Preparation of spherical silica nanoparticles: Stober silica

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Abstract: The diameter of silica nanoparticles is affected by the relative contribution from nucleation and growth processes. Therefore, it is affected by TEOS and NH₃ concentrations. Herein, we have studied the effect of TEOS and NH₃ concentrations on particle size of silica nanoparticles. The size of silica particles increases with increasing TEOS and ammonia concentrations where both the rate of hydrolysis and condensation become faster and affect on the solubility of intermediate [Si $(OC_2H_5)_{4-X}(OH)_X$] and hence affect on the supersaturation for the nucleation process. Also surface modification of the silica nanoparticles by hexamethyldisilazane was studied to prevent the particles aggregation and to give good dispersion of silica nanoparticles in hydrophobic mediums.

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1. Introduction

Silicon is present in environment in different forms. It is not found in nascent form but also it is always present in combination with oxygen (as in silica) or hydroxides (As in silicic acid). 78% of earth's crust consists of silicon and oxygen compounds, both amorphous and crystalline compounds for example quartz, flint, opal, silicates etc. Silicon is also present in dissolved form in the oceans as silicic acid. Also silica is found in living organisms like sponges, grasses, algae (for example, diatoms) (C.G. S. Phillips and R. J. P. Williams, 1965; T. L. Simpson and B. E.Volcani, 1981; R. K. Iler, 1979; S. V. Patwardhan, 2003).

The Stober process is used for the preparation of monodispersed silica colloids 'white carbon black" by means of hydrolysis of alkyl silicates and subsequent condensation of silicic acid in alcoholic solutions using ammonia as catalyst (W. Stober et al., 1968). There are many research groups who applied those monodispersed silica colloids as model material in various applications. Sacks and Tseng utilized those colloids to pack ordered structure membrane and investigated its sintering behavior (M.D. Sacks and T.Y. Tseng, 1984). Unger et al. applied the submicron silica colloids as packing material for capillary chromatography (S. Ludtke et al. 1997; K. K. Unger et al., 2000). Also there are a lot of recent investigations on using those monodispersed silica colloids to fabricate photonic crystals o f 3D periodic structure (V. N. Stratov et al. 1996; H. Miguez et al., 1997). For all applications, it is always desirable to use silica particles with a

specified particle size and extremely narrow distribution.

The diameter of silica particles from the Stober process is controlled by the relative contribution from nucleation and growth processes. The hydrolysis and condensation reactions provide precursor species and the necessary supersaturation for the formation of particles. During the hydrolysis reaction, the ethoxy group of TEOS reacts with the water molecule to form the intermediate [Si $(OC_2H_5)_{4-X}$ $(OH)_X$] with hydroxyl group substituting ethoxy groups. Ammonia works as a basic catalyst to this reaction; the hydrolysis reaction is initiated by the attacks of hydroxyl anions on TEOS molecules (C. J. Brinker and G. W. Scherer, 1990; K.-S Chou and C.-C. Chen, 2006). The chemical reaction is expressed as follows:

$Si (OC_2H_5)_4 + xH_2O \rightarrow Si (OC_2H_5)_{4-x} (OH)_x$ + xC_2H_5OH

Following the hydrolysis reaction, the condensation reaction occurs immediately. Where the hydroxyl group of intermediate [Si (OC₂H₅)_{4-X} $(OH)_X$ reacts with either the ethoxy group of other TEOS "alcohol condensation" or the hydroxyl group another hydrolysis intermediate "water of condensation" to form Si-O-Si bridges. K. S. Kim et al. mentioned that the rate of water condensation is thousands times faster than the alcohol condensation (K. S. Kim et al., 2002; K.-S Chou and C.-C. Chen, 2006). Both condensation reactions is expressed as follows:

 $= Si - OC_2H_5 + HO - Si \Longrightarrow = Si - O - Si =$ $+C_2H_5OH$ $\equiv Si - OH + HO - Si \Longrightarrow = Si - O - Si \equiv +H_2O$

The overall reaction is expressed as follows: $Si (OC_2H_5)_4 + 2H_2O \rightarrow SiO_2 + 4C_2H_5OH$

The reactions of organosilicon compounds in acid–base reactions at oxides with surface OH groups are of technological importance in a lot of fields (D. E. Leyden, 1985). Silica reacted with hexamethyldisilazane (HMDS) to form trimethylsilylgroups which have high reactivity with silica surface silanols and the particles become hydrophobic (E. F. Vansant et al., 1995):

$2 \equiv Si - OH + (CH_3)_3 - Si - NH - Si - (CH_3)_3 \rightarrow$ $2 \equiv Si - O - Si - (CH_3)_3 + NH_3$

This system is widely used for the synthesis of industrially useful materials, the structural element in HMDS most influential in determining its reactivity with silica surface silanols is the basic nitrogen (A. Dabrowski and V. A. Tertykh, 1996).

The effect of various parameters on particle size had been reported in a previous paper (K.-S. Chou and C.-C. Chen, 2003). Herein we discuss the effect of TEOS and catalyst concentrations on the particle size and also the effect of surface modification on the dispersion of the particles was discussed.

2. Material and Methods

2.1 Materials

The materials required for the synthesis of silica nanoparticles are described as follows. Tetraethyl orthosilicate (TEOS 98%) was obtained from the Fischer Company, Ammonium hydroxide solution 31.5% (NH₃) was used as received from the Aldrich Company, Absolute ethanol 99 % from ADWIC Company. The materials required for Preparation of organically modified silica are described as follows. Silane coupling agent (hexamethyldisilazane) was obtained from fluka and used without further purification. Toluene was obtained from ADWIC Company.

2.2 preparations of Silica nanoparticles

Silica nanoparticles were prepared by hydrolysis and condensation of TEOS in ethanol, and in presence of ammonia as catalyst (W. Stober et al., 1968; K.-S Chou and C.-C. Chen, 2006). First, solution containing appropriate quantities of absolute ethanol, ammonia and deionized water were stirred for 5 minutes to ensure complete mixing. Then a proper amount of TEOS in absolute ethanol was added to the above solution and the reaction proceeded at ambient temperature for 24 hours according to reactants concentrations. Thereafter the colloidal solution was separated by high-speed centrifuge, and the silica particles were washed by absolute ethanol for three times to remove undesirable particles, Followed by drying in oven at 100 °C for 2 hrs to prevent continuous reaction.

2.3 Preparation of organically modified silica

After a thermal treatment at 150°C for 2 h to remove physisorbed water, a given amount of silica is put in a glass flask equipped with an amount of toluene then the liquid reagent (10% hexamethyldisilazane in toluene) is added and the mixture is stirred and refluxed at 110°C for 3h. After treatment, the solid is filtered and repeatedly washed with toluene and acetone in order to remove any unreacted silane coupling agent, and finally dried at 150°C for 2h.

2.4 Transmission electron microscope analysis

TEM analyses of silica particles were carried out using JEOL JEM 2010 on silica particles to investigate the diameter of silica particles. To prepare samples for TEM analysis, silica powder is dispersed in absolute ethanol and a drop of silica colloid solution was placed on a copper grid coated with carbon. The solvent was evaporated at room temperature, leaving the silica particles on the grid.

3. Results and Discussions

3.1. Mechanism of particles formation

Depending on the particle formation mechanism in the sol - precipitation process (G.H. Bogush and C. F. Zukoski, 1991), a huge number of primary particles is first nucleated in the initial high supersaturated solution which called the induction period. Then, the primary particles are rapidly aggregated to form stable particles, which grow with the further aggregation of primary particles. After this particle induction period, any further primary particles generated under supersaturation are consumed for the growth of stable particles. In this case, the resulting particles in the product suspension were highly monodispersed in size and spherical in shape, But, if the generation of primary particles by supersaturation exceeds the consumption of primary particles for the growth of stable particles during sol precipitation, new stable particles are spontaneously formed by the self -aggregation of the extra primary particles and a multi -modal distribution of particle sizes will present in the product suspension in this case (S.L. Chen et al., 1997). Herein, the monodispersity of the particle size was maintained over a wide range of TEOS, H_2O , and NH_3 concentrations, implying that the population of stable particles formed during the induction period was sufficient to consume the primary particles nucleated after the induction period. The initial supersaturation level during the induction period is critical in determining the particle size of the product suspension in the sol - precipitation, where the higher particle formation with a higher initial supersaturation results in a smaller particle size in the product suspension (S.-S. Kim et al. 2004).

3.2. Effect of TEOS concentration on size of particles

Figures 1 and 2 show that the prepared silica particles are spherical and there is no wide distribution in the particles sizes. The particle size increases with TEOS concentration, ranging from 0.2 to 0.4M while ammonia and water concentrations are fixed at 0.2M and 1.0 M respectively. When the TEOS concentration is increased; both the rate of hydrolysis and condensation become faster (G.H. Bogush and C. F. Zukoski, 1991). Then the intermediate [Si (OC₂H₅)_{4-X} (OH)_X] will be increased rapidly due to the high hydrolysis reaction; when it reaches the supersaturation region, the consumption rate of intermediate through condensation reaction is also relatively fast (S.L. Chen et al., 1996), which probably shortens the nucleation period. So, the total number of nuclei formed will be less in numbers, and the final particle size of synthetic silica colloids will be relatively larger (K.-S Chou and C.-C. Chen, 2006).



Figure 1 TEM of Silica nanoparticles ~50nm (experimental conditions: TEOS: 0.2M; NH₃: 0.2M; H₂O: 1M)



Figure 2 TEM of Silica nanoparticles ~65nm (experimental conditions: TEOS: 0.4M; NH₃: 0.2M; H₂O: 1M)

3.3. Effect of catalyst concentration on size of particles

Figures 3 and 4 also show that the prepared silica particles are spherical and there is a distribution in the particles sizes at low ammonia concentration. The particle size increases with ammonia concentration, ranging from 0.11 to 0.3 M while TEOS and water concentrations are fixed at 0.28M and 1.0 M respectively. When ammonia is increased, also both the rate of hydrolysis and condensation become faster (G.H. Bogush and C. F. Zukoski, 1991). And the intermediate [Si $(OC_2H_5)_{4-X}$ $(OH)_X$] will be increased rapidly due to the high hydrolysis reaction; when it reaches the supersaturation region, the consumption rate of intermediate through condensation reaction is also relatively fast (S.L. et al., 1996), which probably shortens the Chen nucleation period. So, the total number of nuclei formed will be less in numbers, and the final particle size of synthetic silica colloids will be also relatively larger (K.-S Chou and C.-C. Chen, 2006).



Figure 3 TEM of Silica nanoparticles ~55nm (experimental conditions: NH₃: O.11M; TEOS: 0.28M; H₂O: 1M)



Figure 4 TEM of Silica nanoparticles ~130nm (experimental conditions: NH₃: O.3M; TEOS: 0.28M; H₂O: 1M)

3.4. Effect of surface modification on dispersion of silica particles

Figure 5 shows the TEM image of silica nanoparticles modified with hexamethyldisilazane. The figure shows the good dispersion of the particles. This is attributed to that, the particles posses some organophilic characters after treatment with hexamethyldisilazane where the surface OH groups will convert to $[-(CH_3)_3]$ groups that results in the segregation of the particles.



Figure 5 TEM of Modified Silica (experimental conditions: TEOS: 0.18M; NH₃: 0.2M; H₂O: 1M, 10% HMDS in toluene)

4. Conclusion

Herein, we have studied the effects of TEOS and catalyst (NH_3) concentrations on the resulting particle size of synthetic silica colloids. Our results are discussed in terms of relative contribution from nucleation and growth processes. Where, increase of the rate of hydrolysis, tend to produce fewer nuclei during the nucleation process and therefore a larger particle size in the end. The surface modification by silane coupling agent gives hydrophobic character to the silica nanoparticles.

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