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SPECIFIC SURFACE AREA, CRYSTALLITE SIZE AND THERMOKINETIC OF OXIDE FORMATION $\gamma \rightarrow \alpha$-$Al_2O_3$ NANO POWDERS AT 570 – 1470 K

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Powders where the $\gamma \approx \alpha$-Al_2O_3-nano phases are the priority precursors for catalysts for heterogeneous catalysis with the maximum content of surface 5-coordinated Al centers for Pt attachment. Hydrogenated nano powders (~8 nm) of γ-, γ '-, θ-, κ-Al_2O_3 soluble in hydrochloric acid were obtained from the processing of aluminum boride powders with an icosahedral structure. Samples, which underwent a step-by-step and single heating of 50-100K heat treatment for 2 hours at temperatures of 570-1470K, were received in quantity of 34. The specific surface area of S_{BET}, m^2g^{-1} was measured by the thermal nitrogen desorption express method of gas chromatography through the GC-1 device. X-ray (phase and coherent), fluorescence and phase chemical-analytical evaluation of the samples were performed. The thermokinetic characteristics of the processes are calculated using the exponential Arrhenius law. Dimensional characteristics of crystallites (10.4-48 nm); specific surface area of powders (213-8.6 m^2g^{-1}, S_{BET}); thermokinetic parameters of α-Al_2O_3 crystallite growth process ($V_{\alpha\text{-}Al2O3}$ - $1.44\ 10^{-3}$ - $6.67\ 10^{-3}$ nm s^{-1}; $E_{\alpha\text{-}Al2O3} = 38.7 \pm 2.1$kJ mol^{-1}; $A_0 = 0.16 \pm 0.0\ s^{-1}$ along the temperature line 1220-1470K were determined and calculated. The process of dehydration of two OH-groups occurs in the region 570-720K $E_{a\ H2O\uparrow} = 30.5 \pm 0.5$ kJ mol^{-1} $A_0 = 1.33 \pm 0.3\ s^{-1}$. The last group of OH at temperatures of 820 -1070K and a rate of $2.13\ 10^{-4}$ - $4.93\ 10^{-4}$ mol s^{-1} $E_{a\ H2O\uparrow} = 13.2 \pm 0.8$ kJ mol^{-1} $A_0 = 16.9 \pm 0.9\ s^{-1}$. The activation energy of the phase transition is $E_{a.,\ \gamma \rightarrow \alpha\text{-}Al2O3} = 23.9 \pm 1.0$ kJ mol^{-1} $A_0 = 2.01 \pm 0.72\ s^{-1}$ (770-970K) and $E_{a.,\ \gamma \rightarrow \alpha\text{-}Al2O3} = 83.5 \pm 0.8$ kJ mol^{-1} $A_0 = (2,05 \pm 0,95)\ 10^3\ s^{-1}$ (1070-1170K). It agrees well with the known heat of conversion $E_{a,\ \gamma \rightarrow \alpha\text{-}Al2O3} = 85$ kJ mol^{-1}. The TK of $\gamma \approx \alpha$-Al_2O_3-nano phases is at 1170K.

Keywords: *specific surface area, crystallite size, thermal kinetics, phase transition, powders, $\gamma \rightarrow \alpha$-$Al_2O_3$-nano, dehydration, crystallite growth*

Introduction

The search for ceramic and composite materials resistant to shocking physical impact is relevant. These include related icosahedral compounds such as boron carbide, including reaction products in the system: "Al - B_{15-x} C_x [1] and BN" [2-9].

Powder γ-Al_2O_3-nano, in contrast to α-Al_2O_3 - easily soluble in hydrochloric acid, active sintering material. A solution of sodium tetrahydroxy-aluminate, from waste refining powders AlB_{12}, $AlB_{12}C_2$, $Al_8B_4C_7$ [10, 11] became a precursor to produce γ-Al_2O_3. In the process of $\gamma \rightarrow \alpha$-$Al_2O_3$ phase transition, extended in temperature and time, the state of the powder is special, where the content of γ, octahedrally coordinated aluminum (3+) is proportional to the α-phase of Al_2O_3 with tetrahedral Al (3+). Under these conditions, the surface of the oxide particles according to ^{27}Al MAS-NMR spectroscopy at a magnetic field of 17.6 Tesla [12-14] has up to 20% of intermediate unsaturated 5-coordinated ^{27}Al ionic polyhedral. They act as mounting points for catalytically active materials, such as Pt. The degree of phase transition and the content of 5-coordinated aluminum atoms depends on: the thermokinetic characteristics of the processes of dehydration; phase transformations and growth of α-phase crystallites. The study of the formation of oxides (subject of research) $\gamma \rightarrow \alpha$-$Al_2O_3$ in the temperature range of these processes is relevant. Thermokinetic measurements are inherent in the chemical features of the components of the research object α-Al_2O_3-nano using delicate methods of chemical phase analysis, X-ray diffraction, coherent scattering and methods of nitrogen desorption in the region of heat treatment

570-1470 K. The results of measurements are calculated using Svante Arrhenius equation. Methodologically, such experiments were performed for the first time.

Materials and research methods

Powder 5.0-10.0 nm preferably γ; γ'-Al2O3-nano (RFA) was obtained during the processing of technological waste products of interaction in the system: "BN – Al" [10]. Hydroxyl derivatives of aluminum (3+) were precipitated from alkaline solutions with nitric acid to pH 4.0-5.0. The coagulated product is purified 5 times according to rural cheese production technologies. The difference of osmotic pressure of aqueous solutions and pure aqua at a ratio of 1:10, respectively, was used. According to the known version, the powder is partially dehydrated at 420 and 570 K according to the data [16].[1] Diffractograms of γ-Al_2O_3 samples calcined at 1170 K had reflections of crystalline phases, including α-Al_2O_3. Samples of Al_2O_3 powder are calcined in steps (2 hours) to a temperature of 1470 K sequentially or once. The phases γ-$Al(OH)_3$, γ-AlO(OH), γ-Al_2O_3 and γ'-Al_2O_3, in contrast to α-Al_2O_3, are soluble in hydrochloric acid. [16]. All modifications of alumina are soluble in NaOH melt. Aluminum (3+) was determined by complex-metric direct and inverse titration with fluoride masking [17]. OH-groups after substitution with fluoride (KF) – acid-metrically with phenol-phthalein according to Tananaev [17]. Hydrogen, nitrogen (and oxygen) - pulsed reductive extraction with carbon and gas chromatography [12]. Carbon was measured by oxidative extraction and coulomb-metrically (AN 7529m) [17]. Diffractograms were performed on an X-ray diffractometer DRON-3,0 Cu kα-radiation, monochromator. The *specific* ***surface*** *area* S_{BET}, m^2g^{-1} was determined by express method of thermal *nitrogen* desorption using the GC-1 device. The X-ray fluorescence analyzer EXPERT 3L W207U" (Ukraine) was used, the Al_2O_3 content was 99.69% (wt.), SiO_2 - 0.31%. $\gamma \rightarrow \alpha$-$Al_2O_3$ and growth of α-Al_2O_3-nano crystallites according to Arrhenius exponential law.

Obtained results and discussions

Phase composition. The obtained results do not coincide with the data [16], apparently due to the lack of heat treatment time. The original γ-Al_2O_3 is a mixture of 65.3% of the mass. γ-AlO(OH) and 34.7.7% γ-$Al(OH)_3$. The γ-$Al(OH)_3$ phase decomposes in the region of 770-870K. Phase γ-AlO (OH) - at 1030K. The samples annealed sequentially or once at 1170K had a phase composition of: soluble phases[2] 45.0% γ-Al_2O_3 and 55.0% of other Al_2O_3 phases[3] (1); 58.0% γ-Al_2O_3 and 42.0% α-Al_2O_3 (2), respectively. Al_2O_3 powders without soluble γ-Al_2O_3 were obtained at 1230-1470K heat treatment.

Dehydration. Data from the thermokinetic process of dehydration of Al_2O_3 powders are presented in the table. The total content of bound water in the OH-groups was ≈ 20% of the mass. Dehydration of the 1st (accumulative) and 2nd (single) heating modes in the region 570-870K have a hysteresis of discrepancy. As the temperature increases from 870K to 1470K, the

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[1] In the future, the time of each heat treatment was two hours, respectively.

[2] - conventionally referred to below as γ-Al_2O_3.

[3] - conventionally referred to below as α-Al_2O_3.

dehydration curves merge into one line. The dehydration rate increases from 1.87 10^{-5} to 4.93 10^{-4} mol s^{-1} (Table). The activation energy of dehydration of the two OH-groups (equation 1) in the region 570-730K is $E_{a\ H2O}\uparrow = 30.5 \pm 0.5$ kJ mol^{-1}. The last group of OH (equations 2, 3) at temperatures of 830-1070K and a velocity of 2.13 10-4 - 4.93 10-4 mol s^{-1} dissociates with the activation energy within $E_{a\ H2O}$ $\uparrow = 13.2 \pm 0.8$ kJ mol^{-1}. Above 1070K, Al_2O_3-nano powder becomes virtually anhydrous.

$Al(OH)_{3solid} \rightarrow$ 770-870K $\rightarrow AlO(OH)_{solid} + H2O \uparrow_{gas}$ (1)

$AlO(OH)_{solid} \rightarrow$ 1030K $\rightarrow 0.5\ Al_2O_{3hard} + 0.5\ H_2O \uparrow_{gas}$ (2)

$OH\text{-}_{solid} \rightarrow$ 770-1030K $\rightarrow 0{,}5O^{2-}_{solid} + 0{,}5\ H_2O \uparrow_{gas}$ (3)

The dehydration reaction constant is: $k_{H2O}\uparrow = [H2O]^{0.5}$. Dehydration rate $V_{H2O}\uparrow = [H_2O]$ exposure $time^{-1}$ (s^{-1}). The rate constant kv = $(V_{H2O}\uparrow)^{0.5}$.

Phase transition. The reaction (4; 5) phase transition (Table) can be represented as:

γ-Al_2O_3 → 670-1230K → α-Al_2O_3 (cumulative heating) (4) or

γ-Al_2O_3 → 1130-1230K → α-Al_2O_3 (single-stage heating) (5).

Table 1. Thermokinetic characteristics of hydrated powders $\gamma \rightarrow \alpha$-$Al_2O_3$-nano (9.7-48.0 nm; S_{BET} = 213.0-8.6 m^2g^{-1}) in the field of 570-1470K

N	**T, K**	**Velocity, V, mol s^{-1}, (nm s^{-1})**	**Activation energy E_a kJ mol^{-1}**	**Frequency factor, A_0 s^{-1}**
1	620-670	$H_2O\uparrow 10^6$= 0.58-5.24	$H_2O\uparrow$ = 29.7±1.0	$H_2O\uparrow$ = 0.78±0,04
2	820-1070	$H_2O\uparrow 10^6$= 6.56-15.2	$H_2O\uparrow$ =13.2±1.0	$H_2O\uparrow 10^2$ = 5.8±0.2
3	670-970	$\gamma\rightarrow\alpha$-$Al_2O_3 10^6$= 3.47-12.5	$\gamma\rightarrow\alpha$-Al_2O_3= 23.9±1.0	$\gamma\rightarrow\alpha$-Al_2O_3= 2,0±0,7
4	1070-1200	$\gamma\rightarrow\alpha$-$Al_2O_3 10^5$= 2.78-14.2	$\gamma\rightarrow\alpha$-Al_2O_3= 83.3±1.0	$\gamma\rightarrow\alpha$-Al_2O_3= (2,05±0,95) 10^3
5	700-1120	crystallite growth α-Al_2O_3 10^3nm s^{-1} =1.44-2.79	not an exponential area-	not an exponential area
6	1120-1420	crystallite growth α-Al_2O_3, 10^3nm s^{-1} = 3.36-6.47	crystallite growth =38.7±2.1	crystallite growth =0.16±0.02

Where k = [α-Al_2O_3] (mol) reaction constant. $V_{\gamma\rightarrow\alpha}$ = [α-Al_2O_3] exposure $time^{-1}$ (s^{-1}) formation rate α-Al_2O_3 and $k_{v\ \gamma\rightarrow\alpha} = (V_{\gamma\rightarrow\alpha})^1$ - rate constant $\gamma \rightarrow \alpha$-$Al_2O_3$. The activation energy $E_{a\ \gamma\rightarrow\alpha\ Al2O3\ phase\ transition}$, in the mode of stepwise cumulative heating, is equal to 23.9 ± 0.8 kJ mol^{-1} in the region 670-970K at a process speed of 3.47 10^{-6} - 1.25 10^{-5} mole s^{-1}. Increasing the temperature to 1070-1170K, increases the rate of phase transition $\gamma \rightarrow \alpha$-$Al_2O_3$ to 2.78 10^{-5} - 1.42 10^{-4} mol s^{-1}. The activation energy of the $E_{a\ \gamma\rightarrow\alpha\text{-}Al2O3\ phase\ transition}$ under these conditions is

83.5 ± 0.8 kJ mol^{-1}. The obtained value of $E_{a\ \gamma \rightarrow \alpha\text{-}Al2O3}$ correlates with the known - 85 kJ mol^{-1} [16]. In the mode of single heating, the low-temperature branch γ → α-Al2O3 is absent. The frequency coefficient of the process A_0 phase transition throughout the temperature line remains constant (2.05±0.95)10^3 s^{-1}. Thermokinetic phase transition γ → dehydration → (η-, θ-, γ'-, δ-, χ-, κ-) → α-Al_2O_3 is a complex multistage process of formation of alumina crystallites. The product of the transition is α-modification.

Specific surface *area* and size of crystallites. The specific surface area (S_{BET}, m^2g^{-1}) was measured experimentally in the range of 213.0 - 8.6 m^2g^{-1} in samples maintained at temperatures of 570; 870; 1070; 1220; 1270; 1470K respectively. The temperature dependence of S_{BET} has the form of an inverse Ƨ-shaped dependence with a noticeable inflection at 1170-1220K. The curve, in fact, has the nature of the first derivative of the power function of the specific volume (V, m^3g^{-1}). The ratio S/V in the spherical[4] and cubic approximation is equal to "$6a^{-1}$", where "a" is the average integral length of the diameter or face of geometric figures. As the heat treatment temperature increases, the specific surface area and the parameter a decrease. The S/V ratio increases continuously (in the absence of a jump in the parameters of the martensitic phase transition). The process of agglomeration of crystallites at a segment of high temperatures causes the curve to bend towards the abscissa. The curve acquires an S-shape. The value of the average size of α-Al_2O_3 crystallites in the region of coherent scattering of the diagonal plane hkl_{012} (≈48 nm) at a temperature of 1470K was established. The temperature dependence of S/V allowed to calculate the average size of α-phase crystallites along the temperature line 570-1470K. The increasing region of the α-Al_2O_3 crystallite size curve is similar to the exponent and can be calculated from the Arrhenius equation. The determined thermokinetic parameters of α-Al_2O_3-nano crystallite growth are presented in the table. As can be seen from the table, the specific area of powders decreases from 213.1 to 8.6 m^2g^{-1} in the temperature range 570-1470K. The size of α-Al_2O_3-nano crystallites increases in the form of an S-shaped curve from 9.7 to 48.0 nm from 570 to 1470K at a rate of 2.89 10^{-3} to 1.33 10^{-2} nm s^{-1}. At temperatures of 1220-1370 K, the activation energy is 38.7 ± 2.1 kJ mol^{-1}. Further increase in temperature leads to agglomeration of α-Al_2O_3 crystallites. The frequency growth rate of crystallites A_0 did not exceed 1.83 ± 0.07 s^{-1}.

Conclusions

Considering the obtained data, there is a proportional relationship between the degree of solubility of the phases of aluminum (3+) in hydrochloric acid and dehydration of powders. The higher content of hydroxyl groups correlates with a higher mass fraction of dissolved Al (3+). Reducing the content of OH groups increases the resistance of the powder to dissolution in hydrochloric acid. Dissolution of γ- and γ'-Al_2O_3 was confirmed by X-ray phase analysis. The monograph [16] states that γ'-Al_2O_3 is converted to γ-Al_2O_3 at 1170K. Above 1270 γ-Al_2O_3 is converted to α-Al_2O_3 (heat of conversion 85.9 kJ mol^{-1}). The activation energy of the phase transition γ → α-Al_2O_3 is equal to Ea = 83.5 ± 0.8 kJ mol-1, respectively. The difference in values is < 3.0% relative. For the first time, a low-temperature (670 - 970K) branch of the γ → α-Al_2O_3 phase transition was established under cumulative step heating, with the activation energy of the process being approximately four times lower in comparison with the high-temperature section. Ea = 23.9 ± 0.8 kJ mol^{-1}. The specific surface area of the samples at 570 and 1470K is 213 and 33 m^2g^{-1}, the size of the crystallites is 10.4 and 48.0 nm, respectively. The activation energy of crystallite growth at 1220-1370 K is 38.7 ± 2.1 kJ mol^{-1}, the frequency coefficient of the process A_0 = 0.80 ± 0.02 s^{-1}.

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[4] The sorption properties of the surface of the samples γ≈α-Al_2O_3 (1270K) indicate that the crystallites have a spherical shape.

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ПИТОМА ПЛОЩА ПОВЕРХНІ, КРИСТАЛІТНИЙ РОЗМІР ТА ТЕРМОКІНЕТИКА ФОРМУВАННЯ НАНОПОРОШКІВ ОКСИДУ $\gamma \rightarrow \alpha$-$Al_2O_3$ ПРИ 570 -1470 К

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Проведено рентгенівське (фазове та когерентне), флуоресцентне та фазове хіміко-аналітичне оцінювання $\gamma \approx \alpha$-Al_2O_3-нано порошків. Термокінетичні характеристики процесів обчислюються за допомогою експоненціального закону Арреніуса. Визначено та розраховано розмірні характеристики кристалітів (10,4-48 нм); питома поверхня порошків (213-8,6 $м^2 г^{-1}$, S_{BET}); термокінетичні параметри процесу росту кристалітів α-Al_2O_3 ($V_{\alpha\text{-}Al2O3}$ - 1,44 10^{-3} - 6,67 10^{-3} нм $с^{-1}$; $E_{\alpha\text{-}Al2O3}$ = 38,7 ± 2,1 кДж $моль^{-1}$; A_0 = 0,16 ± 0,0 $с^{-1}$ по лінії температур 1220-1470К). Процес зневоднення двох ОН-груп в області 570-720К Ea $_{H2O\uparrow}$ = 30,5 ± 0,5 кДж $моль^{-1}$; A_0 = 1,33 ± 0,3 $с^{-1}$. Остання група ОН при температурі 820 -1070К і швидкості 2,13 10^{-4} - 4,93 10^{-4} моль $с^{-1}$; Ea $_{H2O\uparrow}$ = 13,2 ± 0,8 кДж $моль^{-1}$; A_0 = 16,9 ± 0,9 $с^{-1}$. Енергія активації фазового переходу - Ea, $_{\gamma \rightarrow \alpha\text{-}Al2O3}$ = 23,9 ± 1,0 кДж $моль^{-1}$; A_0 = 2,01 ± 0,72 $с^{-1}$ (770-970К) та Ea, $_{\gamma \rightarrow \alpha\text{-}Al2O3}$ = 83,5 ± 0,8 кДж $моль^{-1}$; A_0 = (2,05 ± 0,95) 10^3 $с^{-1}$ (1070-1170К). Це добре узгоджується з відомим теплом перетворення Ea, $_{\gamma \rightarrow \alpha\text{-}Al2O3}$ = 85 кДж моль-1. ТК $_{\gamma\approx\alpha\text{-}Al2O3}$-нанофази знаходиться на рівні 1170К.

Ключові слова: *питома площа поверхні, розмір кристаліту, термічна кінетика, фазовий перехід, порошки, $\gamma \rightarrow \alpha$-$Al_2O_3$-нано, дегідратація, ріст кристалітів*

УДЕЛЬНАЯ ПЛОЩАДЬ ПОВЕРХНОСТИ, КРИСТАЛЛИТНЫЙ РАЗМЕР И ТЕРМОКИНЕТИКА ОБРАЗОВАНИЯ НАНОПОРОШКОВ ОКСИДА $\gamma \rightarrow \alpha$-$Al_2O_3$ ПРИ 570 -1470 К

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Проведено рентгеновское (фазовое и когерентное), флуоресцентное и фазовое химико-аналитическое оценивание $\gamma \approx \alpha$-Al_2O_3-нано порошков. Термокинетические характеристики процессов вычисляются с помощью экспоненциального закона Аррениуса. Определены и рассчитаны размерные характеристики кристаллитов (10,4-48 нм); удельная поверхность порошков (213-8,6 $м^2г^{-1}$, S_{BET}); термокинетические параметры процесса роста кристаллитов α-Al_2O_3 ($V_{\alpha\text{-}Al2O3}$ - 1,44 10^{-3} - 6,67 10^{-3} нм $с^{-1}$; $E_{\alpha\text{-}Al2O3}$ = 38,7 ± 2,1 кДж $моль^{-1}$; A_0 = 0,16 ± 0,0 $с^{-1}$ по линии температур 1220-1470K). Процесс обезвоживания двух ОН-групп в области 570-720K Ea $_{H2O\uparrow}$ = 30,5 ± 0,5 кДж $моль^{-1}$; A_0 = 1,33 ± 0,3 $с^{-1}$. Последняя группа ОН при температуре 820 -1070K и скорости 2,13 10^{-4} - 4,93 10^{-4} моль $с^{-1}$; Ea $_{H2O\uparrow}$ = 13,2 ± 0,8 кДж $моль^{-1}$; A_0 = 16,9 ± 0,9 $с^{-1}$. Энергия активации фазового перехода - Ea, $_{\gamma \rightarrow \alpha\text{-}Al2O3}$ = 23,9 ± 1,0 кДж $моль^{-1}$; A_0 = 2,01 ± 0,72 $с^{-1}$ (770-970K) та Ea, $_{\gamma \rightarrow \alpha\text{-}Al2O3}$ = 83,5 ± 0,8 кДж $моль^{-1}$; A_0 = (2,05 ± 0,95) 10^3 $с^{-1}$ (1070-1170K). Это хорошо согласуется с известным теплом преобразования Ea, $_{\gamma \rightarrow \alpha\text{-}Al2O3}$ = 85 кДж моль-1. ТК $_{\gamma \approx \alpha\text{-}Al2O3}$-нанофази находятся на уровне 1170K.

Ключевые слова: *удельная площадь поверхности, размер кристаллита, термическая кинетика, фазовый переход, порошки, $\gamma \rightarrow \alpha$-$Al_2O_3$-нано, дегидратация, рост кристаллитов*