# Aluminium oxide-hydroxides obtained by hydrothermal synthesis: influence of thermal treatment on phase composition and textural characteristics

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**Abstract**. Aluminium oxide-hydroxides obtained by means of the hydrothermal synthesis of aluminium nanopowder are of great interest in terms of the potential supports for heterogeneous catalysts due its high specific surface area (200…300 $m^2/g$) and pore size of 4…17 nm. In this work the influence of thermal treatment (150…1300 °C) on structural and phase composition, specific surface area and porosity of aluminium oxide-hydroxides has been investigated. Nanostructured γ-$Al_2O_3$ ($T$=400 °C) was found to have the specific surface area of 328 $m^2/g$ and average pore size of ~9 nm. The thermal treatment of aluminium oxide-hydroxides at the temperature of higher and lower than 400 °C has caused the reduction of specific surface area and overall pore volume.

## 1. Introduction

Aluminium nanopowders obtained by means of electrical explosion of wires in various atmospheres are extensively investigated and widely used for composite and functional materials production. There is a particular interest in aluminium oxide-hydroxides produced through hydrothermal synthesis of aluminium nanopowder as advanced materials for catalyst supports [1, 2], sorbents [3], ceramics [4, 5] and filters [6]. The main advantages of such aluminium oxide-hydroxides are high specific surface area, high porosity, narrow pore size distribution, and capability to vary phase composition and basic-acid properties of surface. These properties enable using aluminium oxide-hydroxides as supports for heterogeneous catalysts for hydrocarbons reprocessing. That will to a large extent reduce the number of stages required for such catalysts production and help to develop supports and catalysts with desired structural and functional characteristics.

In literature there are more and more papers dedicated to the investigation of hydrothermal synthesis processes from ultradispersed and nanosized aluminium powder [3, 7-11]. However, the information about structure of aluminium oxide-hydroxide formed during hydrothermal synthesis and subsequent thermal treatment, presented in literature, is still diverse and often contradictory. This is because morphological and structural characteristics of aluminium oxide-hydroxides depend on the original nature of material, properties, method and conditions of production, the reactivity of ultra- and

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nanodispersed aluminium powders, conditions of thermal treatment, etc. This work is aimed at the estimation of the thermal treatment impact on the structural and textural characteristics of aluminium oxide-hydroxides produced through hydrothermal synthesis of aluminium nanopowder for further use of them as supports for heterogeneous catalysts.

## 2. Materials and methods

To obtain aluminium oxide-hydroxide (AlOH) the industrial metallic aluminium nanopowder (AlNP) produced by electrical explosion of wires (at LLC Novosibirsk Nanomaterials, Novosibirsk) was used. According to the manufacturer , the average size of AlNP particles was 115 ± 10 nm, specific surface area – 19.4 ± 3 $m^2/g$, loading of active aluminium – 80.8 ± 0.6 %.

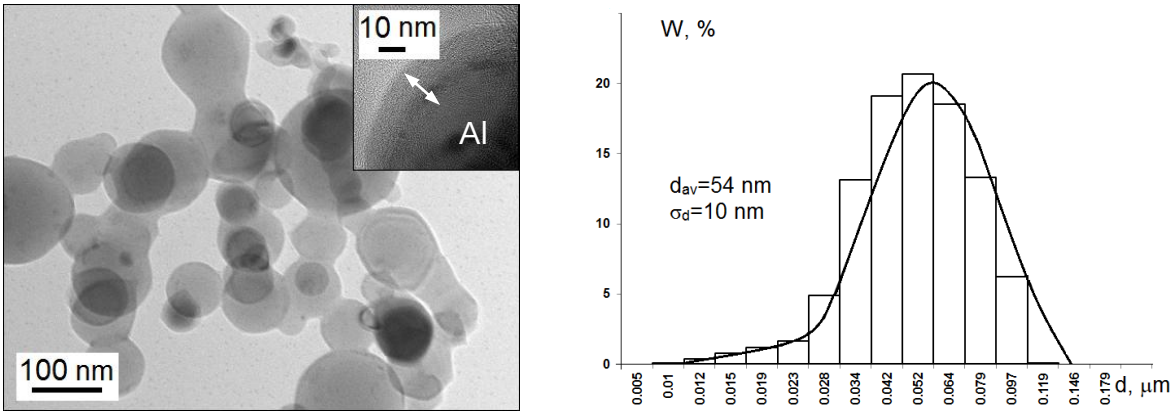
The AlOH was produced using technique described in [12]. That was hydrothermal synthesis of an AlNP implying preparation of a suspension that consisted of the AlNP and preheated (60…65 °C) distilled water with mass ratio $H_2O$:Al=25. The prepared suspension was continuously stirred. After the induction period (3…5 min) the watering oxidation of AlNP was accompanied with self-heating of suspension with temperature growth up to 92…97 °C and intensive hydrogen release. Once the reaction was over the excess of water removed by decantation and solid products of reaction were dried at 21 ± 2 °C. The thermal treatment of the AlOH was conducted in a muffle furnace in the temperature range from 150 to 1300 °C with the heating rate of 10 °C/min and exposure at maximal temperature of 1 h. The size of the AlNP particles was defined using the particle analyzer SALD-7101 in circulation mode with ultrasound (Nano-Center Tomsk Polytechnic University, RF). The shape and size of AlNP particles were investigated by means of high resolution transmission electronic microscopy (HR TEM) using microscope JEM-2100F (Nano-Center Tomsk Polytechnic University, RF). The morphological characteristics of the AlOH were studied by means of scanning electron microscopy (SEM) using system Quanta 200 with focused electronic beam (Center for collective use, Tomsk State University, RF). The phase composition was determined by means of X-ray diffraction (XRD) using the X-ray diffractometer Rigaku Miniflex 600 with $CuK_\alpha$-radiation at the scan rate of 2 °/min. The phase composition analysis was carried out in accordance with PDF-2 database. The AlOH specific surface area and porosity were determined by means of nitrogen low-temperature adsorption using the analyzer Tristar 3020 (Center for collective use, Tomsk State University, RF). The specific surface area ($S_{BET}$) was measured by multipoint BET method with rectifying adsorption isotherm in the relative pressure range of 0.05…0.30 $p/p^o$. The specific surface area of micropores ($S_{micro}$) was determined by t-plot method.

## 3. Characteristics of the original AlNP and products of hydrothermal synthesis

Hydrothermal synthesis of AlNP is accompanied by the huge heat release. Therefore thermal conductivity and heat transfer capability of oxide-hydroxide film of AlNP particles play an important role when AlNP interacts with water [6]. Meanwhile, these processes are accompanied by mass transfer and the formation of solids with totally different morphology and composition when a certain temperature in reaction zone is achieved occur [6]. The heating of aluminium hydroxide results in the following reaction [9, 13]:

$$Al(OH)_3 \xrightarrow{150\,^\circ C} \beta\text{-}Al_2O_3\cdot 3H_2O \xrightarrow{250^\circ C} AlOOH \xrightarrow{400\,^\circ C} \gamma\text{-}Al_2O_3 \xrightarrow{700\,^\circ C} \xrightarrow{700\,^\circ C} \gamma\text{-}Al_2O_3 \xrightarrow{900\,^\circ C} \delta\text{-}Al_2O_3 \xrightarrow{1300\,^\circ C} \alpha\text{-}Al_2O_3$$

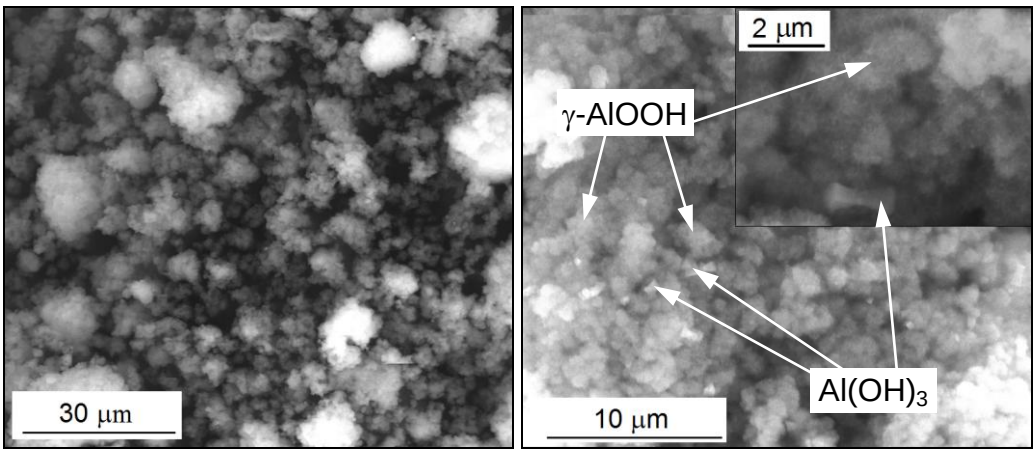
According to TEM data, AlNP particles had spherical shape and represented metallic aluminium with FCC lattice coated with oxide cover with thickness of 7…15 nm (Figure 1a). AlNP particle size distribution is monomodal and lies within the range of 10…150 nm. The average particle size was 54 ± 10 nm (Figure 1b). AlNP particles agglomerate and agglomerations had the size of 200…500 nm as seen from the TEM image (Figure 1a).




a) b)

**Figure 1.** Aluminum nanopowder: *a* – TEM image; *b* – particle size distribution

Hydrothermal synthesis of AlNP leaded to formation of a white friable powder. According to the X-Ray analysis, there were following products of hydrothermal synthesis: AlOOH (boehmite), $Al(OH)_3$ (gibbsite) and residual metallic Al (Table 1). The γ-AlOOH phase was mostly amorphous and have volume percent of 59 % (Figure 2b). The size of coherent scattering region (CSR) of the corresponding γ-AlOOH {020} plane $D_{CSR}$ defined using diffraction line was equal to 1.6 nm. The gibbsite ($Al(OH)_3$) had good crystallinity ($D_{CSR}$=16.4 nm) with hexagonal lattice but its volume percent was negligibly small: ~1 % (Figure 2b). The residual aluminium had a crystalline phase ($D_{CSR}$=14 nm) with FCC lattice and its volume was 40 %. In [6, 10] is the aythors noted that the maximal suspension temperature obtained as the result of aluminium nanoparticles self-heating under hydrothermal synthesis achieved values of 92…94 °C. However, in the current work the maximal temperature of suspension during self-heating achieved 97 °C. The formation of phases γ-AlOOH and $Al(OH)_3$ as the result of the hydrothermal synthesis showed that in reaction zone there were possibly local overheatings with the temperature of at least 250 $^{o}$C, that leaded to the formation of boehmite phase instead of gibbsite one even in the presence of multifold water excess. According to TEM data, the AlOH represented aggregates with the size of ~7.7 μm that consist of smaller particles ($d_{av}$=1 μm, $\sigma_d$=0.5 μm) of various shapes (Figure 2). The microstructure of synthesized AlOH was characterized by formed porous mesh structure with open pores (Figure 2b). In accordance with nitrogen low-temperature adsorption method data, the specific surface area of AlOH particles was 245 $m^2$/g and pore size – 4…17 nm.




a) b)

**Figure 2.** The microstructure of AlOH particles after the hydrothermal synthesis of AlNP

## 4. The influence of thermal treatment on structural phase composition of AlOH

After the AlNP hydrothermal synthesis there were both adsorbed and structural waters in AlOH. The thermal treatment of the synthesized AlOH within the temperature range from 150 to 1300 °C was accompanied by the change of structural water content and phase composition. When heated up to 150 °C the synthesized AlOH loosed adsorbed water. These losses comprised ~3 wt. %. The phase composition of the AlOH heated up to 150 °C was equal to the one of the original AlOH (Figure 3). However, the phase volume percent and CSR size were different (Table 1). In spite of a slight rise of the γ-AlOOH phase CSR ($D_{CSR}$=1.9 nm), the phase stayed mostly amorphous and its volume comprised 49 % (*Sample Al-2* in *the* Table 1). After the thermal treatment the gibbsite ($Al(OH)_3$) and residual Al also had good crystallinity and their CSR rised in 3 and 1.5 times, respectively (Table 1).

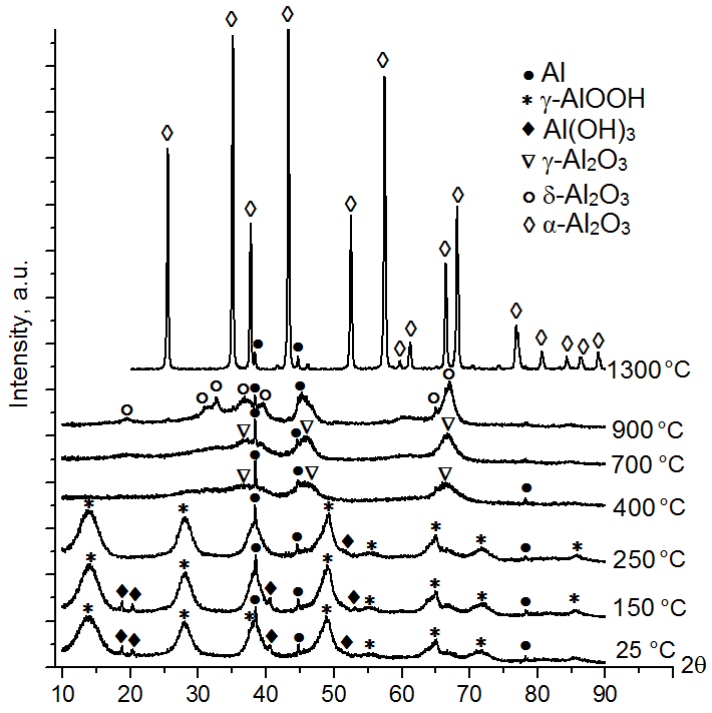



**Figure 3.** X-Ray diagrams for the products of hydrothermal synthesis after thermal treatment within the temperature range of 25…1300 °C.

Within the temperature range of 150…250 °C the structural water volume decreased to the value of ~ 4 wt. %. The basic phases of the *Al-3* sample were γ-AlOOH (boehmite) and residual metallic Al volume percent of which were 85 % and 15 %, respectively. Type, crystalline structure parameters and CSR of the γ-AlOOH phase stayed constant. As the temperature of thermal treatment raised up to the values of 400 °C and 700 °C, the water rating decreased by 9 and 3 wt.% respectively and the formation of γ-$Al_2O_3$ with FCC lattice was observed (*Samples Al-4, Al-5* in Figure 3 and Table 1). Alongside with the γ-$Al_2O_3$ phase in *Al-4* and *Al-5* samples there was residual Al with significantly fewer volume percent of 5 to 7 %. This was possibly due to the partial oxidation of the sample under the heat treatment in the air atmosphere. The γ-$Al_2O_3$ phase of the *Al-4* sample was mostly amorphous. The size of the CSR $D_{CSR}$ defined by means of diffraction line corresponding to the {400} plane of the γ-$Al_2O_3$ structure had the value of 2.6 nm. As the temperature of thermal treatment rised up to 700 °C the CSR size of the γ-$Al_2O_3$ phase increased to the value of 10.5 nm. According to X-Ray data, the further rise of the treatment temperature up to the value of 900 °C resulted in the formation of δ-$Al_2O_3$

with tetragonal lattice (*Sample Al-6* in Table 1). The size of the CSR $D_{CSR}$ defined by means of diffraction line corresponding to the {114} plane had the value of 4.6 nm that means that the δ-$Al_2O_3$ phase had microcrystalline structure (Figure 3 and Table 1).

**Table 1.** Phase composition of the products of hydrothermal synthesis after thermal treatment

| Sample | *T*, °C | Phase | Type of crystal lattice, space group | Volume percent, % | CSR ($D_{CSR}$), nm |
|---|---|---|---|---|---|
| *Al-1* | 25 | Al | FCC, *Fm3m* | 40 | 14 |
| | | γ-AlOOH | Orthorhombic, *Amam* | 59 | 1.6 |
| | | $Al(OH)_3$ | Hexagonal, *P-3* | ~1 | 16.4 |
| *Al-2* | 150 | Al | FCC, *Fm3m* | 50 | 23.2 |
| | | γ-AlOOH | Orthorhombic, *Amam* | 49 | 2 |
| | | $Al(OH)_3$ | Hexagonal, *P-3* | ~1 | 49.9 |
| *Al-3* | 250 | Al | FCC, *Fm3m* | 15 | 23 |
| | | γ-AlOOH | Orthorhombic, *Amam* | 85 | 2 |
| *Al-4* | 400 | Al | FCC, *Fm3m* | 7 | 22.3 |
| | | γ-$Al_2O_3$ | FCC, *Fd3m* | 93 | 2.6 |
| *Al-5* | 700 | Al | FCC, *Fm3m* | 5 | 22.3 |
| | | γ-$Al_2O_3$ | FCC, *Fd3m* | 95 | 10.5 |
| *Al-6* | 900 | Al | FCC, *Fm3m* | 4 | 22 |
| | | δ-$Al_2O_3$ | Tetragonal, *I* | 96 | 4.6 |
| *Al-7* | 1300 | Al | FCC, *Fm3m* | 3 | 21.7 |
| | | α-$Al_2O_3$ | Rhombohedral, $R\bar{3}c$ | 97 | 118 |

In the process of heating AlOH up to 1300 °C the α-$Al_2O_3$ crystalline phase with rhombohedral lattice was formed. According to X-Ray data, all samples contained residual metallic Al within the temperature range from 150 to 1300 °C. Herewith, as the temperature raised from 250 °C to 1300 °C the volume percent of Al dramatically drops from 15 down to 3 % (Table 1). This means that Al oxidizes when sample is heated in the air atmosphere. The presence of metallic aluminium in the sample heated up to 1300 °C indicated the formation of stable structures of core-shell type in which aluminium cores were covered by dense oxide-aluminium shell that prevented its further oxidation.

## 5. The influence of thermal treatment on specific surface area and pore size of AlOH

The porous AlOH structure characteristics before and after thermal treatment were investigated by means of low-temperature nitrogen adsorption (Table 2 and Figure 4). For the *Al-1*, *Al-2* and *Al-3* samples the presence of hysteresis loop at isotherms of nitrogen adsorption-desorption reveals their mesoporous structure (Figure 4a). The pore size distribution for the *Al-1*, *Al-2* and *Al-3* samples was monomodal (Figure 4b) with the average pore size of ~9 nm, $S_{BET}$=243...297 $m^2/g$, $S_{micro}$=33...41 $m^2/g$ (Table 2).

**Table 2**. The textural characteristics of AlOH before and after thermal treatment

| Sample | *T*, °C | Specific surface area, $m^2/g$ | | Pore volume, $cm^3/g$ | | Average pore size, nm |
|---|---|---|---|---|---|---|
| | | $S_{BET}$ | $S_{micro}$ | $V_{pore}$ | $V_{micro}$ | |
| *Al-1* | 25 | 243 | 33 | 0.53 | 0.016 | 8.7 |
| *Al-2* | 150 | 251 | 44 | 0.56 | 0.022 | 8.8 |
| *Al-3* | 250 | 297 | 41 | 0.65 | 0.019 | 8.6 |
| *Al-4* | 400 | 328 | 23 | 0.78 | 0.009 | 9.4 |
| *Al-5* | 700 | 256 | 13 | 0.76 | 0.005 | 11.8 |
| *Al-6* | 900 | 152 | 13 | 0.67 | 0.005 | 17.7 |

| | | | | | | |
|---|---|---|---|---|---|---|
| *Al-7* | 1300 | 6.5 | 2 | 0.23 | 0.001 | 14.7 |

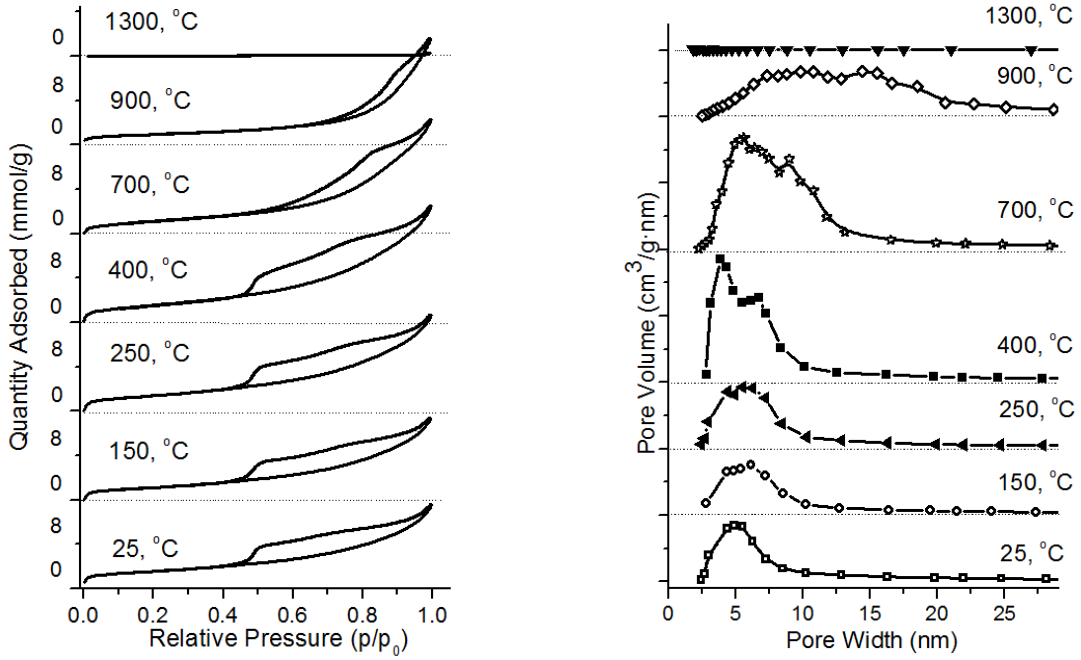



**Figure 4.** The textural characteristics of AlOH before and after thermal treatment: *a* – isotherms of $N_2$ adsorption-desorption; *b* – pore size distributions.

The rise of the AlOH thermal treatment temperature up to 400 °C for the *Al-4* sample resulted in changing of hysteresis loop shape marked by dual loop occurring in different domains of relative pressure (Figure 4a). For this sample we observed bimodal pore size distribution with the average pore size of ~9 nm (Figure 4b and Table 2). Although the values of $S_{micro}$ and $V_{micro}$ for the *Al-4* sample decreased by half comparing to the *Al-1*, *Al-2* and *Al-3* samples, the overall specific surface area ($S_{specific}$) and overall pore volume ($V_{pores}$) raised to the values of 328 $m^2/g$ and 0.78 $cm^3/g$, respectively. The further treatment temperature increased up to 700 and 900 °C (*Al-5* and *Al-6* samples) also results in bimodal pore size distribution. However, the peak points of distribution curve shifted to the domain of pores with large diameter that leads to average pore size growth up to 12 nm for the *Al-5* sample and 18 nm for the *Al-6* sample. The overall specific surface area ($S_{BET}$) for the *Al-5* and *Al-6* samples went significantly down to the values of 256 $m^2/g$ and 152 $m^2/g$, respectively. The AlOH heating up to the temperature of 1300 °C leaded to the porous structure disrupting confirmed by lack of hysteresis loop at the isotherms of nitrogen adsorption-desorption and the corresponding pore size distribution (Figure 4). The temperature growth up to 1300 °C caused the degradation of all textural characteristics due to domination of the α-$Al_2O_3$ phase in the sample structure (Table 2). Therefore the *Al-4* sample ($T$=400 °C) consisting of amorphous γ-AlOOH and residual Al had the most optimal textural characteristics for producing aluminium oxide supports.

## 6. Conclusion

This work investigates the influence of thermal treatment within the temperature range of 150-1300 °C on phase composition, textural characteristics and acid-base properties of aluminium oxide-hydroxides obtained through hydrothermal synthesis of aluminium nanopowder. It was shown that within the temperature range of 150…250 °C the $Al(OH)_3$ passes into γ-AlOOH, adsorbed and structural waters

are eliminated and the porous structure is formed with the average pore size of ~9 nm and specific surface area of 243…297 $m^2/g$. It was established that under the AlOH heating up to 400 °C the amorphous $\gamma$-$Al_2O_3$ is formed that has the overall specific surface area and pore volume of 328 $m^2/g$ and 0.78 $cm^3/g$ respectively. Such structure has low values of $S_{micro}$ и $V_{micro}$ (23 $m^2/g$ и 0.009 $cm^3/g$ respectively) that is very important for developing catalyst supports. It was shown that further rise of treatment temperature (up to 900…1300 °C) results in increasing of pore volume and size and the formation of high-temperature aluminium oxides ($\delta$-$Al_2O_3$, $\alpha$-$Al_2O_3$) that have small specific surface area. It should be noted that in all samples treated within the temperature range of 150…1300 °C the size of particles stays small and residual metallic Al is still present. Therefore the most interesting substance for developing catalyst supports is $\gamma$-$Al_2O_3$ obtained at the temperature of 250…400 °C that has optimal structural and textural characteristics.

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