

# Mechanical modification of silica powders

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Two types of silica powder with different structures, one crystalline (C1) and one amorphous (A1) were mechanically treated using a planetary type mill. Three different rotation speeds (100, 200, 300 rpm), milling times (15, 30, 60 min) and ball sizes (1, 5, 10 mm) were used. The structure and morphology of the powders did not change by milling. The effect of milling conditions on particle size distribution was investigated. By the milling treatment the original particle size of both powders could be effectively reduced. For the amorphous powder rotation speeds of 200 and 300 rpm and prolonged milling causes the formation of a broad range of particles of larger sizes. This behavior is not observed for the crystalline powder. The surface activity of raw and treated powders was measured as the amounts of dissolved  $\text{Si}^{4+}$  ion into ammonia solution. For the crystalline powder the smallest ball size, 1 mm, was the most changing in the amount of dissolved  $\text{Si}^{4+}$  for all milling speeds and milling times and its changing increased by increasing both rotation speed and milling time. In the case of the amorphous powder the 5 mm ball size was the most effective for 100 and 200 rpm rotation speeds almost independently of the milling time. A possible activation reaction mechanism occurring during the milling process is also discussed. The findings indicate that from a technical and economical point of view as the low total energy consumption for milling with 15 min milling time at 200 rpm with a 5 mm ball will be sufficient to considerably reduce the particle size and increase the specific surface activity of the amorphous powder making it suitable for different applications in non-firing ceramics processing.

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## 1. Introduction

Silica ( $\text{SiO}_2$ ) 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 compounds.<sup>1)–3)</sup> The important 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 electron 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).<sup>4),5)</sup> 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.<sup>1),5)–8)</sup>

Recently, Apiluck et al.<sup>9)</sup> has 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 waste paper sludge powder is mechanically activated using a planetary ball-mill. In the present work, two types of silica powder with different structure (one crystalline, one amorphous) were used for activating surface by mechanical treatment. A variety of milling conditions were carried out combining different rotation speeds, milling times and ball sizes. XRD, BET, PSD, ICP, SEM were used for characterization. Possible reaction mechanisms of powder surface activation occurring during milling process are also discussed.

## 2. Experimental procedure

The two types of silica powder (C1 and A1) used in the present investigation were supplied by TOSO Ltd., Japan. Specification of the powders is shown in **Table 1**.

A laboratory planetary mill (A FRITSCH- Pulverisette 5, Germany) was used to mill the silica powders at room temperature. Raw silica powders were milled in a 500 ml zirconia pot using zirconia balls for periods of 15, 30 and 60 min. Rotation speeds of 100, 200 and 300 rpm were applied. Three different ball sizes; 1, 5 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 (Japan) ultrasonically dispersing the powders in distilled water for 20 min.

Particle morphology observation was carried out using Scanning Electron Microscopy (SEM) with JSM-7000F type equipment (Japan). Powders were put into carbon paste and dried in vacuum dryer for 24 h before observation. Optical microscopy was used for observation of raw IOTA powder.

BET (Brunauer-Emmett-Teller, 1938) method was used to measure specific surface area (SSA) of the powders from adsorption-desorption of  $\text{N}_2$  at 77.3 K with BELSORP Max

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Table 1. Specifications of the two as received silica powders

Nomenclature	Particle size/ $\mu\text{m}$	Specific surface area/ $\text{m}^2\text{g}^{-1}$	Structure	State	Shape
C1	750	0.16	Crystal (quartz)	Well dispersed	Free
A1	0.6	9.8	Amorphous	Agglomeration	Spherical

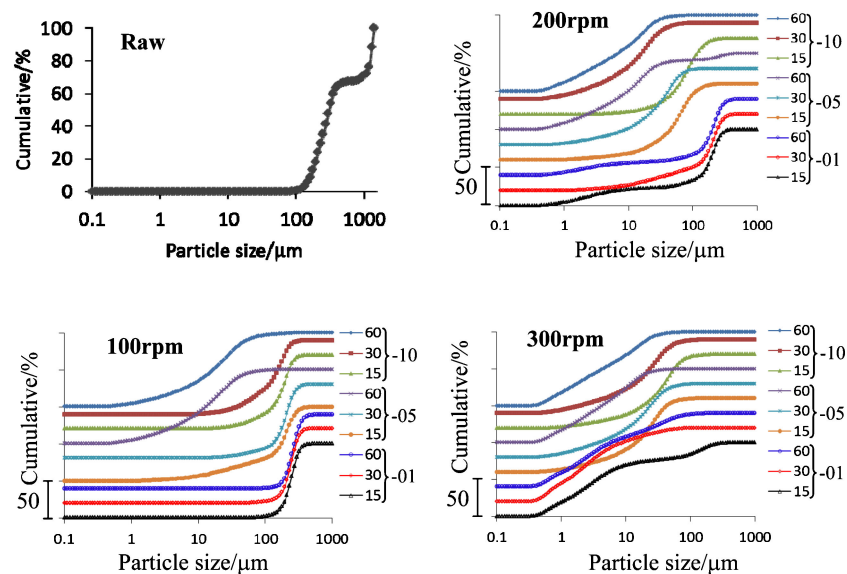


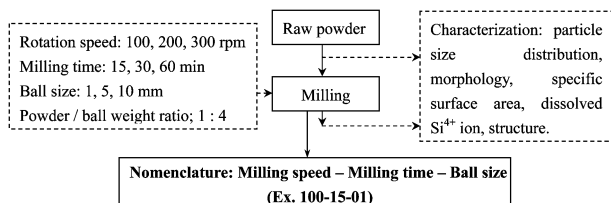
Fig. 1. (Color online) Particle size distribution of raw C1 and milled powders at every milling condition. 60, 30 and 15 indicate milling time in minutes. 1, 5 and 10 correspond to the ball size in mm. The raw powder has an important fraction of large size particles that is reduced in size by milling under any conditions. With same size of ball and milling time the effectiveness increases with increasing rotation speed.

equipment (Japan).

We propose here that the mechanical process induces surface damage with broken bonds and surface silicon ion. The quantitative dissolved loads of cation  $\text{Si}^{4+}$  concentration were estimated by using ICP technique (Inductively Couple Plasma)–SPS-7800 (Japan). The sample for ICP analysis was prepared by dissolving 1 g powder with 100 ml of ammonia solution (3M). The solutions were kept shaking continuously at atmosphere and room temperature (25°C) for 2 h (AS ONE—Shaking baths SB20) and the slurries were separated and centrifuged (KOKUSAN, Japan). The upper portion was filtered with 0.2 micron size filter to remove the remaining particles and the solution was used for ICP measurement.

A normal room temperature XRD (X-ray Diffraction) model RINT 1000-Rigaku analyzer was used for analysis of silica structure. The radiation applied was  $\text{Cu K}\alpha$  operated at 40 kV and 40 mA on a range of  $2\theta$  from 5 to 70°.

Experimental procedures can be summarized as shown below.



### 3. Results and discussions

The changes in the particle size distribution (PSD) of the raw powders produced by milling under different conditions were investigated. The obtained results are presented in **Figs. 1 and 2**

for the C1 and the A1 powders, respectively. Milling conditions are indicated in the figures and the meaning of the nomenclature is explained in the captions such as 60, 30 and 15 indicate milling time in minutes. 1, 5 and 10 correspond to the ball size in mm. 100, 200 and 300 rpm are rotation speeds. By the milling treatment the original particle size of both powders could be effectively reduced. Similar results have been reported for kaolinite powders.<sup>10)</sup>

The raw C1 powder presents a bimodal particle size distribution composed of 31% of very large particles in the size range 913 and 1408  $\mu\text{m}$  and 63% of smaller particles in the range 136–420  $\mu\text{m}$ . After milling at any conditions the large particles are not observed. The resulting distribution of smaller particles strongly depends on the milling speed as seen in Fig. 1. Under a milling speed of 100 rpm for all ball sizes by increasing milling time up to 30 mins the peaks shift to smaller sizes but the obtained particles size distributions are similar. However, a strong effect of ball size is observed when the milling is prolonged to 60 mins. When the speed is increased to 200 rpm ball size and milling time combinations produce different particle size distributions. A general trend is that for 05 and 10 mm ball sizes the peaks shift and broaden gradually to lower particle sizes by increasing the milling time. On the other hand, when using the 1 mm ball, the distribution is almost not affected by the milling time. With a 300 rpm milling speed, the size of the particles is mostly in the range of less than 100  $\mu\text{m}$ . With this speed the shift and broadening effect of peaks with milling time is observed for all ball sizes.

As seen in Fig. 2 the results produced by milling the amorphous silica powder are remarkably different than for the previously discussed behavior of the crystalline powder. As

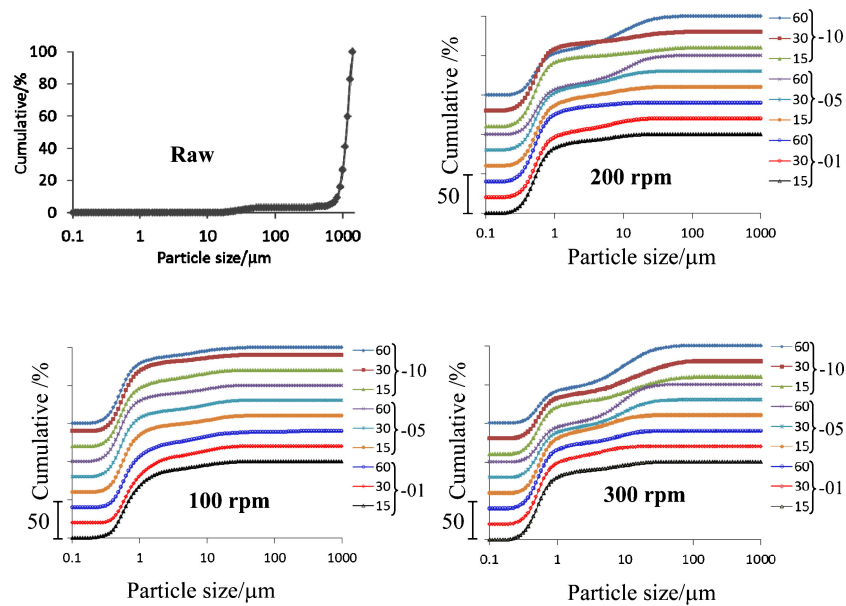


Fig. 2. (Color online) Particle size distribution of raw Al and milled powders at every milling condition. 60, 30 and 15 indicate milling time in minutes. 1, 5 and 10 correspond to the ball size in mm. Raw powder particle size was 1290  $\mu\text{m}$ . By milling the main particle size was reduced to 0.6  $\mu\text{m}$  for all milling conditions at a rotation speed of 100 rpm. By increasing the speed and milling time a broad peak of secondary particles, probably originated by agglomeration of smaller particles, with maximum at around 10  $\mu\text{m}$  is observed.

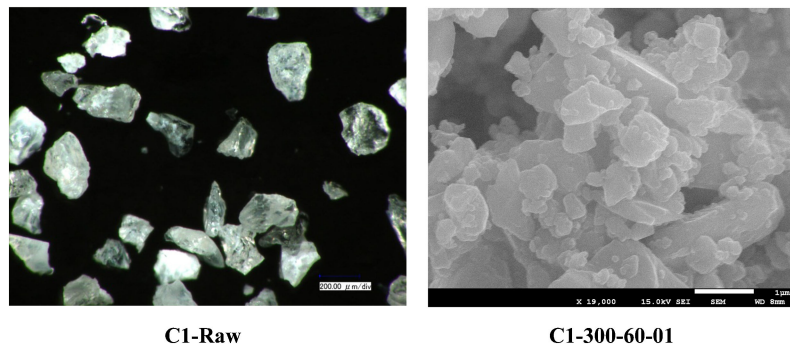


Fig. 3. (Color online) Morphology of raw and mechanically treated, 300-60-01, C1 powders observed by optical and SEM spectroscopy. The observed particle sizes are in agreement with the measured particle size distribution for these treatment conditions.

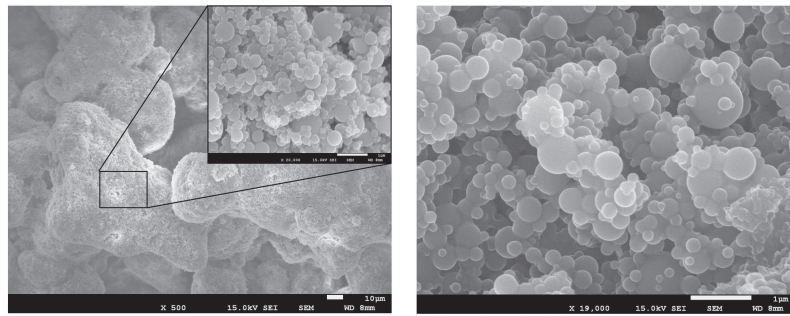
shown in Fig. 2 the raw powder has very large, almost uniform particle size (1290  $\mu\text{m}$ ) but after milling at any conditions even at the lowest rotation speed and shortest time, the particle size was reduced to less than 1  $\mu\text{m}$  (0.6  $\mu\text{m}$ ). At rotation speeds of 200 and 300 rpm prolonged milling causes the formation of a broad range of particles of larger sizes especially for the 5 and 10 mm size balls. This observation may be explained as due to the agglomeration of smaller particles, previously produced as has been observed for kaolinite powders.<sup>11)</sup> These authors stated that during mechanical process three different stages can take place. First the surface area is proportional to the milling time and after that aggregation and agglomeration may occur.

Figure 3 shows electron micrographs of the C1 powders before and after milling for 60 min with a 1 mm ball at a rotation speed of 300 rpm (C1-300-60-01). The observed particle size of the modified powder by SEM is in agreement with the particle size distribution measurements under these conditions shown in Fig. 1. During milling, the particles are broken into smaller pieces and there is an actual decrease in particle size. This

observation has been also reported for kaolinite powders.<sup>12),13)</sup>

As seen in Fig. 4 the raw amorphous powder contains many large agglomerated particles together with a large quantity of small spherical particles. The shape of the original particles did not change but the agglomerated particles were dispersed by the milling modifications. Particle size measurements showed that agglomerated particles could not be dispersed by ultrasound, therefore it could be stated that the milling process is a useful technique for de-agglomeration of powders. However, prolonged milling, high rotation speed and large ball size cause re-agglomeration of particles as seen in the SEM image (A1-300-60-05). This image is in agreement with the particle size distribution shown in Fig. 2 for these milling conditions.

The different response to the mechanical treatment of these two silica powders was also reflected in the specific surface area (SSA) measurements as seen in Figs. 5 and 6. The effects of changing rotation speeds, milling times and ball sizes on the SSA value of the raw C1 powder is shown in Fig. 5. Fixed parameters are indicated in each case. The values of SSA are very big



**A1-Raw**

**A1-300-60-05**

Fig. 4. Morphology of raw and mechanically treated, 300-60-05, A1 powders observed by SEM spectroscopy. The observed particle sizes are in agreement with the measured particle size distribution for these treatment conditions. The shape does not change after treatment but by milling treatment the agglomerated particles can be separated.

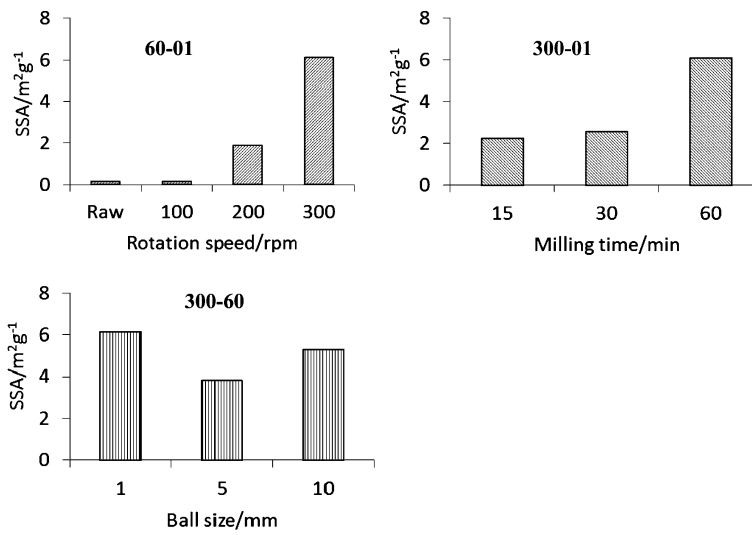


Fig. 5. Specific surface area values of raw and treated C1 powders. Fixed parameters are indicated in each case. The increase in SSA is mostly influenced by the rotation speed.

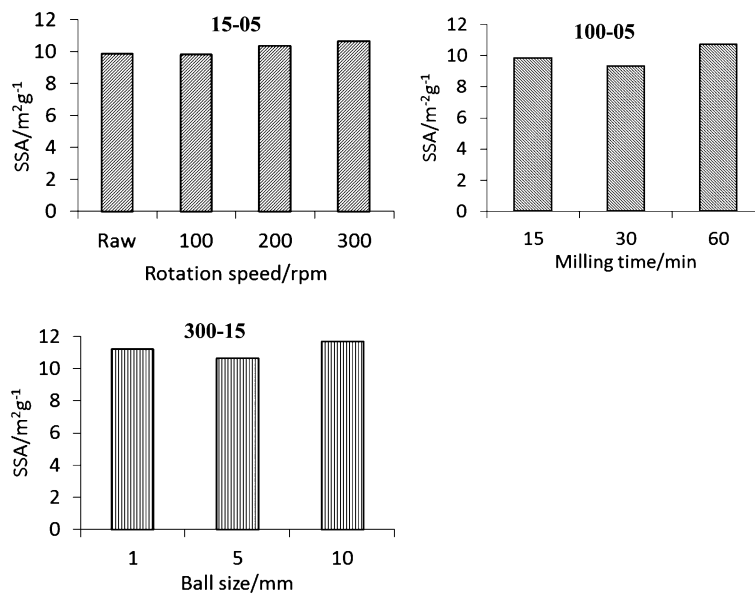


Fig. 6. Specific surface area values of raw and treated A1 powders. Fixed parameters are indicated in each case. There is a very small increase of SSA when the milling speed is increased to 200 and 300 rpm.

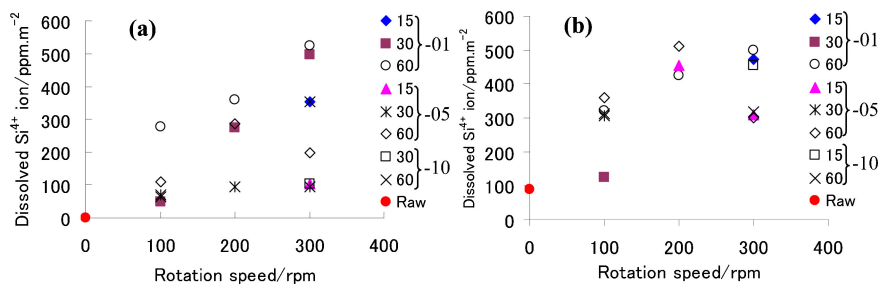


Fig. 7. (Color online) Surface area normalized dissolved Si<sup>4+</sup> ion values for raw and treated (a) crystalline and (b) amorphous silica powders at various milling conditions. 60, 30 and 15 indicate milling time in minutes. 1, 5 and 10 correspond to the ball size in mm. The specific surface activity of both powders could be successfully increased by the mechanical treatment.

different from each powder by milling condition as from 0.15–6 m<sup>2</sup>/g (changing of 97.5%). The increase in SSA is drastically influenced by the rotation speed. The changes of milling times also affected on the SSA, the most effective time is at 60 min, it is hardly to change SSA from 15 to 30 min of milling time. This agrees with reported data for kaolin powders.<sup>11)</sup> Using the 5 mm ball size reduces the SSA compared to the 1 and 10 mm size balls for different powders. Ball size do not clearly effect to SSA. There is agreement between two measurements; particle size distribution and specific surface area for this powder. The total energy transferred to the powder during milling can be correlated to the activation energies of the broken particles that can occur. At higher activation energy more energetic milling condition should correspond.<sup>14)</sup> For longer milling times and higher milling speed give higher level of energy transfer. This is due to the reduction of the ordered size and increase the SSA.

Base on two measurements, rotation milling speed is the most effective factor on the particle size, the second factor is milling time. Because the rotation milling speed is the most effective factor to the total energy consumption and the milling time is the second factor.<sup>14)</sup>

Figure 6 shows specific surface area values of raw and milled amorphous silica A1 powders. The SSA values of all powders were obtained from 9.3–11.6 m<sup>2</sup>/g (changing of 19.8%). SSA increase hardly at rotation speed of 300 rpm and milling time of 60 min. The raw powder has much larger particle size but obtained specific surface area is similar. This can be explained by agglomerated powder, SSA of agglomerated particles is sum of SSA of its contained small spherical particles. At higher rotation speed or long milling time, the harder agglomerated particles are separated causes increasing a little bit of SSA.

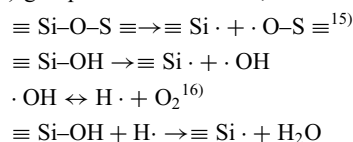
Crystal silica, C1, can be ground by these milling conditions, however, the primary particle of amorphous silica, A1, could not be broken and only aggregates were broken by these milling conditions. A possible reason is the particle size 0.6 μm as minimum size for this milling machine's ability.

The SSA data was used to normalize the surface activity changes of the powders caused by the mechanical treatment discussed below.

The surface activity of raw and treated powders at various conditions was measured as the amounts of dissolved Si<sup>4+</sup> ion into ammonia solution after 2 h shaking time. Surface area normalized dissolved silicon ion values for raw and treated powders are shown in Figs. 7(a) and 7(b) for the crystalline and amorphous silica powders respectively. The specific surface activity increased by the mechanical treatment at every tested condition for both powders. For the crystalline powder the smallest ball size, 1 mm, was the most effective for all milling speeds and milling times and

its effectiveness increased by increasing both rotation speed and milling time. In the case of the amorphous powder the 5 mm ball size was the most effective for 100 and 200 rpm rotation speeds almost independently of the milling time. According to these results, from an economical point of view 15 min milling time at 200 rpm with a 5 mm ball will be sufficient to considerably increase the specific surface activity of this powder.

Primary particles were broken in the case of C1 and de-agglomerated for the A1 powder and generated new surface by these milling conditions, silicon ion concentration will increase. The increasing rate of Si<sup>4+</sup> concentration of the de-agglomerated powder (SFP) is lower than that of broken powder (C1) by milling process. That can be explained by changing behavior in SSA of each powder as mentioned above. Beside that, silicon ion generation during milling process of silica powders can be also generated by the braking of surface silanol (Si–OH) and siloxane (Si–O–Si) groups bonds as follows,



The water produced from these reactions may explain the agglomeration of particles produced as a result of milling at higher speeds and/or prolong times.

Besides surface characterizations, changes in the powders structure caused by milling were also investigated. The X-ray diffraction patterns of the two raw and mechanically treated silica powders milled for 60 min using a 10 mm ball at three different rotation speeds, 100, 200 and 300 rpm are shown in Fig. 8(a) C1 and (b) A1. The structures of the raw C1 and A1 silica powders show crystalline and amorphous patterns, respectively. Basically the structures did not change during milling at any speed but small changes were observed for the crystalline powder as follows.

The C1 powder shows two XRD peaks at 2θ° of 20.6 and 26.7 corresponding to (100) and (101) planes. An extended view of the 26–27 two theta degree region of Fig. 8(a) is shown in Fig. 9(a). Integrated intensities and maxima of the peaks for the raw and treated C1 powders at different rotation speeds are presented in Fig. 9(b). The maximum shifts to lower angles by milling, meanwhile the intensity increases going through a maximum when the milling speed is 100 rpm and then decreases when the speed is increased to 200 and 300 rpm. The large increase in intensity may be explained by the change in particle size, a reduction in particle size would increase the intensity of the X-ray diffraction signal. The decrease in intensity for 200 and 300 rpm rotation speeds may be due to the development of a

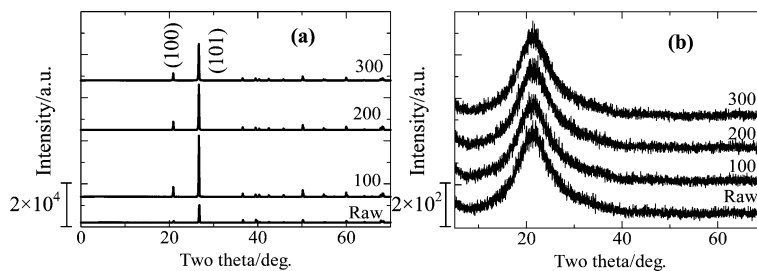


Fig. 8. XRD patterns of raw and treated silica powders: (a) C1 and (b) A1. For both powders 60 min milling with 10 mm size ball at 100, 200 and 300 rpm rotation speed treatments were applied. Crystallized planes are indicated. After milling the structures remain as crystalline and amorphous respectively.

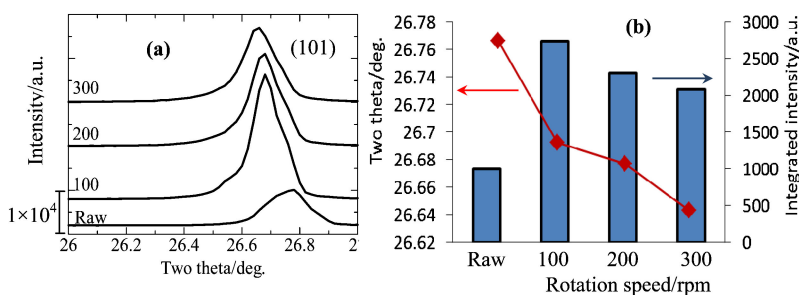


Fig. 9. (Color online) (a) Extended view of the 26–27 two theta degree region of Figs. 6(a) and 6(b) XRD (101) peak position and integrated intensity of raw and after milling at different rotation speeds. The maximum shifts to lower angles by milling. The intensity goes through a maximum when the milling speed is 100 rpm and decreases when the speed is increased to 200 and 300 rpm.

more disordered structure, that is, the background increases as the intensity of the reflections weakens. As discussed above the higher milling speed gives higher consumed energy. At higher level of energy transfer, the structure can be deformed.

Similar observations have been also reported in the literature. Mechanical process induced changes in the regular stacking modes of the silica layer into more random modes, and the structure became more disordered (or poorly crystallized).<sup>16,17</sup> Total degradation of the crystal structure of silica by mechanical treatment probably involves the rupture of the tetrahedral layers. Distortion and rupture of the crystalline silica structure induced by milling reflected in line broadening, increases in mean lattice strain and reduction of peak areas (integrated intensities) has also been reported.<sup>18)</sup>

#### 4. Summary and conclusions

By planetary milling process the particle size and specific surface activity of two silica powders, one crystalline (C1) and one amorphous (A1) 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 two powders did not change by milling modifications.

—By the milling treatment the original particle size of both powders could be effectively reduced but the behavior was different.

The raw crystalline powder presents a bimodal particle size distribution composed of 31% of very large particles in the size range 913 and 1408 μm and 63% of smaller particles in the range 136–420 μm. After milling at any conditions the large particles are not observed. The changes in particle size distribution at each milling speed are influenced by the ball size and milling time combination. A general trend is that increasing milling speed,

ball size and time the peaks shift and broaden gradually to lower particle sizes.

The amorphous raw powder has very large, almost uniform particle size (1290 μm) but after milling at any conditions even at the lowest rotation speed and shortest time, the particle size was reduced to less than 1 μm (0.6 μm). At rotation speeds of 200 and 300 rpm prolonged milling causes the formation of a broad range of particles of larger sizes especially for the 05 and 10 mm size balls. This observation may be explained as due to the agglomeration of smaller particles.

—The specific surface activity of raw and treated powders was calculated using the measured amounts of dissolved Si<sup>4+</sup> ion into ammonia solution after shaking for 2 h and the respective specific surface areas. For the crystalline powder smallest ball size, 01 mm, was the most effective for all milling speeds and milling times and its effectiveness increased by increasing both rotation speed and milling time. In the case of the amorphous powder the 05 mm ball size was the most effective for 100 and 200 rpm rotation speeds almost independently of the milling time.

—According to the results of the present work, from a technical and economical point of view 15 min milling time at 200 rpm with a 5 mm ball will be sufficient to considerably reduce the particle size and increase the specific surface activity of the amorphous powder making it suitable for different applications in non-firing ceramics processing.

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