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Aggregation kinetics of sol-gel process based on titanium tetraisopropoxide

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The kinetics of hydrolysis and condensation of titanium tetraisopropoxide (TTIP) under neutral conditions has been investigated by a light scattering method for different TTIP and water concentrations. The evaluation of kinetics data confirmed the complex nature of the process, which includes hydrolysis, condensation and aggregation of primary particles. Instead of commonly used inverse value of induction time, the rate of an individual particle mass growth for the adequate description of kinetics during induction period was used. Taking into account the initial water consumption allowed a unified description of kinetic data in different ranges of reagent concentrations to be obtained. © *2003 Kluwer Academic Publishers*

1. Introduction

Metal oxide submicron particles with controlled size distribution and high specific area are of considerable interest for production of composite ceramics [1], pigments and components of coating films [2], as well as for catalytic and photocatalytic applications [3]. Whereas the sol-gel process to produce colloidal silica is well understood [4], a clear and complete picture for the formation of transition metal oxide particles has not still been obtained. Understanding the phenomena occurring during the initial stages of particle growth seems to be especially important, because they can determine the properties of final products.

Kinetics of the sol-gel process based on titanium metal alkoxides has been studied in a number of works [5–9]. Different empirical formulae for the dependence of the inverse value of the induction time as a function of reagent concentrations have been obtained. They are often used to determine the order of the hydrolysis reaction, which is found to be different for different ranges of reagent concentrations. This peculiarity has not yet been clearly explained. For description of induction period LaMer's model [10] is often applied, where induction time is explained by accumulation and supersaturation of alkoxyhydroxytitanium molecules (partially or completely hydrolysed molecules of titanium alkoxide). However, it has been shown by Karl Fisher titration method [8] and by Raman spectroscopy [11], that the initial hydrolysis is very fast compared with the induction period. Furthermore, non-monomeric reaction products have been observed during this period in X-ray absorption near edge structures (XANES) [12] and nuclear magnetic resonance (NMR) experiments [13]. From these studies it became clear that the induction time in the case of TTIP based sol-gel process can not be directly related to the hydrolysis reaction, but that it reflects the kinetics of complex processes, including different types of inorganic condensation and aggregation. The presence of nanoparticles of radius 2–4 nanometers throughout the whole induction period of sol-gel process with TTIP was observed by using dynamic light scattering (DLS) [14–16, 17].

The early-stage processes in hydrolysis and condensation of zirconium alkoxides has been studied by Fourier transform infrared spectroscopy (FTIR) and small angle X-ray scattering (SAXS) [18]. A rapid flow-through mixing cell was used for monitoring the reaction within a millisecond time scale. This investigation showed the fast hydrolysis/condensation reactions (<1 sec) and formation of primary particles with a radius about 3–4 nm.

Strictly speaking the term "induction period" must denote a period between the beginning of the reaction and the nucleation of particles. However, in this article the traditional definition of the induction period accepted in sol-gel chemistry as the period until the appearance of a significant turbidity in the system will be used.

The analysis of TTIP based sol-gel reaction kinetics is presented. The early stage rapid hydrolysis and condensation reactions, which precede the formation of primary particles are not studied. Instead, interest is the kinetics for the rest of the induction period, which consists, as hypothesized later, in aggregation of additionally hydrolyzed primary particles. First a conclusive parameter for the description of the kinetics during this part of induction period is found. Then, taking into account the fact that the process occurs in several steps, a general kinetic expression, which is valid during the aggregation stage of the induction period in different ranges of reagent concentrations, is obtained.

2. Experimental method

The sol-gel process has been carried out using TTIP (98 + % Acros Organics), isopropanol (99 + % Acros Organics, 0.05% maximum water content) and distilled water. A solution of TTIP in isopropanol (solution A) and a solution of water in isopropanol (solution B) were prepared. Under intensive stirring the solution B was quickly added to solution A. After 30 sec the stirring stopped and measurements of particle size and intensity of scattered light began. To do this, Photocor DLS system [19] with a 20-mW He-Ne laser (Spectra-Physics) as a light source was used.

To assure the reproducibility of results, it was important to use the same procedure every time: intensity and time of stirring, size of experimental cell etc. Furthermore, the filtration of water and isopropanol with 0.1 micrometer mesh filter was necessary in order to get rid of inevitable presence of dust particles, which could be centers of inhomogeneous nucleation and significantly change the kinetics of the reaction. Since the kinetics depends very strongly on the water concentration, special care was taken for environmental humidity, TTIP being very sensitive towards humidity and isopropanol being highly hydroscopic.

3. Results and discussion

3.1. Conclusive parameter to characterize the kinetics of the process

The usual parameter used to characterize the kinetics of sol-gel processes during the induction period is an inverse value of induction time ($1/t_{\text{ind}}$) [5, 7–9]. This choice was criticized in [6]. It was noted that t_{ind} determined by turbidity measurements can correspond to different states of the system. Furthermore, processes with different particle growth kinetics may result in the same induction time [17].

In this work, attempts will be made to find a more conclusive parameter, which can be related to the kinetics of the process. To do this, the data on the intensity of scattered light will be used. A typical curve of the scattered light intensity during induction period of TTIP based sol-gel process is presented in Fig. 1.

Four stages can be distinguished on this curve: an initial growth or nucleation stage, a linear growth stage, a transitory stage and a fast growth stage. The last stage corresponds to the induction time usually observed in turbidity experiments.

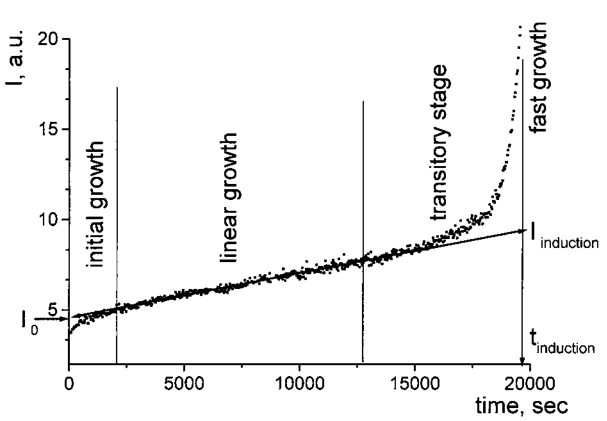

Figure 1 Typical curve of scattered light intensity in TTIP based sol gel process during induction period.

I_0 is denoted as the value obtained by extrapolation of linear part of $I(t)$ towards $t = 0$. The initial growth stage may be much shorter depending on the rate of micromixing [20]. When the reagents are mixed faster than the characteristic times of reactions (typically ~10 ms), this stage is not observed in experiments with temporal resolution >1 sec. Therefore, the initial intensity I_0 rapidly appearing in the reactive solution is due to nuclei. To analyze the kinetics of the process the following expression for kinetic rate is introduced:

$$r = (\mathrm{d}I/\mathrm{d}t)/I_0 \tag{1}$$

where the $\mathrm{d}I/\mathrm{d}t$ is taken on the linear part of $I(t)$.

Now, it will be shown that r is proportional to the rate of mass growth of an individual particle. Since the particle size during the induction period is much smaller then a wavelength of incident radiation Rayleigh scattering is occurring. In this case the intensity of light scattered by individual particles is proportional to the square of their mass (m). Then the total scattered intensity can be written as $I = Am^2N$, where N is the number of particles in a scattering volume and A is a geometrical factor, which is a constant during experiments. If M is the total mass of particles, the particle number N is equal to M/m and $I = AmM$. As it has been shown in the case of TTIP-based sols, the total solid mass appearing after the rapid nucleation stage is conserved during the process and individual particles grow by aggregation [16]. Then, using $M = const$, from (1) it is found that $r = (\mathrm{d}m/\mathrm{d}t)/m_0$, where m_0 is the mass of primary particles. It was shown by DLS measurements that m_0 does not change significantly with changing of reagents concentration [17]. Therefore,

$$r \sim \mathrm{d}m/\mathrm{d}t \tag{2}$$

In what follows the rate of particle mass growth (2) will be used as a kinetic parameter and expression (1) for its calculation will be used. In a real system the particle distribution is polydispersed so that m and r are the average particle mass and the average rate of particle mass growth respectively.

3.2. Analysis of measurements of scattered light intensity

Two parameters determine the composition of the system: the molar concentration of TTIP (c_{t}) and the hydrolysis ratio ($H = c_{\text{h}}/c_{\text{t}}$), where c_{h} is the molar concentration of water. 3 series of experiments were performed. In each series c_{t} was fixed and H was changed. Fig. 2 shows the dependences of r as a function of H for different c_{t} in a double logarithmic scale.

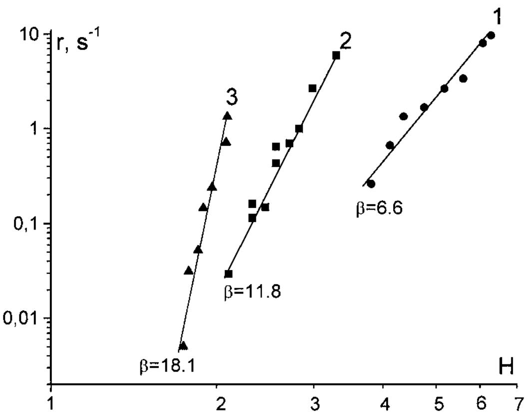

Figure 2 r as a function of H for different c_t: $c_t = 0.08$ M for curve 1, $c_t = 0.15$ M for curve 2, $c_t = 0.28$ M for curve 3.

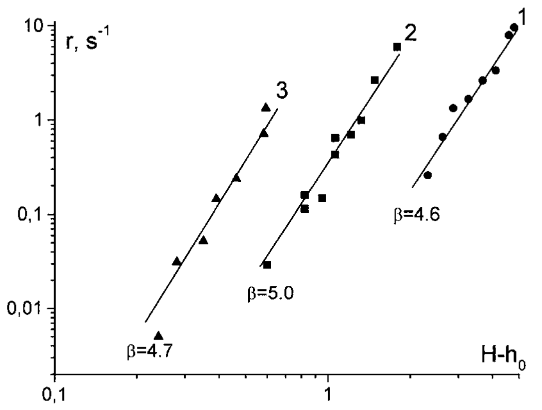

Figure 3 r as a function of $(H - h_0)$ for different c_t: values of c_t correspond to those of Fig. 2.

To analyze these data at first a usual power law expression was applied and the $r(H)$ dependences were approximated by the following formula:

$$r = k \cdot c_t^{\alpha} \cdot c_h^{\beta} = k \cdot c_t^{\alpha+\beta} \cdot H^{\beta} \qquad (3)$$

The $r(H)$ curves were fitted separately for different c_t. The corresponding values of β are shown on Fig. 2. It is seen that β it does not remain constant, but increases progressively with increasing c_t and reaches very high values (β is about 18 for $c_t = 0.28$). It shows that the representation (3) is not adequate in this case.

As it was already mentioned the initial hydrolysis reaction is very fast compared to the whole induction period. Therefore it is supposed that the limiting processes determining the induction time are the reactions of additional hydrolysis and condensation/aggregation. To describe correctly the kinetics of this process, instead of the amount of water put initially in the system, the amount of water remaining after the nucleation must be used. To modify the formula (3), the initial water consumption ratio $h_0 = c_h^0/c_t$, where c_h^0 is the molar concentration of water consumed during the initial hydrolysis and primary particle formation, is introduced. Equation 3 is then replaced by the following modified expression:

$$r = k \cdot c_t^{\alpha} \cdot (c_h - c_t \cdot h_0)^{\beta} = k \cdot c_t^{\alpha+\beta} \cdot (H - h_0)^{\beta} \qquad (4)$$

The results of fitting the data by model (4) and (3) are presented in Table I.

In Table I the values of R^2, which is a coefficient of multiple determination commonly used as a criterion of the adequacy of fitted regression model [21], are presented. The value $R^2 = 0.98$ signifies that these data can be adequately described by formula (4) and $R^2 = 0.72$ obtained for the approximation using expression (3) shows that (3) is an incorrect model. Furthermore the model (3) gives negative value of $\alpha = -4$, which is unacceptable. Adequacy of the model described by Equation 4 is clearly seen from Fig. 3, where the dependences of r as a function of $(H - h_0)$ at different c_t in double logarithmic scale are presented. All the curves in Fig. 3 have almost the same slope. The values of β, which are shown in the Fig. 3, do not depend systematically on c_t and, consequently, the unique value of β about 4.8 can be found, in accordance with fitted value presented in Table I. The value of initial water consumption $h_0 = 1.1 \pm 0.1$ found independently in [20] is in a reasonable agreement with $h_0 = 1.4 \pm 0.1$ found in present work.

TABLE I Reaction rates obtained with and without correction term

Method	α	β	h_0	R^2
With correction term, Equation 4	1.1 ± 0.2	4.8 ± 0.5	1.4 ± 0.1	0.98
Without correction term, Equation 3	-4.0 ± 2.0	7.2 ± 3.0	0	0.72

The kinetics of hydrolysis of titanium alkoxides was studied in a number of articles. The results are summarized in Table II.

It is seen from Table II, that essentially different reaction rates were obtained for the same systems. These discrepancies are caused by two reasons. First, the unmodified formula (3) was used for different concentration ranges and second, rather speculative parameter $1/t_{ind}$ was used for the process description.

3.3. Schematic description of the induction period

It is assumed that shortly after the mixing of reagents the primary particles are formed with radius about 2 nm [15]. Some amount of water is consumed in this process. Afterwards a growth of the primary particle may be described by aggregation.

To find what kind of aggregation regime is present in this system, a sticking coefficient of particles (a part of particle collisions resulting in aggregation) was analyzed. Sticking coefficient W was estimated using the

TABLE II Reaction rates for different alkoxides

Alkoxide	α	β	Reference	Kinetic parameter
Ti(Oet)4	1.23	2.96	[5]	Inverse induction time
Ti(Oet)4	2.0	4.0	[6]	
Ti(Oet)4	2.0	1.0	[8]	
Ti(Obu)4	2.0	5.0	[9]	
Ti(OPri)4	3.5	5.9	[7]	
Ti(OPri)4	1.1	4.8	Present work	Rate of particle mass growth

expression for characteristic time of aggregation [22]:

$$t_a = \frac{3\eta}{4k_B T N_0 W} \qquad (5)$$

η is the viscosity, k_B is the Boltzmann constant and N_0 is the concentration of primary particles (number per cm^3). To estimate N_0 it was assumed that all isopropoxide was transformed into spherical particles with radius of 2 nm. In order to make a rough estimation, primary particles were considered to have a density around the density of anatase bulk phase ($\sim$3.8 g/cm^3). Then knowing the initial concentration of TTIP, N_0 can be found. For an initial molar concentration of TTIP $c_t = 0.28$ mol/L, $N_0 = 1.75 \cdot 10^{17}$ cm^{-3}. Form (5), using viscosity of isopropanol $\eta = 2.4$ cP ($T = 20°$C) and, taking the induction time as a characteristic time of aggregation, $W \sim 10^{-10}$ for an induction time equal to 2×10^4 s. This small value of sticking coefficient suggests that a reaction-limited aggregation (RLA) regime is evident during induction period.

The water remaining after the particle nucleation plays an important role as a driving force in aggregation process. It hydrolyses the surface alkoxy groups, which enables further aggregation of particles via condensation reaction. This is why it is important to use in kinetics formula (4) a relative amount of remaining water $(H - h_0)$ instead of an initial relative amount of water H.

At the end of the induction period the average particle radius is about 4 nm [15]. At this time the particle growth rate increases sharply; the formation of big particles with radius of several hundred nanometers and a sudden increase in solution turbidity are observed.

The following question arises inevitably: if LaMer's model [10] of hydrolyzed monomers accumulation is not valid in this case, how can the phenomenon of the induction period be explained? The aggregative stability of particles depends on their surface charge and on properties of the electrical double layer near the surface. This surface charge can exist even under neutral conditions, because e.g., of protonation of alkoxy and hydroxy surface groups of particles by protons originating from dissociated water molecules. The aggregative stability of growing particles may decrease with their size and be lost when some critical size is reached. Then the RLA (slow aggregation) may change into the diffusion-limited aggregation (DLA) [23] (fast aggregation). This can correspond to the usually observed induction time.

4. Conclusion

The kinetics of TTIP based sol-gel process under neutral conditions has been investigated for different TTIP and water concentrations during induction period. The formation of primary particles (nucleation) takes place short time after the initial hydrolysis and condensation. It is hypothesized that an additional hydrolysis and condensation results in RLA of these particles. Thus, the latter processes may mostly be responsible for the delay time or the induction time, which was often erroneously used for estimation of the hydrolysis reaction rate.

In order to obtain the adequate description of aggregation kinetics during the induction period, instead of inverse value of induction time, the value proportional to the rate of particle mass growth was used. Into the kinetics formula a new parameter was introduced, which is the amount of water consumed during nucleation of particles and in analysis of aggregation kinetics the concentration of water remaining after nucleation instead of the initial water concentration was used. This permitted the general kinetic expression to be obtained in different ranges of reagent concentrations.

The existence of the induction time may be explained by changes in surface charge of particles. Additional experiments on *in situ* measurements of particle zeta-potentials and solution conductivity during induction period could confirm this hypothesis.

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