calcinated at 800 °C have minor crystallinity, while the broad peaks demonstrate the alumina microrods to be nanocrystalline, as is consistent with the previous results.
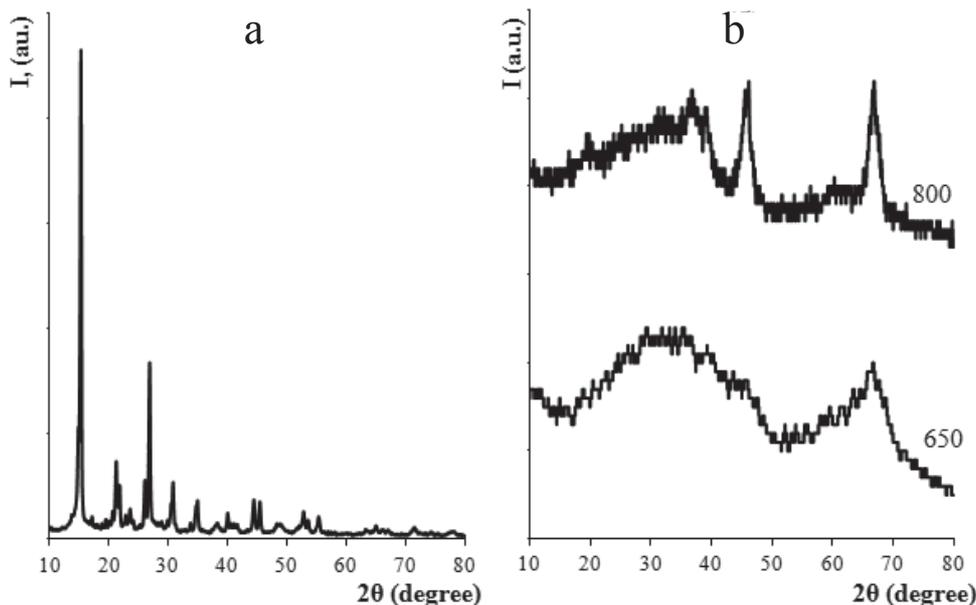
Fig. 3. XRD patterns of gel-precursor (a) and samples calcined at 650 and 800 °C (b)

As is known, the structure of ammonium aluminum carbonate hydroxide crystal is composed of Al-O octahedron chains bonded by covalently sharing oxygen atoms. CO_3^{2-} and NH^{4+} ions are located between the chains bonded by weak hydrogen bonds. During the decomposition of ammonium aluminum carbonate hydroxide, the Al-O bonds remain unchanged, while the weaker bonds between CO_3^{2-} and NH^{4+} ions and Al-O octahedron chains become
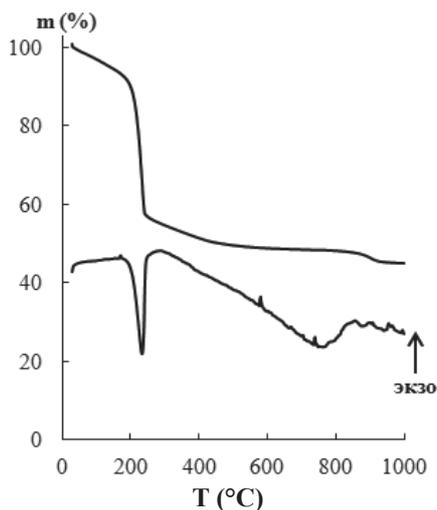

Fig. 4. TG-DSC plot of the ammonium aluminum carbonate hydroxide gel-precursor

broken and release NH_3, CO_2 and H_2O. This special structure of ammonium aluminum carbonate hydroxide endows the alumina microrods with high thermal stability. In the thermal decomposition process, the ammonium aluminum carbonate hydroxide gel-precursor does not cause any dramatic

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change of the framework, and mesopores are formed with the amorphous alumina framework, while the gases burn out. Thus, the pores of the obtained mesoporous alumina microrods are disorderly arranged.

The character of the porous structure can be judged from variations in the hysteresis loop on the low-temperature nitrogen adsorption-desorption isotherms (Fig. 5). The shape of the isotherms is in accord with the IV type of the IUPAC classification (that is, isotherms with clearly expressed capillary condensation typical of mesoporous materials). The hysteresis loop type is combined of H2 and H3, thus indicating that the microrods consist of lamellar structures with slot-like pores and of agglomerates comprised of densely compacted particles with cone-shaped pores between them. As is apparent from the BJH-curves of pore size distribution, the agglomerates comprised of plane-oblong shaped particles are characterized by bimodal pore size distribution caused by availability of slot-like and cone-shaped pores in the specimen, with this phenomenon more markedly expressed in the case of the synthesis from aluminium chloride.

Textural properties (specific surface area S_{BET}, total pore volume Vtot, pore diameter D_{BJH}) of alumina as dependent on the drying method were studied as well. Replacement of the solvent during drying (specimens 3-2N, 3-2Cl) was shown (Fig. 3, Table 1) to contribute to a reduced content of micropores in the specimens and to formation of a mesoporous structure with either homogeneous (specimen 3N-2), or bimodal (specimen 3Cl-2) pore size distribution, as well as to an increased total pore volume V_{tot}.
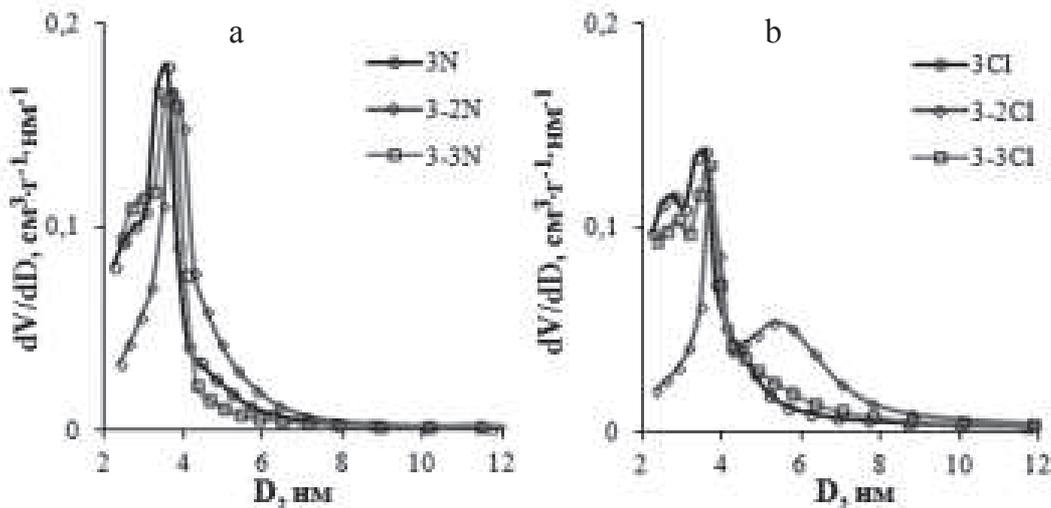

Fig. 5. Differential BJH-curves of pore size distribution for alumina specimens of 3N (a) and и 3Cl (b) series. $T_{calc} = 650$ °C

Table 1

Textural properties of alumina samples obtained during thermal decomposition
of ammonium aluminum carbonate hydroxide gel-precursor at 650 °C

Sample	S_{BET}, $m^2 \cdot g^{-1}$	V_{tot}, $cm^3 \cdot g^{-1}$	D_{BJH}, nm
3N	297	0.298	3.6
3-2N*	257	0.313	3.7
3-3N**	295	0.295	3.5
3-2Cl*	253	0.381	3.7; 5.3
3-3Cl**	301	0.350	2.9; 3.7

* The samples were dried by means of replacement of the solvent with isopropyl alcohol, i-PrOH).

** The samples were dried by means of replacement of the solvent with isopropyl alcohol, i-PrOH) and of subsequent vacuumization. Other samples were dried in the air at 80 °C.

Conclusions

Formation of the ammonium aluminium carbonate hydroxide phase during the HT-synthesis appears to be an indispensable condition for formation of alumina microrods. Thermal decomposition of ammonium aluminium carbonate hydroxide results in formation of amorphous alumina that crystallizes as γ-Al_2O_3 at temperatures over 800 °C. Mesopores within the alumina microrods are formed with alumina framework, while the gases burn out during the thermal calcinations process. Mesoporosity of these alumina microrods can be maintained at 800 °C. Due to mesoporosity and thermal stability, these alumina microrods may have potential applications as catalysts and catalyst supports, even at high temperatures.

References

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