

KINETIC ANALYSIS CRYSTALLIZATION OF α - Al_2O_3 BY DYNAMIC DTA TECHNIQUE

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Abstract

The phase transformation of seeded (5 mass% Fe_2O_3 as a $\text{Fe}(\text{NO}_3)_3$ solution) boehmite derived alumina gel to α - Al_2O_3 was studied with DTA technique and compared with unseeded and α - Al_2O_3 seeded boehmite gels. Data for kinetic analysis of α - Al_2O_3 crystallization were obtained from quantitative DTA curves. The kinetic parameters were analysed by traditional Kissinger analysis and Friedman and Ozawa–Flynn–Wall methods using the Netzsch Thermokinetics program. Results of the comparison of values of activation energies for all three gels and methods are the process of α - Al_2O_3 transformation for originally γ - $\text{AlOOH}/\text{Fe}(\text{NO}_3)_3$ gels goes like that of unseeded boehmite gels, only under lower temperatures (lower about 200°C).

Keywords: crystallization, Friedmann, Kissinger kinetic analyses, Ozawa–Flynn–Wall, seeded alumina, solution effect

Introduction

Aluminium oxide, Al_2O_3 , is one of the most widely used technical ceramic materials. For example, it is used in substrates for electronic circuits, spark plugs, and biomedical applications. Majority applications are made via traditional solid-state process. Synthesis of alumina ceramic fibers, films or membranes is more convenient from solution precursor than via traditional powder techniques.

A sol-gel process, started from alkoxides, makes possible the atomic-scale mixing that is the basis for ‘ultrahomogenization’ and shaping during or after gelation into essentially final shape before firing. However, solution routes as is sol-gel process have some difficulties connected with a series of topotactic metastable phase transformations (γ , δ , θ - Al_2O_3) before final thermodynamically stable corundum phase (α - Al_2O_3) [1–3]. The difficult α - Al_2O_3 nucleation in this system is directly re-

sponsible for unwanted porous microstructure evolution (vermicular microstructure) of boehmite-derived alumina. In order to overcome these problems, additives are often used to lower the nucleation barrier allowing the transformation to occur at a reasonable rate and at lower temperatures [4–8].

Fe_2O_3 additives have been shown to particularly enhance the transformation kinetics of γ - Al_2O_3 to α - Al_2O_3 . Ferric oxide can be introduced into the system in the form of small α - Fe_2O_3 (hematite) particles or as a solution of $\text{Fe}(\text{NO}_3)_3$. For colloidal boehmite seeded with hematite particles or $\text{Fe}(\text{NO}_3)_3$ solution McArdle and Messing [9] reported that nucleation efficiency of ferric nitrate solution is much higher than that of particles seeds. These authors express opinion that the dominant effect in the $\text{Fe}(\text{NO}_3)_3$ seeded $\text{AlOOH}/\text{Al}_2\text{O}_3$ system is the crystallographic and not the solution effect. According to our recent results [10] in agreement with [11], the nucleation effect is prevailing solution one. Characteristic feature of $\text{Fe}(\text{NO}_3)_3$ seeded gels is the presence of two highly dispersed form of iron oxide at temperature above 700°C , substituted hematite (α - $(\text{Fe}, \text{Al})_2\text{O}_3$ of the particle size ≈ 6 nm) and solid solution of γ - $(\text{Al}, \text{Fe})_2\text{O}_3$ occurred before transformation to α - Al_2O_3 phase. Solid solution of γ - $(\text{Al}, \text{Fe})_2\text{O}_3$ is directly transformed into the solid solution of α - $(\text{Al}, \text{Fe})_2\text{O}_3$. The solution effect is further proved by the accelerated crystallization of transient θ - Al_2O_3 in the gels seeded with ferric nitrate [12].

The transformation kinetics and activation energies for transitional aluminas to corundum phase have been extensively studied [8, 13–16]. Activation energies of unseeded alumina gels reported are in the range of 356 – 850 kJ mol^{-1} [12, 14, 17–20, 22] and for seeded alumina gels in the range of 177 – 759 kJ mol^{-1} [12, 14, 21–23]. Direct comparison of activation energies from different studies is problematic because of variations in experimental conditions, starting materials and methods of analysis (DTA, XRD) too.

The aim of this work has been to find out the influence of ferric oxide (originally as a $\text{Fe}(\text{NO}_3)_3$ solution) on the kinetic of crystallization of α - Al_2O_3 by DTA technique. For this purpose is better, if mechanism of α - Al_2O_3 crystallization in γ - $\text{AlOOH}/\text{Fe}(\text{NO}_3)_3$ gels is compared with unseeded boehmite gels and seeded with α - Al_2O_3 crystals.

Series of non-isothermic DTA measurements were made for various heating rates. These measurements led to a series of data showing the same value of conversion for different temperatures.

Experimental

Monolithic seeded ($\text{Fe}(\text{NO}_3)_3$ solution) boehmite gels were prepared from commercial boehmite (Condea, Pural SB ≈ 240 $\text{m}^2 \text{g}^{-1}$, ≈ 10 nm particle size) using the common procedure [10, 12]. Water boehmite suspension (15 mass%) was peptized with nitric acid ($\text{pH} \approx 3$) at 55°C . Unpeptized part of boehmite (≈ 2 mass%) was eliminated from the sol by centrifugation (9000 rpm during 10 min). In the case of seeded boehmite sols, it was mixed with solution of $\text{Fe}(\text{NO}_3)_3$ (5 mass% Fe_2O_3 on Al_2O_3) or α - Al_2O_3 crystals. The sol was poured into plastic planed dishes. This layer of sol (≈ 1 mm)

gelled in about 1 h. Gel allowed to dry at room temperature for 4 days and then it was cracked to fragments (cm^2).

Gel fragments were calcined in electric furnace at 550°C during 1h and then were ground. Mean size of the particles has been $28\ \mu\text{m}$.

Thermal analyses (DTA, TG) of gels were carried out in the air, at a various heating rate (1, 2.5, 5, 10 and $20^\circ\text{C}\ \text{min}^{-1}$) to the temperature 1300°C using Netzsch STA 409 equipment.

Results and discussion

The basic data for kinetic analysis was obtained from DTA curves for different boehmite gel samples for heating rates $1.0, 2.5, 5.0, 10.0$ and $20.0^\circ\text{C}\ \text{min}^{-1}$ (Fig. 1a, b). Figure 1a shows that exothermic effect of crystallization of corundum phase is shifted to lower temperature by seeding with Fe_2O_3 (as a $\text{Fe}(\text{NO}_3)_3$ solution) and α - Al_2O_3 crystals. The exothermic effect of α - Al_2O_3 crystallization at the lowest temperature has been displayed for originally γ - $\text{AlOOH}/\text{Fe}(\text{NO}_3)_3$ gels. As is known [24], position of exothermic peak depends on the heating rate. Exothermic peaks as a function of temperature for unseeded boehmite gels and the different heating rates are shown in Fig. 1b. The data for calculation of kinetic parameters of α - Al_2O_3 crystallization have been obtained by analyzing these curves.

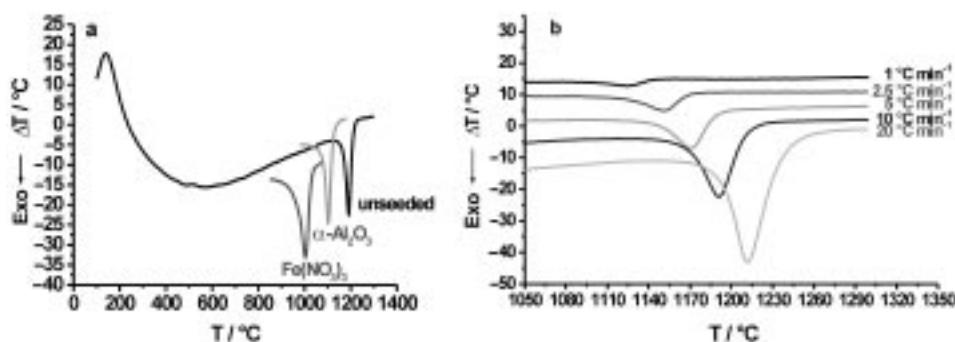


Fig. 1 DTA curves of calcined ($550^\circ\text{C}\ \text{h}^{-1}$) gel samples; a – crystallization exothermic peaks of unseeded and seeded gels with 5.0 mass% Fe_2O_3 (as a $\text{Fe}(\text{NO}_3)_3$ solution) and with α - Al_2O_3 (5.0 mass%) crystals – heating rate $10^\circ\text{C}\ \text{min}^{-1}$; b – DTA curves taken at various heating rates – for unseeded boehmite gels

The transformation of a degree of conversion, x , at time, t , is calculated according to Eq. (1) for DTA measurements:

$$x = \frac{\int_{t_f}^t [S(t) - B(t)] dt}{\int_{t_s}^{t_s} [S(t) - B(t)] dt} \quad (1)$$

where, $S(t)$ – the signal at time t , $B(t)$ – the baseline at time t , t_s – the start time, t_e – the end time. The calculations lead to the graphs of conversion degree, x , and conversion rate, dx/dt , as a function of temperature (Figs 2 and 3).

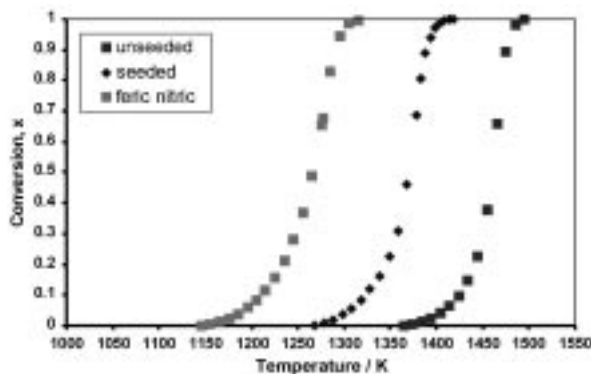


Fig. 2 Conversion to α -Al₂O₃, x , as a function of temperature for unseeded and seeded (5.0 mass% Fe₂O₃ – as a Fe(NO₃)₃ solution and 5.0 mass% of α -Al₂O₃ crystals) boehmite gels

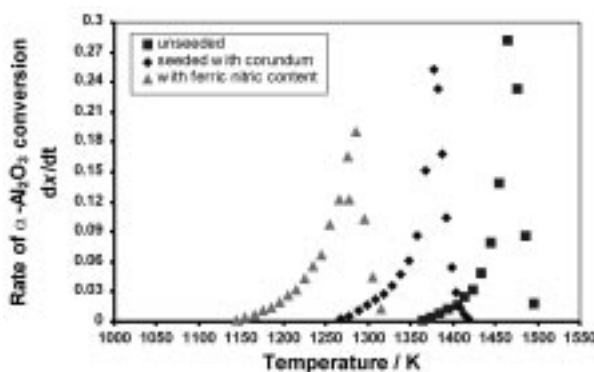


Fig. 3 Rate of α -Al₂O₃ conversion (dx/dt), as a function of temperature for unseeded and seeded gels with 5.0 mass% Fe₂O₃ (as a Fe(NO₃)₃ solution) and with α -Al₂O₃ (5.0 mass%) crystals

Effect of seeding is evident from comparison of curves in Figs 2 and 3 for unseeded boehmite gels, gels seeded with α -Al₂O₃ crystals and boehmite gels with Fe(NO₃)₃ content. The values of kinetic parameters and activation energies for Friedman and Ozawa–Flynn–Wall methods have obtained by the Netzsch Thermokinetics program [25]. An advantage of these methods is their ability to specify kinetic parameters and activation energies without necessity of certain kinetic model.

Friedman analysis

Friedman [26] proposed application of the logarithm of the conversion rate, dx/dt , (with x given) as a function of the reciprocal temperature (2):

$$\ln\left(\frac{dx}{dt}\right)_x = \ln A - \frac{E}{RT_{kj}} + \ln f(x) \quad (2)$$

where, A – pre-exponential factor, E – activation energy, R – gas constant, T – temperature, $f(x)=1-x$. As $f(x)$ is constant in the last term of (2) for given x , the plot of $\ln(dx/dt)$ over $1/T$ results in a straight line with the slope E/R . For each partial value of the conversion x , the value of activation energy (Fig. 4a) and pre-exponential factor (Fig. 4b) of α -Al₂O₃ crystallization was obtained.

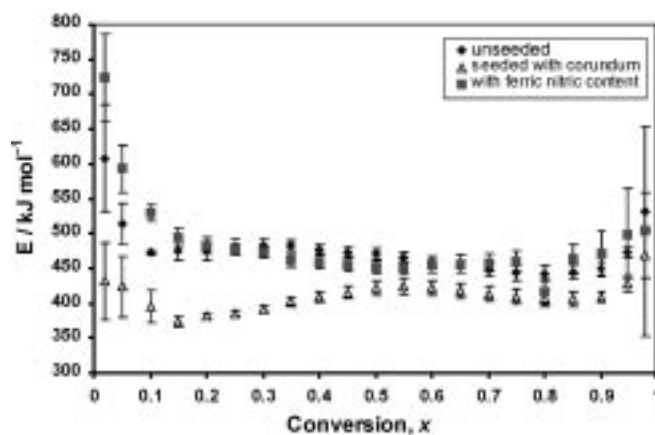


Fig. 4a Activation energy, E , as a function of α -Al₂O₃ conversion, x , for Friedman analysis

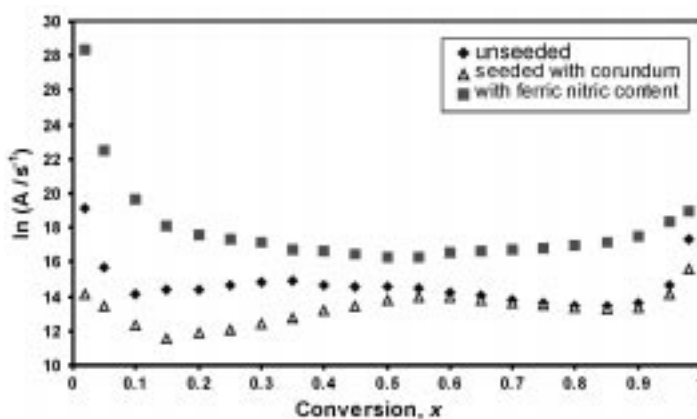


Fig. 4b Pre-exponential factor, A as function of α -Al₂O₃ conversion, x , for Friedman analysis

Ozawa–Flynn–Wall analysis

Ozawa–Flynn–Wall [27, 28] analysis is based on the equation:

$$G(x) = \int_0^1 \frac{dx}{f(x)} = \frac{A}{\beta} \int_{T_0}^T \exp\left(-\frac{E}{RT}\right) dt \quad (3)$$

After transformation and using the approximation given by Doyle [29], it can be determinate an activation energy for different temperatures, but constant heating rates, β , (4):

$$\ln(\beta) = \ln\left(\frac{AE}{R}\right) - \ln G(x) - 5.3305 + 1.052\left(\frac{E}{RT}\right) \quad (4)$$

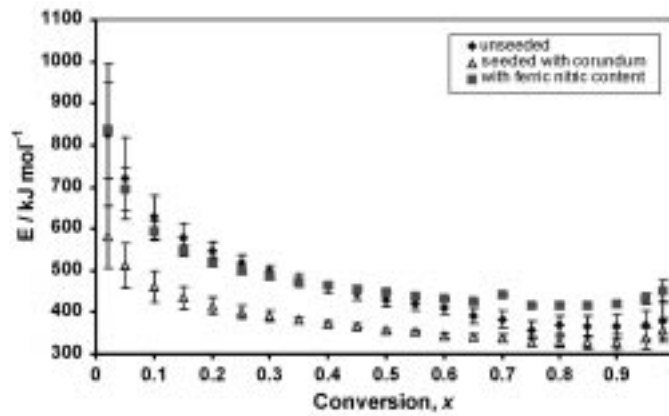


Fig. 5a Activation energy, E , as a function of α - Al_2O_3 conversion, x , for Ozawa–Flynn–Wall analysis

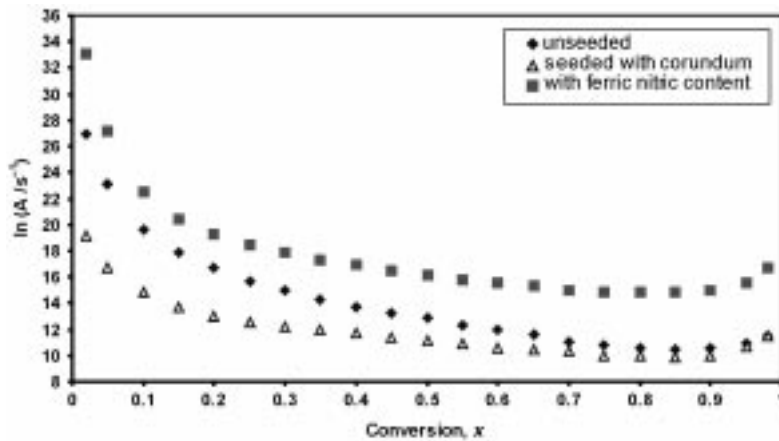


Fig. 5b Pre-exponential factor, A as a function of α - Al_2O_3 conversion, x , for Ozawa–Flynn–Wall analysis

Table 1 Characteristic values of DTA peaks and activation energies for unseeded boehmite gels, seeded with α -Al₂O₃ crystals and originally γ -AlOOH/Fe(NO₃)₃ gels; x – degree of conversion

Sample	Heating rate/ °C min ⁻¹	Temperatures of DTA peaks/°C			Conversion x_m at T_{max}	Activation energy of α -Al ₂ O ₃ crystallization/kJ mol ⁻¹		
		start	maximum	end		Kissinger/ $n=1$	Friedman/ $x=0.2-0.9$	Ozawa–Flynn– Wall/ $x=0.2-0.9$
γ -AlOOH	1.0	1070.6	1124.3	1149.9	0.6202			
	2.5	1088.0	1151.1	1181.2	0.6421			
	5.0	1094.6	1170.4	1206.2	0.6348	571±17	463±10	433±20
	10.0	1081.8	1190.6	1227.7	0.6253			
	20.0	1117.0	1211.5	1258.0	0.5225			
γ -AlOOH- α -Al ₂ O ₃	1.0	943.2	1028.7	1061.0	0.6997			
	2.5	972.2	1058.5	1091.7	0.6605			
	5.0	981.1	1080.2	1125.2	0.6397	449±14	407±10	359±12
	10.0	985.2	1102.4	1150.2	0.6248			
	20.0	998.4	1125.1	1185.6	0.5652			
γ -AlOOH-Fe(NO ₃) ₃	1.0	859.4	942.8	974.3	0.6575			
	2.5	872.4	967.7	1007.9	0.6818			
	5.0	868.3	986.4	1021.9	0.6882	481±13	464±14	451±6
	10.0	862.0	1004.0	1054.6	0.6872			
	20.0	866.0	1020.5	1080.2	0.6487			

For series of measurements at heating rates, β_1, \dots, β , for fixed degree of conversion, $x=x_k$, the plot of $\ln\beta=f(1/T_k)$ results in a straight lines with the slope $-1.052E/R$. T_k represents the temperatures at which the conversion x_k is reached at the heating rate β .

Similarly to the case Friedman analysis the activation energy (Fig. 5a) and pre-exponential factor (Fig. 5b) was obtained as a function of degree of conversion.

Both of these methods can give activation energy for partial degree of α -Al₂O₃ conversion.

Kissinger analysis

The activation energy for all three boehmite samples has been calculated by Kissinger method too [24]. In the Kissinger's method, it is assumed that the rate of conversion is proportional to the concentration of uncreated part. Therefore, $f(x)$ takes the form:

$$f(x) = (1-x)^n \quad (5)$$

in which n is the apparent reaction order and is assumed to be constant through the greater part of the reaction. The conversion rate can be expressed by equation:

$$\frac{dx}{dt} = A \exp\left(-\frac{E}{RT}\right) f(x), \quad (6)$$

When the temperature increases during the reaction, the reaction rate dx/dt will rise to a maximum value, and then return to zero as the reactant is exhausted. The maximum rate occurs when d^2x/dt^2 is zero. Replacing $f(x)$ in Eq. (6) with $(1-x)^n$ and differentiating the equation obtained with the respect to time and setting the resulting expression equal to zero gives (7):

$$\frac{\beta}{T_m^2} = \frac{RA}{E} n(1-x)_m^{n-1} \exp\left(-\frac{E}{RT_m}\right) \quad (7)$$

where T_m is the temperature at which maximum reaction rate takes place and the footnote m denotes the value at this point.

Thus, Eq. (8) is obtained by taking the logarithm of previous equation:

$$\ln\left(\frac{\beta}{T_m^2}\right) = -\frac{E}{RT_m} + \ln\left(\frac{RA}{E}\right) + C \quad (8)$$

A plot of $\ln(\beta/T_m^2)$ vs. $1/T_m$, should give straight line with the slope $-E/R$ (Fig. 6).

Characteristic values of DTA peaks and activation energies are summarized in Table 1 and Figs 4 and 5 for all types of gel samples. The data have been compared for all three methods. It can be seen, that activation energy of α -Al₂O₃ crystallization is the lowest for boehmite gels seeded with α -Al₂O₃ crystals.

The activation energy of α -Al₂O₃ crystallization as a function of conversion for unseeded boehmite gels and γ -AlOOH/Fe(NO₃)₃ gels have got even course (Figs 4, 5). High starting values of α -Al₂O₃ conversion are rapidly decreasing to

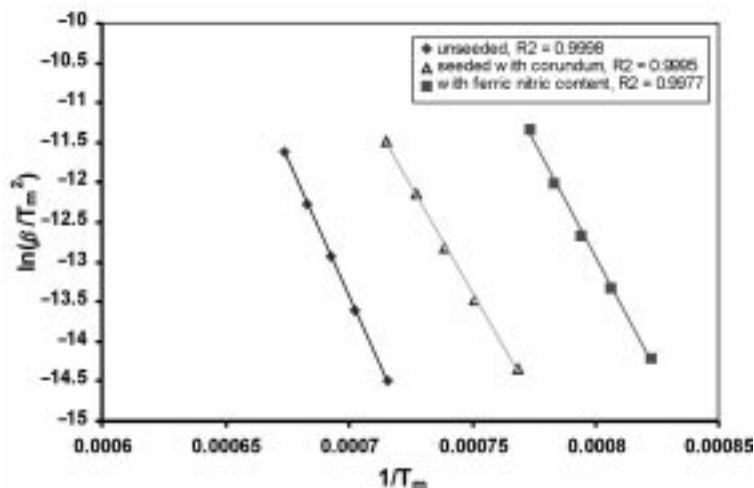


Fig. 6 Kissinger's analysis for unseeded and seeded gels with α - Al_2O_3 crystals and $\text{Fe}(\text{NO}_3)_3$ solution (oxide seeds content 5.0 mass%)

$x \approx 0.2$ and further drop is slight. Different values of activation energy of α - Al_2O_3 crystallization for conversion in a range between 0.2 and 0.9 indicate similar course of processes in both gels but different with boehmite gels seeded with α - Al_2O_3 particles. As it is known [30], α - Al_2O_3 homogeneous nucleation is not applied in gels seeded with α - Al_2O_3 seeds. While the seeds growth in θ - Al_2O_3 matrix, defect Al_2O_3 phases disappear. The transformation of θ to α - Al_2O_3 is controlled by volume diffusion of ions through θ/α - Al_2O_3 interface [8, 31]. The activation energies of α - Al_2O_3 transformation and grain growth are even in this system.

In the unseeded boehmite gels α - Al_2O_3 transformation begins by homogeneous nucleation of α - Al_2O_3 phase. This transformation is properly proceeding of topotactic sequence, forming several increasingly ordered transition aluminas (γ , δ , θ - Al_2O_3), before final rearrangement into α - Al_2O_3 structure in the form of single-crystal colonies [32]. The beginning of α - Al_2O_3 transformation seems to be only the rearrangement process in originally defect structure. It is not certainly a leap of ions through θ/α - Al_2O_3 interface. The rearrangement and the shift of ions into α - Al_2O_3 structure are broken by major θ - Al_2O_3 phase. That is the reason why the activation energy of α - Al_2O_3 crystallization in unseeded boehmite gels up to value of conversion 0.2 is higher than in the following sequence. However, it is interesting that the activation energy in γ - $\text{AlOOH}/\text{Fe}(\text{NO}_3)_3$ gels is closer to the unseeded gels than to α - Al_2O_3 seeded gels.

This result is very significant and is in good agreement with previous work [10], ions of iron (originally γ - $\text{AlOOH}/\text{Fe}(\text{NO}_3)_3$ system) dispersed into the transitions aluminas do not work as crystal seeds (α - Al_2O_3 , α - Fe_2O_3), but process of α - Al_2O_3 transformation can be attributed prevailing to the solution, ionic effect.

On the contrary boehmite gels seeded with α - Al_2O_3 particles behaved in agreement with works [33–35], which affirm that the nucleation effect of α - Al_2O_3 or α - Fe_2O_3 seeds is purely crystallographic.

Conclusions

Ions of iron (originally γ - $\text{AlOOH}/\text{Fe}(\text{NO}_3)_3$ system) dispersed into the transitions aluminas do not work as crystal seeds (α - Al_2O_3 , α - Fe_2O_3). The activation energy of α - Al_2O_3 crystallization was $481 \pm 13 \text{ kJ mol}^{-1}$ (Kissinger analysis), $464 \pm 14 \text{ kJ mol}^{-1}$ (Friedman analysis) and $451 \pm 6 \text{ kJ mol}^{-1}$ (Ozawa–Flynn–Wall analysis) for γ - $\text{AlOOH}/\text{Fe}(\text{NO}_3)_3$ system. Similar values of the activation energies of α - Al_2O_3 crystallization have been obtained for unseeded boehmite gels for Friedman ($463 \pm 10 \text{ kJ mol}^{-1}$) and Ozawa–Flynn–Wall analysis ($433 \pm 20 \text{ kJ mol}^{-1}$). The values of activation energies of α - Al_2O_3 crystallization for all three methods have been the lowest for boehmite gels seeded with α - Al_2O_3 crystals.

Result of that is the process of α - Al_2O_3 transformation for originally γ - $\text{AlOOH}/\text{Fe}(\text{NO}_3)_3$ gels goes like that for unseeded system, but at lower temperatures (lower about 200°C).

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