Nanoscale Silicon Dioxide Prepared by Sol-Gel Process

Hui Gao (Corresponding author) & Junling Yang

College of Material Science and Chemical Engineering

Tianjin Polytechnic University, Tianjin 300160, China

E-mail: gh8404@yahoo.com.cn

Abstract

Nanoscale silicon dioxide has been prepared with tetraethyl orthosilicate (TEOS) by sol-gel process. The optimum process conditions have been obtained by investigating the effect of formulation, temperature, catalyst and etc. on its gel morphology, gel time, and particle size.

Keywords: Nanoscale silicon dioxide, Sol-gel process, Tetraethyl orthosilicate (TEOS)

Preface

Nanoscale silicon dioxide, with the presence of hydroxyl and absorbed water on the surface, is an amorphous, non-toxic, odorless and eco-friendly white powder. It is characterized by fine particle size, high purity, low density, large specific surface area, and good dispersing performance. As a result, it has excellent stability, reinforcing ability, thixotropy, optical and mechanical properties. Therefore, it is widely applied in ceramics, rubber, plastics, paint, pigment and catalyst carrier, and plays an important role in improving the properties of final products (Milin, Zhang et al, 2003, p. 11-13; Lide Zhang et al, 2001; Liangzhen Cai et al, 2002, p. 20-23). At present, there are quite a few methods for preparing nanoscale silicon dioxide, such as precipitation process, sol-gel process, micro-emulsification process, as well as vacuum distillation and condensation process (Chanli, Zhou et al, 2001, p. 22-24; Qishu, Zhai et al, 2000, p. 57-62; Junmin, Qian et al, 2001, p. 1-5). However, sol-gel process is easy to control, and the obtained particles are evenly distributed (Yu, Guo et al, 2005, p. 34-35; Ning, Zhang et al, 2003, p. 267-269; Yang, Li et al, 2007, p. 707-710).

1. Experiment

1.1 Reagents

TEOS, hydrochloride, distilled water and absolute alcohol.

1.2 Equipments

DF-101S Heat-Collecting Electromagnetic Stirrer, DL-101-2 Electric Blast Drying Oven, and SX2-2.5-10 Box-Type Resistance Furnace.

1.3 Preparation of nanoscale silicon dioxide

Add a certain amount of TEOS and absolute alcohol into beaker, and drop slowly the mixture of distilled water, absolute alcohol, and hydrochloride at a proper ratio under the conditions of constant temperature and magnetic stirring. Place the obtained sol in fume hood for 1 h to evolve gradually towards the formation of a gel, which is in turn grinded after drying for 4 h in an oven, and then calcined for 3 h in the box-type resistance furnace to achieve the nanoscale silicon dioxide powder.

2. Results and discussions

2.1 Effect of the ratio of TEOS to alcohol on the preparation of nanoscale silicon dioxide

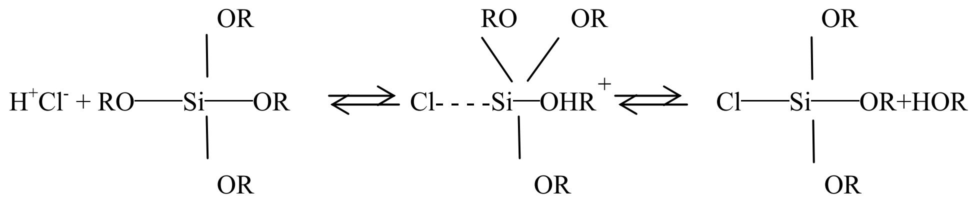
Table 1 shows the effect of the ratio of TEOS to alcohol on the preparation of nanoscale silicon dioxide.

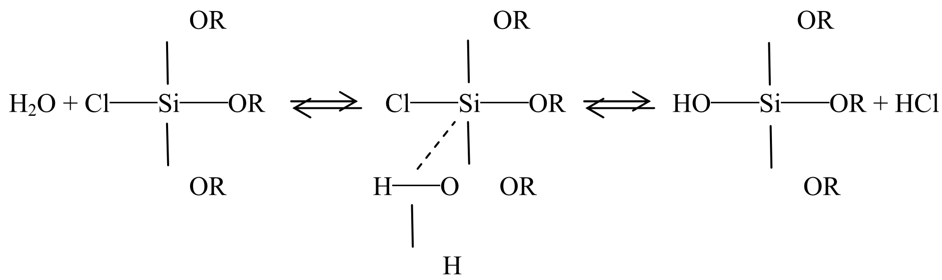
The results indicate that the gel time becomes longer as the dosage of alcohol increases. It's because the alcohol-diluted sol reacts slower as the concentration decreases, which lead to the increase of gel time. However, TEOS is insoluble in water before reaction, and absolute alcohol, as a solvent, can increase the contact surface area between TEOS and water, which results in the shortening of sol-gel reaction time. Therefore, the dosage of absolute alcohol must be enough. A small amount of light blue powder is observed on the surface of porcelain boat, this is because the powder in porcelain boat is too much to be completely processed, and leads to overload. All powder is ivory white when the processing amount is relatively appropriate. It is concluded that the proper ratio of TEOS to alcohol is 1 to 2.

2.2 Effect of the dosage of distilled water on the preparation of nanoscale silicon dioxide

Table 2 shows the effect of the dosage of distilled water on the preparation of nanoscale silicon dioxide.

The results indicate that the gel time becomes longer as the ratio of TEOS to water rises from 1/1 to 1/5, and the ivory white powder can be obtained. However, with the increase of the water dosage, the concentration of condensate polymer and viscosity of sol decrease, and gel time increases. The reaction procedure is expressed with following formula.





It is concluded from the above hydrolysis procedure of TEOS that in the presence of acidic catalyst, hydrolysis rate of TEOS increases with the reduction of steric hindrance around silicon atom. In addition, electron donor group attached to silicon atom, such as −OR, can stabilize the cationic intermediate formed during the hydrolysis, and in turn increase the hydrolysis rate to some extend. Likewise, electron acceptor group next to silicon atom, such as −OH and −OSi, results in the decrease of hydrolysis rate of TEOS. For this reason, it is almost impossible for −OH substituted TEOS or TEOS polymer to be further substituted with −OH. Therefore, the hydrolysate of TEOS comprises no more than 2 hydroxyl group per molecule.

The hydrolysis rate of TEOS slows down and $Si(OR)_3OH$ dominates when the dosage of distilled water is not enough for the further hydrolysis of TEOS. Water produced from the dehydration condensation of silicon alkoxide can partially promote the hydrolysis of TEOS. Therefore, the dealcoholization condensation dominates over the dehydration condensation. However, it is directly affected by the hydrolysis of TEOS. Due to steric hindrance around silicon atom, the terminal Si−O bond is hydrolyzed much more easily. Hydrolysis promotes the formation of Si−O−Si linear chains, which in turn interact with each other, and form a linear polymer structure.

Excess distilled water can increase the hydrolysis rate of TEOS. However, excess distilled water results in low concentration of reactants, which, on the other hand, leads to the decrease of condensation rate. Thus, hydrolysis of TEOS is almost completed during the early stage of polymerization. As a result, the concentration of hydrolysate and hydroxyl group per molecule increase, and $Si(OR)_2(OH)_2$ dominates over $Si(OR)_3OH$ in the reaction system. Therefore, dealcoholization condensation is dominant when excess water is used, and promotes the formation of short crosslinked network structures, which in turn interact with each other to form a gel. Ge, Manzhen et al analyzed the structure of silicate polymer by gel permeation chromatography, and observed that in the presence of acidic catalyst, the formed gel exhibited a linear polymer structure when water is not enough; whereas a crosslinked network structure when water is excess.

The test results indicate that the best volume ratio of TEOS to water is 1 to 2.

2.3 Effect of temperature on the preparation of nanoscale silicon dioxide

Table 3 shows the effect of temperature on the preparation of nanoscale silicon dioxide.

From Table 3, we can see that the higher the temperature, the shorter the gel time, and the lower the stability of sol. It is because collision probability of the condensation product of low molecular increases with the rise of hydrolysis temperature, and small particles grow bigger by aggregation. On the other hand, the higher the temperature, the faster the volatile compounds evaporate, and the larger the concentration of reactants and products. Consequently, the increase of concentration should induce further aggregation of condensation product, thereby further accelerating the gelation.

The following formula exhibits the effect of reaction temperature on the particle size of monodisperse gel.

$$J=J_0\exp[-\triangle G_D/KT]\exp[-\triangle G^*/KT]$$

Here, J represents the nucleation rate; J_0 represents the initial nucleation rate; $\triangle G_D$ represents the change of diffusion activation free energy; $\triangle G^*$ represents the change of critical nucleation free energy; K represents Boltzmann constant; and T represents the reaction temperature.

The above formula indicates that the nucleation rate increases by geometric progression with the rise of reaction temperature, which leads to the formation of small particles in a narrow size range. The reaction temperature has an obvious effect on the particle size of silicon dioxide. It is concluded that the best reaction temperature is between 60 ℃ and 70 ℃.

2.4 Effect of the dosage of hydrochloride on the preparation of nanoscale silicon dioxide

Table 4 shows the effect of the dosage of hydrochloride on the preparation of nanoscale silicon dioxide.

The test results indicate that the gel time decreases with the increase of the dosage of hydrochloride. It is because water molecular directly attacks TEOS in an acid medium, and induces the hydrolysis reaction. The higher the concentration of HCl, the faster the rate of reaction, thus the less time it takes for the formation of gel. In an acid medium, H^+ attacks −OR group in TEOS molecular, its protonation induces the electron cloud to migrate towards −OR, and enlarges the surface interspace on the reverse side of silicon nuclei, which in turn increases the electrophilic ability of Si, and accelerates the attack of negative charged species, such as Cl^-. It is concluded that the best dosage of HCl is 2 mL.

3. Conclusion

(1) The proper volume ratio of TEOS to alcohol is 1 to 2.

(2) The best volume ratio of TEOS to distilled water is 1/1~1/ 2.

(3) The best reaction temperature is between 60 ℃ and 70 ℃.

(4) The best volume ratio of TEOS to HCl is 5 to 2.

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Table 1. The effect of the ratio of TEOS to alcohol on the preparation of nanoscale silicon dioxide

Solvent	Dosage (mL)	Gel time (min)	Gel morphology	Color of sol	Appearance after calcination
Absolute alcohol	5	30	Sol	White and transparent	Ivory white powder
Absolute alcohol	10	45	Sol	White and transparent	Ivory white powder
Absolute alcohol	15	48	Sol	White and transparent	Ivory white powder
Absolute alcohol	20	52	Sol	White and transparent	Ivory white powder, and light blue powder on the surface of porcelain boat
Absolute alcohol	25	56	Sol	White and transparent	Ivory white powder, and light blue powder on the surface of porcelain boat

Table 2. The effect of the dosage of distilled water on the preparation of nanoscale silicon dioxide

	Dosage (mL)	Gel time (min)	Gel morphology	Color of sol	Appearance after calcination
Distilled water	5	26	Sol	White and transparent	Ivory white powder
Distilled water	10	45	Sol	White and transparent	Ivory white powder
Distilled water	15	65	Sol	White and transparent	Ivory white powder
Distilled water	20	75	Sol	White and transparent	Ivory white powder
Distilled water	25	95	Sol	White and transparent	Ivory white powder

Table 3. The effect of temperature on the preparation of nanoscale silicon dioxide

Temperature (℃)	Gel time (min)	Gel morphology	Color of sol	Appearance after calcination
30	150	Sol	White and transparent	Ivory white powder
40	75	Sol	White and transparent	Ivory white powder
50	62	Sol	White and transparent	Ivory white powder
60	45	Sol	White and transparent	Ivory white powder
70	27	Gel	White and transparent	Ivory white powder

Table 4. The effect of the dosage of hydrochloride on the preparation of nanoscale silicon dioxide

Catalyst	Dosage (mL)	Gel time (min)	Gel morphology	Color of sol	Appearance after calcination
Hydrochloride	1	48	Sol	White and transparent	Ivory white powder
Hydrochloride	2	45	Sol	White and transparent	Ivory white powder
Hydrochloride	3	42	Sol	White and transparent	Ivory white powder
Hydrochloride	4	43	Sol	White and transparent	Ivory white powder
Hydrochloride	5	33	Gel	White and transparent	Ivory white powder