Paper

Mechanical Treatment of Silica Powder

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ABSTRACT

An amorphous silica powder (A2) was mechanically treated using a planetary type mill. Four different rotation speeds (50, 100, 200, 300 rpm), milling times (15, 30, 60 min) and ball sizes (01, 05, 10 mm) were used. The structure and morphology of the powder did not change by milling. The effect of milling conditions on particle size distribution and specific surface area was investigated. By the milling treatment the original particle size of the powder was not effectively reduced. Rotation speeds of more than 200 rpm and prolonged milling causes the formation of a broad range of particles of larger sizes. The surface activity of raw and treated powders was measured as the amounts of dissolved Si^{4+} ion into ammonia solution. The 10 mm ball size was the most effective for 200 and 50 rpm rotation speeds almost independently of the milling time. Comparison of the effect of milling conditions on particle features of this powder with previously investigated powder is also discussed. The findings indicate that from a technical and economical point of view each powder has its own optimum milling condition, which will be sufficient to considerably increase the specific surface activity of the original amorphous powder making it suitable for different applications in non-firing ceramics processing.

KEY WORDS

Silica powder, mechanical treatment, surface activities, modifications

1 Introduction

Silica (SiO_2) is one of the most abundant minerals on the earth's surface and is an important technological material. It can have application in numerous areas especially in glass. The functionalization of the silica particle surface can be used to enhance and/or control the overall properties of the particles for desired applications. The nature of the functional groups on the particle surface usually plays a critical role in the surface properties of particles such as hydrophobicity and chemical reactivity. There has been increasing interest in the synthesis and application of oxide materials whose surface is modified by organic, inorganic and metal-complex compounds¹⁻³⁾. The significant property of these materials is that they combine the physical properties of solids and the chemical behavior of surface compounds.

The surface silicon atoms tend to have a complete tetrahedral configuration and in an aqueous medium their free valence becomes saturated with hydroxyl groups (surface OH groups: isolated, germinal, H-bonded), siloxane groups (Si-O-Si or bridges with oxygen atoms on the surface)^{4,5)}. Deposition of different compounds on the surface of SiO based materials

is usually achieved by adsorption, the adsorption efficiency increases proportionally to the quantity of surface active sites. Many investigations have been reported on surface treatment and characterization of silica powders^{1,5-8)}.

Recently, Apiluck et al.⁹⁾ have proposed a novel ceramic fabrication method without firing and/or debinding process, in order to reduce the cost and energy for post-forming processes. In this method, the surface of a raw powder is mechanically activated using a planetary ball-mill. In the present work, the surface of an amorphous silica powder was activated by mechanical treatment for further applications in synthesis of non-firing ceramic. A variety of milling conditions were carried out combining different rotation speeds, milling times and ball sizes. BET, PSD, ICP, SEM were used for characterization. The optimum milling conditions to activate the surface of the present powder are compared with the results obtained previously for another amorphous silica powder.

2 Experimental Procedure

The silica powder IFX (A2) used in the present investigation was supplied by TOSO Ltd., Japan.

A FRITSCH-Pulverisette 5-Germany type laboratory planetary mill was used to mill the silica under air at room temperature. Raw

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Fig. 1 Particle size distribution of raw and milled powder at every milling condition. 60, 30 and 15 indicate milling time in minutes. 01, 05 and 10 correspond to the ball size in mm. Raw powder particle size was 10 μm . By increasing the speed and milling time a peak of small size particles disappeared, probably due to agglomeration of smaller particles.

silica powder samples were milled in a 500 ml zirconia pot using zirconia balls for periods of 15, 30 and 60 minutes. Rotation speeds of 50, 100, 200 and 300 rpm were applied. Three different ball sizes; 01, 05 and 10 mm were used. For all the experiments 25 g of raw powder was used with a weight ratio to the zirconia ball of 1:4.

Particle size distribution (PSD) measurements were carried out on a MICROTRAC Particle Size Analyzer after ultrasonically dispersing the powders in distilled water for 20 minutes.

Particle morphology observation was carried out using Scanning Electron Microscopy (SEM) with JSM-7000F type equipment. Powders were put into carbon paste and dried in vacuum dryer for 24 hours before observation.

BET method was used to measure specific surface area (SSA) of the powders from adsorption–desorption of N_2 at 77.3 K with BELSORP Max type equipment.

The quantitative dissolved loads of cation Si^{4+} concentration were estimated by using ICP technique (Inductively Couple Plasma)–SPS-7800 type. The sample for ICP analysis was prepared by dissolving 1 g powder with 100 ml of ammonia solution (NH_3 3M). The solutions were kept shaking continuously at atmosphere and room temperature (25 $^\circ\text{C}$) for 2 hours (AS ONE–Shaking baths SB20) and the slurries were separated and centrifuged (KOKUSAN type). The upper portion was filtered with 0.2 micron size filter to

remove the remaining particles and the solution was used for ICP measurement.

3 Results and Discussions

The changes in the particle size distribution (PSD) of the raw and treated powder under different milling conditions are presented in Fig. 1. Milling conditions are indicated in the figures and the meaning of the nomenclature is explained in the captions. The powder presents a bimodal particle size distribution composed of 70 % of larger particles in the size range 4 and 22 μm and 15 % of smaller particles in the range 0.3–0.8 μm . The particle size distributions of milled powders at rotation speed of 50 rpm are similar to that of raw powder. The peak of small size particles disappeared at high rotation speed of 200 rpm. At 100 rpm prolonged milling causes changes in the range of particles of smaller sizes. This observation may be explained as due to the agglomeration of smaller particles as discussed in¹⁰.

As seen in Fig. 2 the shape and size of the original particles did not change by the milling modifications. This image is in agreement with the particle size distribution shown in Fig. 1 for these milling conditions. This feature was also observed for previously investigated powders (A1)¹⁰.

Fig. 3 shows specific surface area values of raw and milled

Fig. 2 Morphology of raw and mechanically treated (rotation 100 rpm-milling time 15 min- ball size 01 mm) powders observed using SEM spectroscopy. The observed particle sizes are in agreement with the measured particle size distribution for these treatment conditions. The shape did not change after milling process.

Fig. 3 Specific surface area values of raw and treated powders. Fixed parameters are indicated in each case. 60, 30 and 15 indicate milling time in minutes. 01, 05 and 10 correspond to the ball size in mm. 50, 100 and 200 are rotation speeds. There is a very small increased of SSA when the milling speed, milling time, ball size is increased to 100 rpm, 30 min and 5 mm, respectively. SSA decreased when prolonged milling speed, milling time or big ball size.

amorphous silica A2 powders. 1, 5 and 10 indicate ball size in mm. 15, 30 and 60 correspond to milling time in min. 50, 100 and 200 rpm are rotation speeds. The fixed parameter is also shown. The SSA values of all powders were in the range of 23–26 m²/g (within 11.5 % difference). The behavior of small change in SSA was also reported in the modification of another powder¹⁰. SSA increased a little at a rotation speed of 100 rpm, milling time of

30 min and ball size of 5 mm. When prolonged milling time, high milling speed and large ball size corresponding to 60 min, 200 rpm and 10 mm are used, re-agglomeration occurs and the SSA decreases. From these results, long time milling is not only unsuitable for economical reasons but also because the particle features are not appropriate for application. The particle size distribution and specific surface area of the original power hardly

changed by the milling treatment but prolonged milling time, high milling speed and large ball size caused detrimental agglomeration of small particles.

These features were also observed for a previously investigated powder (A1) but milled conditions are different. SSA for the A1 studied powder also increase hardly but at higher rotation speed (300 rpm) and higher milling time (60 min) compare to the present A2 powder. The powder A1 is agglomerated stated so that it needs more energy to break the aggregated particles in order to increase SSA. In the case of A2 powder, original particles are well dispersed, it enhances less used energy to separate the aggregated particles. In generally, at higher rotation speed or milling time, the harder agglomerated particles are broken to induce increasing of SSA but for each powder has its own curtain milling conditions¹⁰⁾.

As we proposed in an earlier communication, the mechanical process induces surface damage resulting in broken bonds and generation of surface silicon ions¹⁰⁾. The surface activity of raw and treated powders at various conditions was measured as the amounts of dissolved Si^{4+} ion into ammonia solution after 2 hours shaking time. Surface area normalized dissolved silicon ion values for raw and treated silica powder is shown in Fig. 4. The specific surface activity increased by the mechanical treatment at every tested condition. For this powder the highest ball size, 10 mm was the most effective for 100 and 200 rpm rotation speeds almost independently of the milling time. At 300 rpm of milling speed, surface activities decreased because of re-agglomeration of small particles. According to these results, from an economical point of view 15 min milling time at 200 rpm with a 10 mm ball will be sufficient to considerably increase the specific surface activity of this powder (A2). In the case of A1 investigated powder, the optimum conditions were different in ball size as shown 15 min milling time at 200 rpm with a 05 mm. As results in dissolved Si^{4+} in ammonia solution, the ball size is the most effective factor to activate the surface activity but each powder gives different results in ball sizes. It may possible the original surface state, surface features or further production method of the powders, the optimum conditions for sufficiently increasing the surface activity of the powder investigated in the present study are different from the one previously studied indicating that the effect of milling on the surface activity may be different for each powder and the conditions can not be generalized. The difference of original surface state for each powder will be shown in further publication.

4 Summary and Conclusions

By planetary milling process the particle size and specific surface activity of amorphous silica powder were successfully modified. Milling at different rotation speeds, milling times and ball sizes was applied and the results can be summarized as follows:

- The particles morphology of the original powder did not change by the milling treatment. This feature was also

Fig. 4 Surface area normalized dissolved Si^{4+} ion values for raw and treated amorphous silica powder at various milling conditions. 60, 30 and 15 indicate milling time in minutes. 01, 05 and 10 correspond to the ball size in mm. The specific surface activity of the powder could be successfully increased by the mechanical treatment. The maximum activities are seen at 200 rpm of rotation speed.

observed for a previously investigated powder.

- The particle size distribution and specific surface area of the original powder hardly changed by the milling treatment but prolonged milling time, high milling speed and large ball size caused detrimental agglomeration of small particles. These features were also observed for a previously investigated powder.
- According to the results of the present work, from a technical and economical point of view 15 min milling time at 200 rpm rotation speed with a 10 mm ball size will be sufficient to increase the specific surface activity of the powder making it suitable for different applications in non-firing ceramics processing.

By planetary milling process the particle size and specific surface activity of amorphous silica powder were successfully modified.

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