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Preparation of highly dispersed precipitated nanosilica in a membrane dispersion microreactor

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HIGHLIGHTS

- A novel method for the preparation of highly dispersed precipitated nanosilica was proposed.
- The dispersion of silica was characterized quantitatively by the dispersion index.
- The nanosilica with the narrow size distribution and excellent dispersion was obtained.

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ABSTRACT

A novel process was developed for the preparation of highly dispersed precipitated nanosilica in a membrane dispersion reactor with H_2SO_4 and Na_2SiO_3 as the reactants. The particle size and extent of aggregation were significantly reduced by improving mixing performance and controlling the reaction environment. The effects of the surfactant and the final pH on the properties of the precipitated silica were investigated. By adding the surfactants sodium carboxymethylcellulose (CMC) and polyethyleneglycol (PEG) to the reaction system, silica precipitates with a surface area of 126.2 m^2/g and primary particle size of approximately 20 nm were obtained. The dispersion index D_I at 1.12 and the coordination number between 1 and 2 indicate an effective dispersion performance of the obtained SiO_2. This study provides a controllable, economical and easily scaled up method for the production of this important additive for the tire, paint and toothpaste industry.

1. Introduction

Precipitated silica with specific properties has been widely used in the rubber, plastic, paint, and toothpaste industries as effective filler [1–3]. In particular, highly dispersed precipitated nanosilica has been widely used as a green filler in the tire industry for manufacturing "green tire" with highly reinforced rubber composites and low rolling resistance [4,5].

At present, highly dispersed nanosilica is prepared mainly via the precipitation method because of its cost-effectiveness. However, silica synthesized by the precipitation method produces large particles and a high degree of aggregation [6–8]. Thus, the development of a new process for the preparation of highly dispersed silica with a suitable particle size distribution and low aggregation is very important.

Silica powders typically possess high free energies and easily adsorb water, which leads to hydroxylation. Different silanol groups can form hydrogen bonds or siloxane bridges via dehydration. Therefore, if no measures are taken to prevent the polymerization of highly active silanol groups on the surface of silica, these groups will form particles that aggregate and eventually produce a silica gel with a net structure. The net structure, which is formed by the loose accumulation of silica particles, can maintain large amounts of water. After dehydration, the structure maintains high pore volume and high specific surface area [9–11]. If proper measures can be taken to block the polymerization of silanol groups, highly dispersed silica precipitates with a lower specific surface area can be obtained.

Several prior studies have already demonstrated methods for the preparation of precipitated silica with low particle aggregation. Teofil Jesionowski et al. [12] prepared silica via precipitation from sodium silicate solutions using ammonium bicarbonate or ammonium chloride solutions. Silane coupling agents were added to the reaction system for surface modification, and silica with a surface area of 220 m^2/g was obtained. Bozena Rager et al. [13] prepared highly dispersed silica with a surface area ranging from 70 to 140 m^2/g from sodium silicate and carbon dioxide with the

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addition of ionic or nonionic surfactants. Dang Viet Quang et al. [14] prepared precipitated silica powder with a surface area between 200 and 350 m^2/g by adding sulfuric acid to a mixture of sodium silicate and sodium chloride in two stages. The previous studies indicate that silane coupling agents, mineral salts, or surfactants can be used to change the chemical environment of the precipitation reaction thereby reducing silica particle aggregation and leading to a more optimized performance of the precipitated silica product. When silica particles remain in the surfactant solution, which contains oxygen-polar groups, the sodium silicate and sulfuric acid react in distinct areas along the length of the molecular chains of the surfactants. After the formation of silica precipitates, the silanol groups of the silica nanoparticles and the hydroxyl groups of the surfactant molecules can form hydrogen bonds. Because the silica particles are surrounded by the surfactant molecules, the stereo-hindrance effect of the molecular chains prohibits the polymerization of silanols. Thus, silica precipitates with a high dispersion can successfully be prepared. However, in a typical stir-tank reactor, the poor mixing performance significantly affects the uniformity of the supersaturation of solution, which can still lead to large particle size distribution.

Previously, membrane dispersion microreactors have shown significant, practical value for the preparation of nanoparticles because of their excellent mixing performance, low energy consumption, continuous production, and high scaling-up potential [15–17]. Particle size depends on the supersaturation of the solution, which is related to the mass transfer rate. In a membrane dispersion reactor, as the dispersed phase is divided uniformly by the membrane, homogeneous supersaturation is achieved while avoiding high local supersaturation, and nanoparticles with a small size and narrow distribution can be successfully prepared. Wang et al. successfully prepared a series of inorganic metal materials, such as γ-Al_2O_3 [18], $CaCO_3$ [19], and ZnO [20–22]. However, membrane dispersion microreactors have not yet been applied in methods for the preparation of porous materials.

In this study, a new process for the preparation of highly dispersed nanosilica particles using a membrane dispersion microreactor was developed. Sulfuric acid and sodium silicate solution were used as the reactants, and surfactants were added to the reaction system to prepare highly dispersed nanosilica precipitates. The influence of the surfactants on the properties of silica particles was investigated and the most suitable surfactants were identified. The operating parameters were optimized and their influence on the morphology of the silica particles, specific surface area, and dispersion performance was investigated. Silica nanoparticles with a low surface area and high dispersion were successfully prepared. This study aims to provide an economical method for the production of this important additive for the tire, paint and toothpaste industry.

2. Experiment

2.1. Preparation of precipitated silica

The reactants included sodium silicate ($Na_2SiO_3 \cdot 9H_2O$, Xilong Chemical Co., Ltd.) and sulfuric acid (H_2SO_4, Beijing Modern Eastern Fine Chemical Co., Ltd.). The objective of this study is to produce precipitated silica (SiO_2). The experimental device was a membrane dispersion microreactor (Fig. 1a) in which a 5 μm stainless steel microfiltration membrane (Zhen Yuan Purification Technology Co., Ltd.) was utilized. The mixing chamber was 12 mm × 4 mm × 1 mm in size.

Surfactants were added to the continuous phase 0.75 mol/L Na_2SiO_3 solution. The Na_2SiO_3 solution was then mixed with the 1 mol/L H_2SO_4 dispersed phase solution in the membrane dispersion microreactor. The type of surfactant added to the reaction system is listed in Table 1. The SiO_2 precipitates were synthesized when the two phases came into contact with each other and were immediately delivered to the product reservoir with mechanical agitation. The pH of the SiO_2 suspension was then adjusted to approximately 7 and kept aging for 0.5 h at room temperature. The resulting slurry was suction filtered, washed three times with distilled water and ethanol, and dried with a spray dryer (L-117, Laiheng Scientific Co., Ltd). The slurry with a pH of approximately 7 and a solid content of approximately 5% was injected by a nozzle with a tip diameter of 0.7 mm, and rapidly dried by preheated air. The inlet and outlet air temperatures were maintained at 100 °C and 70 °C, respectively. The dried powder was cyclone separated from the flowing air stream and SiO_2 were obtained (Fig. 1b).

2.2. Characterization

The pH value in silica slurry was measured with a PHS-3C pH meter (Shsan-xin, Shanghai, China), using a MODEL E-900 pH electrode (RUOSULL, Shanghai, China). The specific surface area and pore volume of the precipitated silica were determined by the Brunauer–Emmet–Teller (BET) (Quantachrome autosorb-1) method. The morphology of nanoparticles was observed using scanning electron microscopy (SEM, JEM-630F, Japan) and transmission electron microscopy (TEM, JEOL-2010, Japan). A laser particle size analyzer (Malvern, Mastersizer 2000) was used to determine the diameter distribution of the silica particles.

2.3. Calculation of dispersion index

The dispersion index D_I was defined to represent the dispersion performance of the silica particles quantitatively as follows:

$$D_I = \frac{S_C}{S_{BET}}. \quad (1)$$

Here, the theoretical surface area, S_C, for spheres can be calculated if the primary particle diameter, d, can be measured in the following manner:

$$S_C = \frac{6000}{\rho d}. \quad (2)$$

The units of d and S_C are nm and m^2/g, respectively. The value of silica density (ρ) is 2.18 g/mL. The particle diameter d was obtained from TEM photos using Image Tool software. The actual surface area, S_{BET}, was measured with the BET method. The ratio S_C/S_{BET} serves as a measure of the extent of nanoparticle

Table 1
Type of surfactants added to the reactive system.

Sample	Supplements (based on the quality of the precipitated silica)		Flow rate of reactants		Temperature (°C)	Final pH
			F_C (mL/min)	F_D (mL/min)		
1	0.15 wt% PEG	0.05 wt% SDS	60	37	70	9.3
2	0.15 wt% PVA	0.05 wt% PEG	60	37	70	8.9
3	0.15 wt% PVP	0.05 wt% PEG	60	37	70	8.8
4	0.15 wt% CMC	0.05 wt% PEG	60	37	70	9.2