Preparation of Silica Nanoparticles via Two-Step Process Utilizing Mixed Chlorosilane Residues

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ABSTRACT

We propose an economic and facile method for the preparation of silica nanoparticles through a two-step process utilizing chlorosilane residues. Mixed chlorosilane residue was alcoholized with absolute ethanol as a first step to form tetraethoxysilane (TEOS). The TEOS was then utilized as a silicon source to synthesize silica nanoparticles in a sol-gel method. The alcoholysis process was designed and optimized utilizing the Taguchi experimental design method and the yield of TEOS was as high as 82.2% under optimal synthetic conditions. Similarly, the Taguchi method was also utilized to study the effects of synthesis factors on the particle size of silica nanoparticles. The results of statistical analysis indicate that the concentration of ammonia has a greater influence on particle size compared to the mass fractions of TEOS and polyethylene glycol (4.6% and 9.7%). The purity of the silica particles synthesized in our experiments is high, but the specific surface area and pore volume are small.

Key words : Mixed chlorosilane residues, Taguchi method, Alcoholysis, TEOS, Silica nanoparticles

1. Introduction

With the rapid development of the polysilicon industry, a large number of industrial by-product mixed chlorosilane residues are produced in China. Silicon tetrachloride (SiCl_4) and trichlorosilane (SiHCl_3) liquids account for up to 80% of these residues. For each ton of polysilicon produced, the process generates a minimum of approximately 18 tons of SiCl_4 liquid waste in some Chinese enterprises.^{1,2)} Mixed chlorosilane residues react violently with water and transform into acids and poisonous hydrogen chloride gas when exposed to humid air, which can not only irritate eyes and respiratory tract systems, but also endanger the environment.³⁾ Currently, hydrolysis is the most common method for treating mixed chlorosilane residues in domestic processes. Although acid hydrolysis is capable of recovering a portion of the hydrogen chloride gas, the silica-containing solid waste produced by hydrolysis is typically landfilled, which results in a significant waste of silica. Therefore, it has become an urgent issue to explore a method for treating mixed chlorosilane residues in accordance with China's Sustainable Development Strategy.

SiCl_4 is the most commonly used raw material for the production of silica nanoparticles. The synthesis of silica nanoparticles based on SiCl_4 materials is typically achieved through vapor-phase or vapor-liquid reactions. For example, fumed silica nanoparticles are prepared through vapor-

phase reactions in which SiCl_4 is burned in a hydrogen-oxygen flame, but this technology involves high energy consumption, harsh reaction conditions, and large investment.⁴⁾ Yan *et al.* successfully prepared silica nanoparticles via hydrolysis of SiCl_4 vapor with water vapor at low temperature ($\sim 150^\circ\text{C}$).⁵⁾ Luo *et al.* reported the production of silica nanoparticles through the hydrolysis of SiCl_4 vapor in an alkaline solution.⁶⁾ Hong *et al.* reported the synthesis of silica nanoparticles through the hydrolysis of SiCl_4 vapor in a diffusion flame of air and liquid petrol gas.⁷⁾ In liquid-phase approaches, silica nanoparticles are typically prepared through a precipitation reaction utilizing SiCl_4 in a micro-emulsion system,⁸⁾ but it is difficult to perform such production on a large scale. Xu *et al.* and Cai *et al.* synthesized silica particles with particle sizes in the range of tens of microns via hydrolysis of chlorosilane residue in aqueous solutions.^{9,10)} Overall, many studies on mixed chlorosilane residues as silicon sources utilizing liquid-liquid reactions to prepare silica nanoparticles have been performed, but methods that can be utilized for amplification have rarely been reported.

The sol-gel-based Stöber method is currently the most popularity and widely used method for the synthesis of silica nanoparticles. This method involves the hydrolysis and polymerization of TEOS in a mixed solution of water, solvent, and admixture. Lee *et al.* prepared silica nanoparticles induced by non-alcoholic solvent addition with TEOS as a precursor.¹¹⁾ Mily *et al.* prepared silica nanoparticles through a sol-gel process in an alcoholic solution under microwave irradiation in the presence of an ammonium catalyst.¹²⁾ Based on these studies, one can determine that TEOS is an

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ideal precursor for the preparation of silica nanoparticles.

To the best of our knowledge, SiCl_4 and SiHCl_3 are the optimal precursors for TEOS preparation, where the relevant reactions are defined by the following equations (1–4):

A method utilizing mixed chlorosilane residue alcoholized at low temperature as a first step to form TEOS, which is then converted into silica nanoparticles through further hydrolysis and condensation, has not been reported previously. Additionally, there have been no comprehensive studies on the effects of alcoholysis conditions on TEOS yield.

The Taguchi method is a statistical and efficient approach for developing, improving, and optimizing experimental processes. The basic principle of this method is to employ orthogonal arrays to minimize the number of experiments required to analyze the effects of experimental variables on synthetic processes.¹³⁾ This method can be utilized to determine the optimal conditions for performing a few well-defined experimental sets. In this study, the Taguchi method was utilized to investigate the effects of various reaction parameters on the yield of TEOS, as well as the effects of the synthesis conditions of silica nanoparticles on the final silica particles.

2. Experimental Procedure

In this study, the initial solutions were absolute ethanol, ammonium hydroxide, deionized water, hexane, polyethylene glycol (PEG) 1000, calcium oxide, and mixed chlorosilane residues (SiCl_4 : 80.67 wt%, SiHCl_3 : 9.86 wt%, and HCl : 9.86 wt%). All materials were utilized without further purification.

2.1. Experimental design

Various parameters of the alcoholysis process can affect the yield of TEOS. In this study, experimental design was performed based on the $\text{L}_9 (3^4)$ Taguchi orthogonal design process to investigate the influences of various parameters and the optimal conditions for the alcoholysis process. We selected four factors, namely the (1) mass ratio of absolute ethanol to mixed chlorosilane residues, (2) mass ratio of hexane to mixed chlorosilane residues, (3) reaction temperature, and (4) feed rate of absolute ethanol, to study their effects on TEOS yield. For each parameter, we set up three test levels. The four factors and their levels are listed in Table 1. The numbers “1,” “2,” and “3” in Table 1 represent the first, second, and third levels of each factor, respectively. Similarly, the $\text{L}_9 (3^4)$ Taguchi orthogonal design process for the preparation of nanometer silica from TEOS is detailed in Table 2.

2.2. Alcoholysis and synthesis

The alcoholysis reaction was performed in a four-necked flask with a capacity of 500 mL, equipped with a magnetic stirrer, feed pump, and nitrogen supply system. The following summary represents a typical alcoholysis experiment. First, 0.7 M of mixed chlorosilane residues and 0.457 M of hexane were mixed at 20°C via magnetic stirring for 10 min. Next, 1.96 M of absolute ethanol was added to the mixture in droplets at a rate of 60 mL/min under a nitrogen flow rate of 100 mL/min. The reaction solution was collected when the reaction was completed and an appropriate amount of calcium oxide was added to remove any remaining hydrochloric acid until the reaction solution became neutral. The calcium oxide was then removed via filtration. Finally, the reaction solution was analyzed via gas chromatography and the TEOS yield was calculated utilizing the external standard method, followed by purification via distillation to extract the TEOS.

Next, hydrolysis and condensation reactions of the TEOS were performed in an alcohol solvent in the presence of

Table 1. Experimental Factors and Levels for Alcoholysis Experiments

Parameter	Levels		
	Low (1)	Medium (2)	High (3)
A: Mass ratio of absolute ethanol to mixed chlorosilane residues	2.8 : 1	3 : 1	3.2 : 1
B: Temperature [°C]	20	30	40
C: Feed rate [ml/min]	60	90	120
D: Mass ratio of hexane to mixed chlorosilane residues	1 : 1.53	1.30 : 1	1.95 : 1

Table 2. Experimental Factors and Levels for the Synthesis of Silica Particles from TEOS

Parameter	Levels		
	Low (1)	Medium (2)	High (3)
E: Molar concentration of TEOS [mol/L]	0.2	0.3	0.4
F: Molar concentration of NH_3 [mol/L]	0.2	0.3	0.4
G: Mass fraction of PEG 1000 [%]	1.69	2.11	2.53

ammonium hydroxide. In a typical procedure, 150 mL of absolute ethanol and an appropriate amount of NH_4OH were blended in a four-necked flask at 25°C via magnetic stirring. A known volume of TEOS, absolute ethanol, and PEG 1000 mixture was then added in drops to the above solution. The mixture was then agitated for 48 h at 25°C to obtain white precipitate, which was collected via filtration and washed with deionized water and ethanol several times. Finally, the samples were dried in an oven overnight at 80°C .

2.3. Analysis and characterization

The components of the mixed solution prepared through the alcoholysis reaction were tested and analyzed using a gas chromatography analyzer (Agilent 1790). The yield of TEOS was calculated based on Eq. (5). The compositions of the silica samples were analyzed based on their X-ray fluorescence (XRF, Axios-mAX). The crystal structures of the silica nanoparticles were measured via X-ray diffraction (XRD, EMPYREAN). The morphology of the products was observed via scanning electron microscopy (SEM, Nova NANOSEM-450). The size of the as-synthesized silica particles was measured via dynamic light scattering (MS2000). The surface area and porosity of the products were analyzed by a Quantachrome (USA) device using the adsorption/desorption isotherms of nitrogen. Thermogravimetric (TG) analysis and differential thermal scanning (DSC) analysis of the sample were performed utilizing a simultaneous thermal analyzer (STA 449F3) with a heating rate of $5^\circ\text{C}/\text{min}$ from 30°C to 1000°C in an atmosphere of argon gas. The surface structures of samples were analyzed via Fourier transform infrared spectrometer (FTIR, NICOLET-IS10).

$$y = \frac{m_1/M_1}{m_2/M_2 + m_3/M_3} \times 100\% \quad (5)$$

y : yield of TEOS.

M_1 : relative molecular mass of TEOS.

m_1 : mass of TEOS in the reaction mixture.

m_2 : mass of SiCl_4 in chlorosilane residues.

M_2 : relative molecular mass of SiCl_4 .

m_3 : mass of SiHCl_3 in chlorosilane residues.

M_3 : relative molecular mass of SiHCl_3 .

3. Results and Discussion

3.1. Determination of optimal alcoholysis conditions

To identify the optimal alcoholysis conditions and most important factors affecting the yield of TEOS, the signal-to-noise (S/N) ratio was utilized in the Taguchi method. The S/N ratios are calculated by Eq. (6) when a smaller value is desirable.¹⁴⁾

$$\text{S/N} = -10 \log \left(\frac{1}{n} \sum_{i=1}^n Y_i^2 \right) \quad (6)$$

In the case where a larger value is desirable, S/N ratios are calculated by Eq. (7).

$$\text{S/N} = -10 \log \left(\frac{1}{n} \sum_{i=1}^n \frac{1}{Y_i^2} \right) \quad (7)$$

When a nominal value is desirable, S/N ratios are calculated by Eq. (8).

$$\text{S/N} = 10 \log \left(\frac{\mu^2}{\sigma^2} \right), \quad (8)$$

where

$$\mu^2 = \frac{1}{n} \sum_{i=1}^n Y_i^2 \quad (9)$$

$$\sigma^2 = \frac{1}{n-1} \sum_{i=1}^n (Y_i - \mu)^2. \quad (10)$$

In Eqs. (6)–(10), n is the replication number of the experiment in the orthogonal array and Y_i is the measured value of each response. The units of S/N ratios are decibels (dB). To identify the optimal conditions for alcoholysis reactions, Eq. (7) (larger value desirable) was utilized to optimize the TEOS yield. Table 3 lists the TEOS yields and S/N values for the TEOS obtained in our experiments. Additionally, the mean S/N ratio was utilized to estimate the effectiveness of each factor at different levels. For example, the mean S/N ratios for the mass ratios of absolute ethanol to mixed chlorosilane residues at levels one, two, and three can be calculated by averaging the S/N ratios for experiments 1–3, 4–6, and 7–9, respectively. The mean S/N ratios for each level of the other parameters can be computed in a similar manner (Table 4). The S/N responses for the yields of TEOS are summarized in Table 3.

From Table 4, one can see that the highest maximum-minimum value is associated with the feed rate of absolute ethanol, indicating that the most significant influencing factor on the yield of TEOS is the feed rate of absolute ethanol. The order of the influence of each factor on the yield of

Table 3. TEOS Yields and the Corresponding S/N Values Obtained from the Alcoholysis Experiments

Experiment	A	B	C	D	TEOS yield (%)	S/N ratio (dB)
1	1	1	1	1	59.67	35.52
2	1	2	2	2	68.31	36.69
3	1	3	3	3	43.52	33.13
4	2	1	2	3	79.95	38.06
5	2	2	3	1	50.65	34.09
6	2	3	1	2	48.82	33.77
7	3	1	3	2	44.24	32.92
8	3	2	1	3	44.07	32.88
9	3	3	2	1	74.5	37.44

Table 4. S/N Response Table for TEOS Yields from the Experiments

Effect	Parameter	Mean S/N ratio (dB)			
		Level 1	Level 2	Level 3	Maximum-minimum
A	Mass ratio of ethanol to mixed chlorosilane residues	35.11	35.31	34.41	0.90
B	Reaction temperature [°C]	35.50	34.55	34.78	0.95
C	Feed rate [ml/min]	34.06	37.40	33.38	4.02
D	Mass ratio of hexane to mixed chlorosilane residues	35.68	34.46	34.69	1.22

Fig. 1. Mean effect plot for signal-to-noise ratios for TEOS yields.

TEOS is as follows: $C > D > B > A$. Based on our analysis of S/N responses (Fig. 1), the optimal level for each parameter is A2B1C2D1 (B and D at level 1, A and C at level 2). To estimate the yield of TEOS under these optimal conditions, another experiment was performed. The results revealed that the yield of TEOS reached 82.2% under optimal conditions.

3.2. Statistical analysis of the impacts of various factors on silica particle size

Table 5 lists the mean silica particle sizes and standard deviations calculated in our eight reported experiments. One can see that the mean silica sizes of the samples ranged from 145–381 nm, which proves that the preparation of nanoscale silica is feasible through a two-step process utilizing chlorosilane residue. To quantify the importance of each synthesis factor, analysis of variables (ANOVA) was performed based on the measured mean silica particle sizes.¹⁵⁾ The analysis results are listed in Table 6, with headings

Table 5. Mean Silica Particle Sizes Prepared by the Sol-Gel Method

Experiment	E	F	G	Mean particle size (nm)	SD ($\pm$ nm)
1	1	1	1	145	7.8
2	1	2	2	227	Bimodal
3	1	3	3	381	1.2
4	2	1	2	148	2.3
5	2	2	3	251	Bimodal
6	2	3	1	298	Bimodal
7	3	1	3	157	1.2
8	3	2	1	165	2.9
9	3	3	2	306	Bimodal

representing the sum of squares (SS), degrees of freedom (df), root mean squares (MS), factor of variance-to-error variance ratio (F), and contribution percent (p) of each factor to mean silica size. The results reveal that among the three factors investigated in this study, the molar concentration of NH_3 had the greatest impact (85.6%) on mean silica size, followed by the mass fraction of PEG 1000 (9.7%) and molar concentration of TEOS (4.6%). Here, the pH value mainly affects the sample size by affecting the hydrolysis and condensation rate of TEOS. At high pH values, the hydrolysis rate is higher than the condensation rate, which leads to the growth of particles dominating nucleation, meaning the synthesized particles are larger. PEG was utilized as a nanostructure control agent because it can adsorb on the surface of particles to exert a steric effect during their preparation, thereby controlling the generation of crystals and suppressing the agglomeration of particles. Finally, small silica particles with good dispersibility were prepared. For the TEOS reactant, under certain conditions, the greater its concentration, the larger the particle size of the synthesized silica particles.

Table 6. Analysis of Variance for Mean Silica Particle Size

Source	SS	df	MS	F-Value	Contribution percent (p)[%]
E	2613.556	2	1306.778	38.688	4.6
F	48937.556	2	24468.778	724.405	85.6
G	5528.222	2	2764.111	81.832	9.7
Residual	67.556	2	33.778		0.1
Total	57146.889	2

Fig. 2. SEM photographs of synthesized silica nanoparticles designed by the Taguchi method (panels a–i represent samples 1–9, respectively).

3.3. Characterization of silica particles

3.3.1. Chemical composition and morphology of samples

The chemical compositions of the samples were analyzed based on XRF. Excluding the H_2O and PEG 1000 contents, the SiO_2 content of the samples was greater than or equal to 99.8 wt%. Very few impurities were detected, including Fe_2O_3 , Na_2O , K_2O , CaO , P_2O_5 , and Cl . The content of these impurities was very consistent across different samples. Fig. 2 presents the SEM images of the nine samples synthesized based on the Taguchi experimental design. All samples were composed of small silica particles, but aggregation was significant.

3.3.2. Structural properties of silica nanoparticles

To identify the amorphous or crystalline structures of the as-prepared silica powders, powder XRD patterns were utilized. A single broad peak centered at approximately $2\theta=23^\circ$ is shown in Fig. 3, which may be caused by the smaller particle sizes and incomplete inner structures of the spherical nanoparticles.¹⁶⁾ This result indicates that the samples were amorphous.

The above analysis reveals that pH level had the greatest influence on the particle size of the samples. In order to

Fig. 3. XRD patterns of samples six, seven, eight, and nine.

understand the characteristics of specific surface area, the pore volumes and pore sizes of the samples synthesized at different pH values (samples one, two, and three) were investigated via nitrogen adsorption and desorption analysis. The nitrogen adsorption-desorption isotherms and pore distributions of samples one, two, and three are presented

Fig. 4. (a) Nitrogen adsorption-desorption isotherms and pore-size distribution plots for sample one, (b) nitrogen adsorption-desorption isotherms and pore-size distribution plots for sample two, and (c) nitrogen adsorption-desorption isotherms and pore-size distribution plots for sample three.

in Fig. 4. In this experiment, samples were calcined in air at 550°C for 8 h to ensure complete removal of the PEG 1000. The nitrogen isotherms for the samples can be divided into two types. Sample one yielded the typical type IV isotherms with H1 hysteresis loops according to the IUPAC classification. The presence of type H1 hysteresis loops indicates that sample one is a mesoporous material with relatively small pore diameters. The pore size distribution also supports this conclusion (Fig. 4(a)). Additionally, a sharp peak centered at 17.6 nm in the pore-size distribution curve was observed.

Samples two and three exhibited type IV isotherms with an H3 hysteresis loop, which represents macroporous solids with multilayered adsorption. The macropores likely resulted from the interspaces between small silica nanoparticles, which are also indicated by the hysteresis at high relative pressures.¹⁷⁾ A small type of H3 hysteresis loop at a high relative pressure of approximately 0.8 was observed, which may be a result of the random distribution of pores and interconnecting pore systems.¹⁸⁾ The pore size distribution reveals that samples one and two both have relatively wide

Fig. 5. FT-IR spectra for samples five and six.

size distributions. The average pore sizes of samples one and two were calculated via the Barrett–Joyner–Halenda method, with results of 27.2 nm and 33.8 nm, respectively. Samples one, two, and three have low specific surface areas and low pore volumes.

FTIR spectra were utilized to investigate the surface structures of the silica nanoparticles (Fig. 5). The band around 3421 (3419) cm^{-1} is caused by the stretching vibrations of OH in adsorbed water molecules.¹⁹⁾ Three bands at 459 (458) cm^{-1} , 570 (574) cm^{-1} , 802 (803) cm^{-1} , and 1088 (1087) cm^{-1} are related to the bending and stretching vibrations of Si and O.^{19,20)} The peak at 459 (458) cm^{-1} can be attributed to the bending vibrations of Si-O-Si. The band at 802 (803) cm^{-1} can be attributed to the symmetric stretching vibrations of Si-O-Si. The very intense and broad peak appearing at 1088 (1087) cm^{-1} is related to the asymmetric vibrations of Si-O-Si, which reveals that a dense silica network was formed. The band at 1637 (1640) cm^{-1} corresponds to Si-H₂O flexion.¹⁹⁾ The bands at 1396 (1395) cm^{-1} , 1446 (1451) cm^{-1} , 2934 (2926) cm^{-1} , and 2986 (2985) cm^{-1} can be attributed to the bending vibrations of -CH₃ and -CH₂ groups.^{21,22)} Additionally, a band at 2321 (2311) cm^{-1} was also detected, which corresponds to Si-H stretching vibrations.

3.3.3. Thermal analysis

The TG and DSC results, as well as their respective thermograms were utilized to evaluate the incidence of physical and chemical changes in the silica nanoparticles in sample three (Fig. 6). The TG curve of the sample reveals three major weight losses. The first weight loss of 2.27 wt% occurred in the temperature range of 94.0–348.9°C and involved the removal of physically combined water. The second weight loss of 15.67 wt% in the temperature range of 348.9–559°C is related to the loss of chemically combined water, pyrolysis of PEG 1000, and silanol group dehydration. The final weight loss of 1.57 wt% is associated with the dehydration of isolated hydroxyl groups.²⁰⁾ Additionally, the DTS curve reveals that endothermic and exothermic reactions occurred during the heating of the sample. The endothermic peaks at 398.1°C correspond to the evaporation of

combined water, pyrolysis of PEG 1000 and silanol group dehydration, with a total peak area of 69.26 J/g. The exothermic peak at 805.8°C is associated with phase transition.

4. Conclusions

In this paper, a two-step process utilizing chlorosilane residues for the preparation of silica nanoparticles was proposed. This process has great significance for achieving optimal resource utilization. The results of alcoholysis experiments on chlorosilane residues revealed that the feed rate of absolute ethanol is the most significant parameters affecting the yield of TEOS. In descending order of importance, the other parameters affected TEOS yield are the mass ratio of mixed chlorosilane residues to hexane, reaction temperature, and mass ratio of absolute ethanol to mixed chlorosilane residues. The yield of TEOS can reach 82.2% under optimal alcoholysis conditions.

Silica nanoparticles with mean particle sizes ranging from 145–381 nm were successfully synthesized by controlling the concentrations of TEOS and ammonia, and the mass fraction of PEG 1000. The sequence of parameters influencing particle size was the concentration of ammonia (85.6%), the mass fraction of PEG 1000 (9.7%) and concentration of TEOS (4.6%). XRF and XRD results indicated that the as-synthesized silica nanoparticles were amorphous with a purity over 98.8%. SEM results revealed that most of the SiO₂ nanoparticles were agglomerated and spherical in shape. Additionally, the synthesized silica created a mesoporous material with low surface area and low pore volume. The proposed two-step process utilizing chlorosilane residues provides a simple and environmentally friendly method for the large-scale production of nanostructured silica materials, which will play a crucial role in the future development of the polysilicon industry.

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