The Kinetics of The Process of Pepitization During the Hydrolysis of Titanium Nanoparticle
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1.Introduction

Titania powder can be applied in a wide range of industries like pigments, catalyst support and photocatalysts because of its interesting optical, dielectric and catalytic properties. Many methods of preparing the nanometer titanium have been put forward. Among these, the chemical methods draw the scientific interesting because of their advantages of low cost and low reaction temperature. The Sol-gel method is a very important process to produce the nanometer titania powder. Many researches show that it has great value for the final product by controlling the size, shape and structure of titania precursors. Peptization process has the merit to control the reaction at molecular level [1].

2.The peptization in the process of hydrolysis

Basically, TiO_2 colloids grow through the hydrolysis and condensation of titanium alkoxides in aqueous media [2,3]. In the presence of water, a spatial oxide network is formed by alkoxide hydrolysis and condensation. The process of hydrolysis and condensation is showed in the following reaction:

$Ti(OR)_4+4H_2O\_Ti(OH)_4+4ROH$ (hydrolysis)   (1)
$Ti(OH)_4\_TiO_2·xH_2O+(2-x)H_2O$ (condensation)   (2)
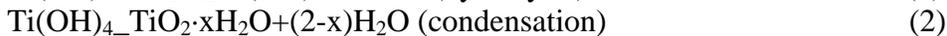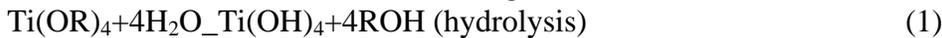
As the alkoxy chain becomes long, the reactivity of hydrolysis becomes less since the long alkoxy chain affects the rate of particle formation limitedly[4].

The mole rate of the water-to-tianium ($r=[H_2O]/[Ti]$) has a great effect on the size, stability and morphology of the sol generated from alkoxides. Usually, there are two distinguish ranges of r: _ at low r(r 10), 0.5-1__m diameter spherical, relatively monodisperse particles are obtained [5,6] _ at high r value, the particles (usually <100nm in diameter) tend to precipitate to form large aggregates which can be broken up to final size by peptization [7,8].

The process of forming stable colloidal TiO_2 nanoparticles from alkoxides is very complex and includes several steps. The results of the paper [2] show that usually there are several steps involved. During hydrolysis of the alkoxides, the first step is the nucleation and growth of primary particles which then aggregate to form large clusters and precipitates rapidly. Second step is slow peptization of the aggregates. In the end this step precipitates disappear completely and a translucent suspension forms. The third step is that the nucleation, growth and precipitation are completed within a very short time under high-r hydrolysis and pepitization occurs nearly at time zero.

3. Kinetics
The formation of nanometer TiO_2 at high r rates remains poorly understand because of the rapid precipitation, which makes kinetics studies very difficult.

The kinetics involve the two processes the agglomeration and fragmentation (peptization). We will introduce the relative theories and experiments results.

3.1 Scaling theory of fragmentation
3.1.1The Irreversible Process
Many theoretical works focus on the description of fragmentation by a system of linear rate equation. It assumes that the breakup process is driven by an external source. Cheng and Rander [9] found that the asymptotic form of the cluster-size distribution at large size is strongly determined by the homogeneity index of the breakup kernel. According to the model of Cheng and Rander [9], the rate of fragmentation is relative to the size distribution function. The shape of this curve can give the information about both the rate of disappearance of large aggregates and the rate of formation of small fragments. This fragmentation rate may be deduced from the variation with time of the weight and number of average of the aggregate.

Eric Ringenbach et al. [10] research the mechanism and kinetics of fragmentation of colloidal alumna by using the model of Cheng and Radner. They take advantage of the linear fragmentation concept which means, at the absorbed polymer layer, the dispersive forces which act between opposing portions of grains have no relationship with their localization inside the grain agglomerate or fragment. The main driving force controlling the rate of grain dispersion is the layer modification acting uniformly at each interparticle link. They also neglect the influences of other forces on the rate of fragmentation. The following equation is used to describe a linear fragmentation process. Here we use the same note of the document [8].

(3)

where c(n,t) is the concentration of n-mers size cluster at time t, a(n) is the rate of fragmentation and f(n/m) is the rate at which cluster of size n are generated from cluster of size m. For homogeneous kernel:

$$a(n)=n^{-}$$
(4)

where _ is the homogeneity index. For homogeneity, the f(n/m) has the form $m^{-1}b(n/m)$.The mass conservation holds the condition $\int_0^1 xb(x)dx=1$, and the average number of fragments engendered by particle breakup, $\int_0^1 xb(x)dx$ is given to be finite. Theoretically, the breakup rate is related to the changing of the mean cluster size which decreases conforming to
$$S(t) \sim N(t) \sim t^{-1/-}$$
(5)

By using the usual cluster size distribution, Eq.(3) can be modified as:

$$C(n,t)S^{2}(t) \sim \_[n/S(t)]$$
(6)

Where S(t) is the weight average size of the colloid. Substituting the Eq.(6) into Eq.(3) and by some mathematical treatment, we get

$$\boxed{} \quad (\_>0, \text{ the separation constanat}) \qquad\qquad (7)$$

Where the overdot denotes the time derivative. In the case of linear fragmentation, the exponent _ is related to the slope of _(n) for large value of this variable.

$$\_(n) \ \ n^{-2}\exp(-an^-) \qquad\qquad (8)$$

3.1.2 The Reversible Process

The model of Cheng and Render [8] treats the situation of irreversible fragmentation but the polymer-induced fragmentation in the case of preparation of TiO_2 may be reversible, since S(t)and N(t) do not vary with $t^{-1/-}$as required by Eq.(5).

The paper [11] shows that the aggregation rate will increase greatly by stirring the suspension, so Eric Ringenbach et al. [10] think that the weakly stabilized fragment undergoes supplement aggregation by stirring and the stirring of the mixture will decrease the fragmentation rate, i.e no fragmentation emerges. Therefore the exponents of S(t) and N(t) and the rate of breakup a(n) must be different. This means the mechanism of aggregation/fragmentation would be reversible.

When we consider the reversible process, the agglomeration rate and fragmentation rate must be considered together. Fereydoom Family et al [12] give the following result.

For the reaction:

$$Ai+Aj \; \underset{F(i,j)}{\overset{K(i,j)}{\rightleftharpoons}} \; Ai+j \qquad\qquad (9)$$

where Ai is a cluster containing i monomers and K(i,j) and F(i,j) are the fragmentation and agglomeration rates, respectively. When the F(i,j)=0, the process is irreversible and the scaling theory is given in the above discussion. During the reversible process, the K(i,j) and F(i,j) are the inverse factors so there must have a crossover time _, after a long time t>>_, the reaction reaching a equilibrium state. The F(i,j), the rate of a cluster of size i+j breaking into a cluster of size of I and cluster j, has the form:

$$F(i,j)=k\_(i,j) \qquad\qquad (10)$$

Here k is the breakup constant, _(i,j) is the function representing the relationship of the fragmentation rate on the cluster size i and j, and _(1,1)=1. By defining the mean cluster size:

$$S(k,t) = \; {}_s \, s^2 Ns(k,t) \qquad\qquad (11)$$

where $N_s(k,t)$ denotes the number of cluster of size s in the system at time t.

$$N_s(k,t)=s^{-2}f(S(k,t)/s) \qquad\qquad (12)$$

f(x) depends on the detail process. For the steady-state cluster-size distribution, Ns(k,) and its moments depend on S(k,). Assuming the S(k,) scaling with k, at t>>_,

$$S(k,)\sim k^{-y} \tag{13}$$

If at steady state, S(k,) scaling k^{-y}, the following equation holds in the steady state,

$$Ns(k,)=s^{-2}f(sk^{y}) \tag{14}$$

this means N(k,)~k^{y} for the whole clusters N(k,t)= sNs(k,t).

Danijela Vokapic and Themis Matsoukas [2] simplify the above model by providing a hypothesis that the deaggregation of the colloid is caused by the competing effect of two opposing mechanisms: peptization(fragmentation), which causes the slow migrate out of primary particles and possibly small clusters from large precipitates and reaggragation whereby the peptized primary particles and clusters reattach onto large aggregates. The slow time scales of peptization suggest that this process is limited by the rate of breakdown of the bonds that hold the primary particles together. The possible reason may be Ti-O-Ti bridges between touching particles or the result of a deep secondary minimum in the pair-potential interaction.
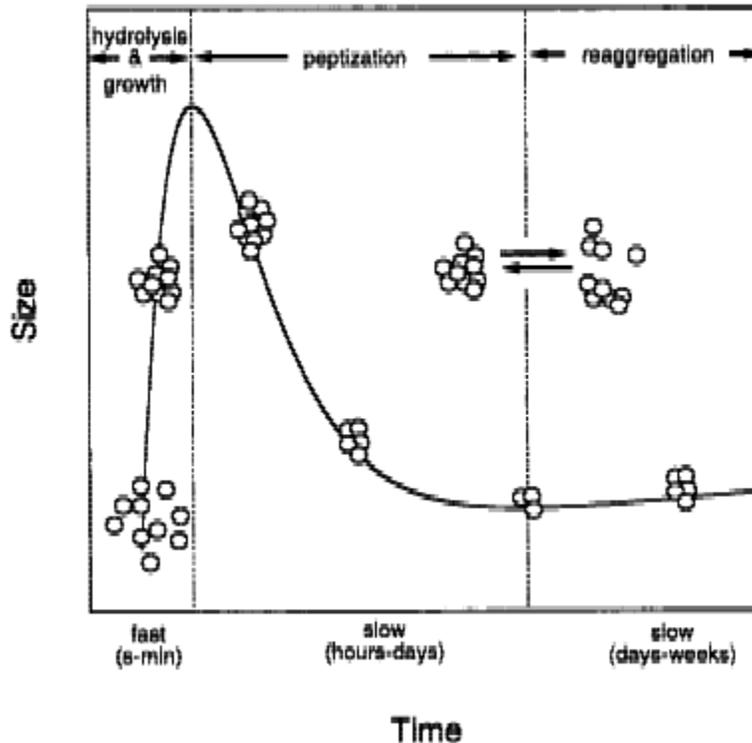

Figure 1 Schematic depiction of the growth and peptization of TiO_2 Colloids. Size and time are not drawn to the scale[2].

Their experiment shows that the formation of TiO_2 colloids at high $[H_2O]/[Ti]$ (r) ratios is dominated by process that occur during the peptization step. The final size is determined by the competing actions of peptization and reaggregation, peptized particles may further growth by aggregation over extended periods of time. This process is schematically showed in figure1. Their results show that high alcohol concentration or molecular weight cause the colloidal destabilization.

This model assumes that breakup and reagglomeration proceed at the same time during peptization. In term of the concentration of particles agglomeration is a second-order process. In diffusion-limited agglomeration we can calculate its rate constant from the pair interaction in the suspension [13]. The deagglomeration is more complex and till now has not understood clearly. For the deagglomeration of titania, both electrostatic repulsion and chemical split band competes, the first action excluding particles in agglomerate and second action combining these particles together. Under the situation of not too high concentration, we can neglect the effect of colloisions in the breakup process so the rate of deagglomeratie can be treated as the first order in the number concentration of particles

$$dN/dt = 1/2K_a N^2 - K_d N \qquad (15)$$

where N is the total number concentration in the suspension at time t. The average rate constants for agglomeration, K_a, and deagglomeration, K_d, are defined as

$$K_a = 1/N^2 \quad Kij \ NiNj \qquad (16)$$
$$K_d = 1/N \quad (f_i-1)KiNi \qquad (17)$$

Where Ni is the number concentration of particles containing i particles, K_{ij} is the agglomeration rate for the pair i and j, K_i is the fragmentation rate of an agglomerate particle of size i and f_i is the mean number of fragments produced by its fragmentation. Here f_i-1 represents the net change in the total number concentration of a particle of size i. By defining the average agglomerate particle size, n, the number of primary particles per cluster is

$$n = N_0/N = (R/r_o)^{df} \qquad (18)$$

Where r_0 is the size of the primary particles, R is the size of the mean agglomerate particle, and d_f is the fractal dimension. In the whole process, the total number concentration of primary particles, N_0, keeps constant and is given by

$$N_0 = 3C/(4 \_ r_o 3) \qquad (19)$$

where C is the mass concentration of titania and _ is the density of the primary particle. Substituting these equations into equation (15), we get
$$dn/dt = N_0 K_a/2 - K_d n \qquad (20)$$

Generally, the different order in N of agglomeration and deagglomeration make botch systems reach steady state.

_At steady state, the particle size is obtained from equation (15) with dn/dt=0:

$$n = K_a N_0 / (2 K_d) \tag{21}$$

By combining Eqs. (18) and (19), Eq.(21) expresses the mass-equivalent sphere radius of the peptized particle

$$R / r_0 = [3C/(8 \, \_r_0 3) \cdot K_a / K_d]^{1/df} \tag{22}$$

From this equation, the final size (linear dimension) scales as $C^{1/df}$ given that K_a and K_d are remained constant.

_Kinetics
By assuming K_a and K_d is independent of size, Eq.(20) can be expressed as

$$n/n = 1 + (n_0 - n)/n \cdot e^{-K_d(t - t_0)} \tag{23}$$

where n_o is the number concentration of agglomerates at time t_0 and n is the steady-state mean size which is got from Eq.(21). By some mathematic treatment, the following equation is given:

$$R/R = 1 + a e^{-K_d t}, \quad (t \gg \ln(a/K_d)) \tag{24}$$

From the above equation, the radius approaches the steady state value as a first-order process whose time constant is equal to the deagglomeration rate constant. The agglomeration rate can be got from from Eq. (24) and the agglomeration rate is obtained from K_d and the final size can be got by using Eq.(22). We can use the parameter *a* to check the validity of the condition t≫ln(a/Kd).

Conclusion:
_ The experiment shows[2], the formation of TiO_2 nanocolloid from alkoxides is dominated by colloidal interaction. It is more efficient to control the aggregation/fragmentation by avoid the presence of the alcohol.
_Since the mechanism of aggregation/fragmentation may be reversible, its evolution would be expected to follow four successive steps. In the first step, the aggregation predominates, in the second step, aggregation and fragmentation of equal important lead to a steady-state situation and in the third step, fragmentation predominates over aggregation. In the last step, fragmentation to control the variation of the average sizes S(t) and N(t).
_ The simplified model get the results that the first order decreases of size and power-law scaling of the form $R \sim C^{1/df}$ between the particle and concentration and size.

Reference:
1. B.L.Bischoff, M.A. Anderson, Chem, Mater., 7 (1995),1772
2. Vorkapic D, Matasonkas T., "Effect of temperature and alcohols in the preparation of titania nanoparticles form alkoxides", J.Am. Ceram. Soc., 81,(11), 2815-20, 1998

3. Zeng T. Y., Qiu Y et al., "Microstructure and phase evolution of TiO_2 precursors prepared by peptization—hydrolysis method using polycarboxylic acid as peptizing agent", Mat. Chem. and Phys., 56 (2) 163-170, 1998
4. C. Sanchez, F.Ribot et al., "Design of hybrid organic-inorganic materials synthesized via sol-gel chemistry, New J. Chem. 18, 1007-47, (1994)
5. J.-L Look and C.F. Zukoski, "Colloidal Stability of Titania precipitate Morphology: Influence of Short-Range Depulsion", J.Am. Ceram. Soc., 78[1]21-32 (1995)
6. V.J.Nagpal, R.M.Davis and J.S.Riffee, "In Situ Steric Stabilization of Titanium Dioxide Particles Synthesized by a sol-gel process", Collids Sur., 87, 25-31, (1994)
7. Q.Wu, M.J. Gieselmann and M.A.Anderson, "The Colloid Stabilization of Titannium Dioxide Particles Synthesized by a Sol-Gel Process", Collids. Surf., 87. 25-31 (1994);
8. C.Lijzengh, V.T.Zaspalis et al., "Nanostructure Charactrization of Titannia Membranes", Key. Eng. Mater., 61 & 62, 379-82 (1991)
9. Cheng, Z., and Redner, S., Phys. Rev. Lett. 60, 2450 (1988)
10. Eric Ringenbach, Guy Chanveteau and Emile Pefferkorn, Aggregation/Fragmentaiion of Colloidal Aluminum, J. Colloid and Interface Sci., 172, 208-213, (1995)
11. Quali, L., and Pefferkorn, E., J.Collid. Interface. Sci., 161,237, (1995)
12. Fereydoom Familly, Paul Meakin and John Deutch, "Kinetics of Coagulation with Fragmentation: Scaling Behavior and Fluctuation", Phy. Rev. Lett., vol.57, 6, 727-730, 1986
13. Hunter R.J., Electroviscous and Ciscoelectric Effects, "Zeta Potential in Colloid Science", P190-205,Edited by Ottewill R.H and Rowell R.L, Academic Press, New York, 1981