



Study on the preparation of silica particles from chlorosilane residues



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ABSTRACT

In order to achieve resource utilization of chlorosilane residues, a facile method was proposed for the preparation of silica particles by the hydrolysis of chlorosilane residues in an aqueous solution. The synthesized silica powders were characterized by X-ray fluorescence (XRF), X-ray diffraction (XRD), scanning electron microscope (SEM), dynamic light scattering (DLS) and infrared spectroscopy (IR). Additionally, the combination of thermogravimetry and mass spectrometry (TG-DSC-MS) was employed to study the variation of mass, energy and pyrolysis gas products of silica particles in the thermal decomposition process. Furthermore, to further understand hydrolysis process of chlorosilane residues, the hydrolysis and condensation mechanisms of chlorosilane residues were studied by analyzing the surface structure of the silica particles prepared from the hydrolysis of chlorosilane residues in an aqueous solution. At the same time, the three-dimensional network structures of the silica were proposed. The results shown that the prepared silica was an amorphous material, with high purity (exceed 96.46 wt% SiO₂), low, and the median diameter of 17.2 to 33.8 μm, has the potential to be used as a rubber additive, which could lay the foundation for the commercialization of silica product produced by the hydrolysis of aqueous chlorosilane residues.

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1. Introduction

During the production of polysilicon using the improved Siemens method, chlorosilane residues is inevitably generated from the processes of synthesis, purification and cold (or hot) hydrogenation of trichlorosilane. Generally, chlorosilane residues are mainly composed of silicon tetrachloride (SiCl₄), trichlorosilane (SiHCl₃), dichlorosilane (Si₂H₂Cl₂), hexachlorodisilane (Si₂Cl₆) and metal chlorides [1]. Some of these components (such as, SiCl₄, Si₂H₂Cl₂, and Si₂HCl₃) have a strong tendency to hydrolyze and are characterized by the release of hydrogen chloride and heat, which can easily cause damage to skin, eyes and mucous membrane to a certain extent [2,3]. In addition, both hydrogen chloride and heat can cause severe environmental pollution, if directly discharged into the atmosphere. For each ton of polysilicon produced, approximately 3–5 tons of chlorosilane residues are generated. In consideration of the hazards and resource utilization of chlorosilane residues, the study of an economic and environmental-benign approach for treating chlorosilane residues is of great significance, which can boost the sustainable development of polysilicon industry.

A series of methods have been reported for the treatment of chlorosilane residues, including hydrolysis [1], combustion [4], filtration [5], drying [6] and crystallization [7]. Among these methods, hydrolysis

and combustion are the most commonly used methods to achieve a sound residue management. An aqueous lime slurry bath and contaminated chlorosilane residues are introduced into the reactor to carry out the hydrolysis reaction as described by Breneman et al. After drying the solids, silica content of 80–98% is obtained in this process [1]. The combustion of chlorosilane residues originated from the fumed silica technology [8]. The main objective of the technology is to transform chlorosilane residue into harmless silica by burning chlorosilane residues in a hydrogen-oxygen flame. The process of combustion produces almost no waste water and residues as compared to the hydrolysis process. However, the combustion technology is expensive due to the cost of fuel, is carried out at relatively complicated high temperature processing facilities and results in severe corrosion to equipment [1,9].

Furthermore, the alkaline hydrolysis may lead to complex post-processing requirements. Therefore, the authors focused mainly on acidic hydrolysis of chlorosilane residues in an aqueous solution. According to the best of our knowledge, studies on the hydrolysis mechanism and properties of silica produced by the hydrolysis of chlorosilane residue have never been reported previously. Based on the excellent reinforcing, thickening and thixotropic properties, silica particles have been widely used in the fields of elastomers [10], films [11], coating [12] and toothpaste [13]. In addition, silica particles have also been applied in the fields of catalysis [14], electrochemistry [15] and biomedical engineering [16]. As a result, it is necessary to study the properties of silica and its preparation process, which can provide theoretical basis for the resource utilization of chlorosilane residues.

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2. Experimental section

2.1. Materials

Distilled water; sodium hydroxide (NaOH) (AR grade; Hangzhou Print-Rite Industry & Trade Co., Ltd., China), Chlorosilane residues (SiCl_4 :93%; SiHCl_3 :4.85%; SiHCl_2 :2.13% and HCl : 0.02%; from the Kunming Metallurgical Institute New Materials Co., Ltd).

2.2. Preparation of silica

Fig. 1 shows the schematic of the experimental setup used to prepare the silica. Firstly, a certain amount of distilled water was poured into the three-necked flask (500 mL). Then, the chlorosilane residues were added to the three-necked flask by an injection pump (LSP01-1A) at a flow rate of 2 mL/min under mechanical stirring at a speed of 350 r/min and a temperature of 35 °C. A neck of the three-necked flask was connected to a portable multi gas detector (GX-2003-xhcy) to detect the composition of the mixed gases. The off-gas was moved to a conical flask containing 10% NaOH solution to absorb the HCl by-product after the mixed gases were detected. The obtained suspension was kept aging for 2 h at 35 °C, and then filtered through a vacuum pump. The white precipitate was washed with distilled water or 1% sodium hydroxide solution, and then, with distilled water for several times. After the final wash, white solid material was dried in an electrothermal blowing dry box at 103 °C for 10 h. The molar ratio of distilled water to chlorosilane residues was set as 152:1, 73:1, 47:1 and 34:1 in various repeats of the hydrolysis process.

Silica particles were obtained under different molar ratio and at different washing conditions. Thus, samples were given names according to their preparation conditions (for example, SiO_2 -152 for 152:1 M ratio of water to chlorosilane residues, respectively; SiO_2 -H₂O for the sample which was washed with distilled water; SiO_2 -NaOH-H₂O for the sample which was washed with NaOH solution and distilled water).

2.3. Characterization

Crystal structure of the silica particles was characterized by using an XRD equipment (Empyrean) which used Cu radiation in the 2θ range of 5–80°, a current of 40 mA and voltage of 40 kV. The morphology of samples was observed by using an SEM (TESCAN VEGA3). Chemical components were detected using an XRF instrument (EDX8300). Chemical structure was determined by using infrared spectrometer (TENSOR 27) with a scan wave number ranging between 400 and 4000 cm^{-1} .

The DLS examination was performed with particles dispersed in the distilled water. In order to obtain a homogeneous suspension before the measurements, ultrasonic oscillation was used to treat the suspension for 60 min. The TG-DSC-MS (STA 449 F3 - QMS 403 C) was applied to determine the thermal stability of silica and the compositions of pyrolysis mixed gases. The TG-DSC-MS curves were obtained with a heating rate of 10 °C·min⁻¹ from 50 °C to 1500 °C in an argon environment.

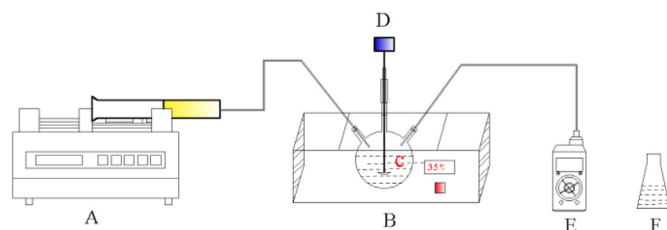


Fig. 1. Schematic of the experimental setup used to prepare silica particles. (A) Injection pump, (B) water bath, (C) three-necked flask (D) mechanical agitator, (E) portable multi gas detector, (F) NaOH solution.

Table 1

Chemical composition of samples.

Sample	SiO ₂ (wt%)	Na ₂ O (wt%)	Cl (wt%)	Fe ₂ O ₃ (wt%)	CuO (wt%)	MnO (wt%)	Cr ₂ O ₃ (wt%)
SiO ₂ -152-H ₂ O	97.51		2.480	0.0022	0.00078	0.00064	0.0058
SiO ₂ -73-H ₂ O	96.68		3.309	0.0025	0.00084	0.00058	0.0062
SiO ₂ -47-H ₂ O	96.46		3.528	0.0028	0.0011	0.00062	0.0071
SiO ₂ -152-NaOH-H ₂ O	97.88	1.282	0.830	0.0019	0.00067	0.00054	0.0046
SiO ₂ -73-NaOH-H ₂ O	97.82	1.312	0.860	0.0014	0.00070	0.00051	0.0053
SiO ₂ -47-NaOH-H ₂ O	97.66	1.344	0.987	0.0017	0.00072	0.00058	0.0057

3. Results and discussion

3.1. Chemical composition and crystal structure of samples

Because severe gelation occurred during the experiment of SiO_2 -34, no silica particles were prepared in this experiment, which resulted in SiO_2 -34 being not used to characterize and analyze. Except for H₂O content, the chemical components of samples were determined by XRF (Table 1). The results indicated that all samples exceeded 96.46% silica. Very few impurities were detected, including Fe₂O₃, MnO, CuO. Additionally, the impurities might come from the chlorosilane residues because the content of these impurities were nearly equal in different samples. Samples SiO_2 -152(73, 47)-NaOH-H₂O compared with samples SiO_2 -152(73, 47)-H₂O, although the silica content was increased to a certain extent and Cl content was significantly decreased, impurity Na₂O was introduced. No narrow and sharp diffraction peaks were observed in the XRD pattern of the silica powder (Fig. 2). A broad diffraction peak with a wide 2θ range confirmed that the silica powder produced by the experiments was amorphous.

3.2. Effect of the hydrolyzing water on silica particles

Fig. 3 shows the size distribution of the silica particles prepared at different molar ratios of hydrolyzing water as determined by the dynamic light scattering. It can be seen that different molar ratio of distilled water to chlorosilane residues (152:1, 73:1 and 47:1, respectively) yielded 17.2, 27.4, and 33.8 μm median diameters respectively, whereas a polydispersity index (PDI) of 0.716 (for 152:1), 0.757 (for 73:1) and 0.852 (for 47:1), indicating a decrease in the particle size and polydispersity with the increase in the quantity of the water.

3.3. Properties of silica particles

3.3.1. Morphology

The morphology of samples has been examined by SEM images (Fig. 4). The highly-aggregated structure of the particles was observed in the SEM micrographs, which is attributed to the strong polarity and high permittivity of water that allowed small silica particles with high surface energies to form hydrogen bonds more easily and to aggregate

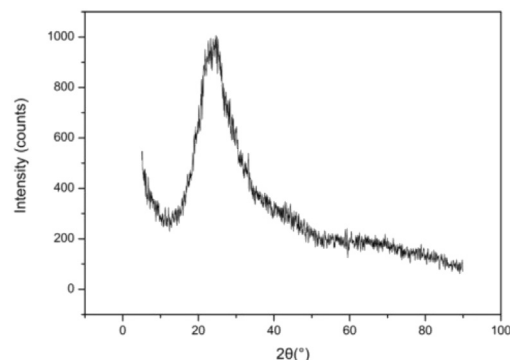


Fig. 2. XRD pattern of the produced silica particles.

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