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Short communication

Effect of the gelation on the properties of precipitated silica powder produced by acidizing sodium silicate solution at the pilot scale

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HIGHLIGHTS

- ▶ BET surface area and porosity of precipitated silica decrease as Δ*t* and temperature increase.
- ▶ The size of the primary particles is larger as reaction temperature increases.
- ▶ The percolation model was successfully applied for the flocculation of precipitated silica.

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ABSTRACT

Controlling the properties of precipitated silica (PS) synthesized by acidizing sodium silicate solution is a significant challenge. Here, we report the effect of gelation on the BET surface area and pore volume of the PS produced at the pilot scale. H_2SO_4 was added to a mixture of sodium silicate and sodium chloride in two stages: the first stage ends before the gelation point and the second one ends as pH of solution reached to 5. The interval (Δ*t*) from the end of the first stage to the gelation point was recorded to evaluate its effect on the properties of the resulting PS. The obtained samples were characterized by nitrogen adsorption–desorption method, field emission scanning electron microscopy (FE-SEM), and field emission scanning transmission electron microscopy (FE-STEM). The results revealed that the BET surface area and pore volume of the prepared PS decreases with the increase of Δ*t* and temperature, while the pore size is not affected. The variations in the properties of the PS were successfully explained by the application of a percolation model to the flocculation and bridging of the primary particles.

1. Introduction

Precipitated silica (PS) has been widely used as effective filler for plastic, rubber, and paint [1–5]. In particular, it has been considered as a green filler in the tire industry where it is assumed to contribute to the reduction of energy consumption and the emission of CO_2 [6]. Precipitation of silica from sodium silicate and sulfuric acid is an economic way to synthesize PS. In this method, sulfuric acid and sodium silicate solution are simultaneously fed into the well mixing solution of a salt [7] or only sulfuric acid is added into a reactor containing a mixture of salt and sodium silicate solutions [8,9]. To control the porosity and pore size of the resulting PS, surfactants can be added [10,11] or the reaction parameters such us pH and temperature can be modified [12,13].

Previous studies have indicated that the properties of sodium silica solution and silica gel change abruptly at the proximity of the gelation point [14–16]. Before the gelation point, the viscosity of the sol exponentially increases as the threshold is approached. After the gelation point, the elasticity of the gel appears and increases continuously from zero. The variation in the properties of sol near the gelation point is due to the divergence of the size of silica aggregates. When $Si(OH)_4$ monomers are supplemented, the size of aggregates expands as a result of the condensation of these monomers with aggregates and the coalescence among the aggregates [17]. The increase in the size of the aggregates is well described by the percolation model [14,18] and was experimentally observed by Schlomach and Kind [19].

Near the gelation point, the size of the aggregates increases sharply by the bridging flocculation of the primary particles and secondary aggregates [20]. The rate of flocculation and the gelation time depends on the concentration of the primary particles and the

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secondary aggregates. We consider them as building blocks, which are ready to join together randomly. When the flocculation happens at a low rate, the building blocks are arranged in a packed manner to reduce free energy. This reduces porosity and surface area of the resulting product. In contrast, when a flocculation occurs at a high rate, the building blocks are arranged in a more random manner. This enhances porosity and the surface area of the resulting product. Therefore, although the properties of PS are affected by the post treatment following gelation, the effect of the flocculation and the treatment of sol around the gelation point are of utmost importance.

The production of PS by acidizing sodium silicate solution usually undergoes two acidizing stages: before and after the gelation point. The end of the first stage is right before the gelation point to prevent the formation of the strong gel, which may be hard to break by mechanical mixing. The second stage ends at a desired pH of the resulting product. The addition of acid after gelation does not have a significant effect on the properties of PS, but the stage before the gelation point dominates the properties of the resulting product. Several works have studied the variation of physical properties of silica sol and gel at the temporal proximity to the gelation point [15,16,19–24]. However, the effect of the gelation on the surface area and porosity of PS has not yet been discussed, particularly at the pilot and industrial production scale. Therefore, we report the effect of the gelation on the surface area and porosity of the PS produced at the pilot scale, specifically the time from the end of the first acidizing stage to the gelation point (Δt).

2. Experimental

2.1. Preparation of PS by acidizing sodium silicate solution

The synthesis of PS was carried out in a 100 L reactor where the mixing speed and temperature are automatically adjustable by a digital control panel. Initially, 40945 g of water was put in the reactor, followed by the addition of 1712 g of NaCl (99.5%, Showa Chemical Co., Ltd.). Solution was mixed until all NaCl was dissolved and a homogeneous mixture was obtained. Then, 11778 g of sodium silicate with a molar ratio of $3.4SiO_2{\cdot}NaO_2$ (24% SiO_2, Shinwoo Materials Co., Ltd.) was added. The heater was turned on and when the desired temperature (40 and 60 °C) was approached, 8% H_2SO_4 was fed into the reactor by a digital quantitative pump with a flow rate of 1560 ml/min under a constant stirring rate of 45 rpm. The 8% H_2SO_4 was fed into the reactor with a two stage process. The first stage ended before the gelation point at a pH below 10.5, the feeding time t and the gelation time t_c were recorded. The gelation point was determined at the time when the size of the silica aggregates is large enough to be distinguished by the naked eye. At this point, mixing force was used to break the early-formed gel, and therefore, the aggregates observed were the formed aggregates and the pieces of broken gel. To prevent the formation of strong gel, the second stage was conducted after 10 min since the gelation appeared, and it ended when the pH of silica slurry reached 5. The resulting silica slurry was aged at 85 °C for 30 min and cooled to room temperature (25 °C). The silica slurry was thoroughly washed with water to eliminate the by-product ions, mainly including Na^+, SO_4^{2-}, and Cl^-. The slurry was simultaneously filtered and washed using a filter press until the concentration of Na^+ ions in 5% silica slurry measured less than 100 ppm. The PS was obtained as a silica wet-cake, which was then mixed with water (with a ratio of 2:1) for spray drying as described in our previous publication [8]. All of the experiments carried out in this work were done in a pilot plant fabricated by E&B Nanotech. Co., Ltd.

2.2. Characterization

The surface area, pore volume, and pore size were measured by nitrogen adsorption–desorption method using Micromeritics Surface and Porosity Analyzer (ASAP 2020). All of the samples were degassed at 250 °C for 2 h before analyzing. The pore volume and pore size were calculated by the BJH method using the adsorption isothermal data. The microstructure of the PS was observed on field emission scanning electron microscope (FESEM, Hitachi, S4800). The TEM images were taken on field emission scanning transmission electron microscope (FJEOL 2000 FX).

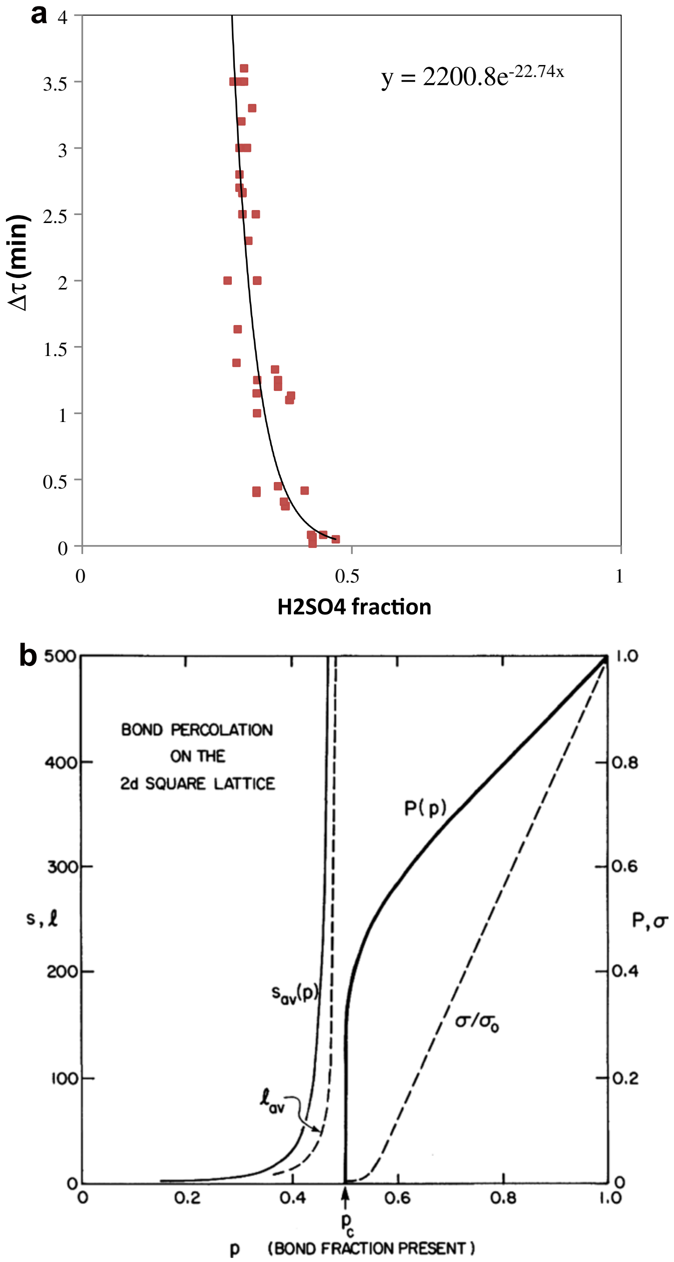

Fig. 1. The variation of ΔT near the gelation point at 40 °C (a) and the behavior, as a function of the fraction of filled bonds, of the key properties that characterize the bond percolation on the square lattice in two dimensions (b). The percolation of probability (P_p) and the average luster size s_{ave} are results of computer studies; the random-network conductivity σ is from the work of Kirkpatrice [23] and the spanning length is schematic. From Zallen [18].