Characteristics of crystalline silica (SiO$_2$) particles prepared by simple solution method using sodium silicate (Na$_2$SiO$_3$) precursor

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Abstract. The crystalline silica (SiO$_2$) particle is successfully prepared using simple solution method from sodium silicate (Na$_2$SiO$_3$) precursor. The FTIR spectrum of the sample confirms the presence of SiO$_2$. The X-ray diffraction (XRD) shows that the sample is cristobalite type of SiO$_2$ which is comparable with ICSD ref. number of 01-076-0941. The crystallite size is about 28 nm as calculated by Scherrer method and the average particle diameter was about 697 nm as confirmed by Particle Size Analyzer (PSA) measurement. The Scanning Electron Microscope (SEM) image reveals that the sample reveal micro-flake with irregular rod-shaped morphology. The purity of sample is examined by X-ray Fluorescence (XRF) which shows about 93.1 mass % of pure SiO$_2$ whereas, the purity of the raw precursor Na$_2$SiO$_3$ before synthesis is about 60.5 Mass %. The synthesized SiO$_2$ particles can be used for several applications, where SiO$_2$ is used in its crystalline phase.

1. Introduction
In the last few years, there has been growing interest in the preparation of SiO$_2$ particle for a variety of applications where the purity of materials is one of the important key parameters. Pure SiO$_2$ particles with crystalline phase can be applied as the material source in photovoltaic [1], semiconductor electronic devices, catalysis, film substrates, ceramics, humidity sensors, etc. [2, 3]. Synthesis of the SiO$_2$ particle can be done by several methods such as chemical vapour deposition, plasma and combustion synthesis, hydrothermal method and also sol-gel processing. Among these methods, the simple solution method as a part of sol-gel has advantages of low cost in processing and also ease in controlling the properties of SiO$_2$, i.e., purity and homogeneity or modification of material composition. The report of simple solution method can be seen in Ref. [4-6]. In recent reports, the silica particle was prepared from an expensive raw material such as tetraethyl orthosilicate (TEOS) [7-8]. However, a simple method using inexpensive source materials is required for the mass production of the SiO$_2$ particle. In this work, the SiO$_2$ particle was prepared using simple solution method from an economic raw material, i.e., Na$_2$SiO$_3$ and its result were described.
2. Experiments
The starting material for synthesizing SiO$_2$ is Na$_2$SiO$_3$ solution. Firstly, the precursor (Na$_2$SiO$_3$) was mixed with distilled water (with fraction 1:2) and then 2 M HCl was added and stirred at room temperature (RT) until a clear homogeneous mixture was obtained. The white powder was recovered by filtration followed by cleaning with distilled water in order to neutralize the acid and dried at a temperature of 60°C for about 12 h. In order to form crystalline phase of SiO$_2$, 2 g of the obtained white powder is mixed with PEG 6000 and distilled water in RT. The amount of SiO$_2$: H$_2$O: PEG 6000 fraction was about 1: 50: 5. The mixture of material was calcined at 900°C for about 2 h. Finally, the powder sample was characterized by various sophisticated techniques. The presence of SiO$_2$ in the sample was characterized by Fourier-transform infrared (FTIR) analysis (Shimadzu prestige 21). The structure and phase of silica were examined by X-ray Diffraction (XRD) Rigaku with Cu Kα with $\lambda = 1.54060$ Å. The average of particle diameter was measured by Particle Size Analyzer (PSA) Beckman Coulter LS 13 320. The purity of SiO$_2$ and its traces (Mass %) was measured by X-ray Fluorescence (XRF) Rigaku NEX CG. The morphology and elemental analysis of the sample were characterized by using Scanning Electron Microscopy (SEM) equipped with energy dispersive X-ray (EDX), FEI-Inspect 550, EDAX Ametek.

3. Results and Discussion
In order to confirm the presence of SiO$_2$, the sample was characterized using FTIR analysis. The spectrum of the sample after calcination at a temperature of 900 °C is shown in figure 1. It can be seen that two main characteristics peak were observed at around 794 cm$^{-1}$ and 1079 cm$^{-1}$ which is attributed to Si-O bending vibration band and asymmetric stretching vibration of the siloxane bonds (Si-O-Si) [9, 10], respectively. The band at about 473 cm$^{-1}$ was associated with bending vibration modes in O-Si-O network [11]. On the other hand, the band at around 2357 cm$^{-1}$ is concomitant to Si-C stretching (interaction of C from PEG with Si) and the band at around 3450 cm$^{-1}$ is concomitant with Si-OH, characteristics of -OH group which commonly exists in water [12]. This peak still prevails even though the sample was calcined at high temperature. The reason for Si-OH existence is the physically absorbed water molecules from the environment by silica.

![Figure 1. The FTIR Spectra of crystalline SiO$_2$ prepared by simple solution method.](image-url)

Secondly, the structural property of sample was examined by XRD. The results showed that the SiO$_2$ exhibits a crystalline nature (figure 2(a)), representing cristobalite low type of SiO$_2$ (figure 2(b)). It matches with the reference of 01-076-0941 number (Calculated from ICSD using POWD-12++,
1997) [13]. The crystal phase of this type of silica is tetragonal with a lattice parameter of $a$-axis about 4.99 Å, $b$-axis 4.99 Å, and $c$-axis 7.02 Å, respectively. The alpha, beta and gamma were 90 degrees, respectively. However, the addition of PEG and calcination in high-temperature influences the crystallinity and structural phase of the material. The crystallite size ($D$) of the sample was calculated using Debye-Scherer’s equation (1).

$$D = \frac{0.9 \lambda}{\beta \cos \theta}$$

where $\lambda$ is the wavelength of X-ray beam ($\lambda$=1.5406 Å), $\beta$ is the full width at half maximum (FWHM) of the intense peak and $\theta$ is the Braggs angle. Based on the above calculation, crystalline SiO$_2$ has crystallite size of about 28 nm.

Figure 2. The XRD pattern of (a) SiO$_2$ powder, and (b) the standard SiO$_2$ pattern, cristobalite low type.

On the other hand, the particle diameter of the sample was measured by PSA analysis. The result (figure 3) showed that the average particle diameter was about 697 nm while volume median diameter of $d_{50}$ (represent 50% of the total volume) was about 305 nm. This result was still larger compared to the crystallite size. Theoretically, it should be noted that the particle diameter will always be higher than that of crystallite size. We predict that this particle diameter was influenced by the existence of many agglomerations of particles on the sample which was detected by PSA. The existence of agglomeration and morphology of sample can be seen in figure 4.

The SEM characterization showed the surface morphology of silica particle at different magnification, (a) 100.000×, (b) 50.000×, (c) 20.000×, and (d) 150.000× (figure 4). The morphology of sample depicts mostly micro-flake and irregular rod-shape with agglomeration.
**Figure 3.** The particle diameter for crystalline SiO$_2$ prepared by simple solution method.

**Figure 4.** The SEM image of SiO$_2$ with various magnifications, (a) 100.000×, (b) 50.000×, (c) 20.000×, and (d) 150.000×.

The elemental analysis of SiO$_2$ particle is shown in figure 5. The presence of silica is confirmed by elemental analysis. The presence of oxygen in the EDX result indicates that the formation of silica as silicon dioxide. The element of oxygen is about 62 at% and Si is about 38 at%.
Figure 5. The result of EDX measurement of SiO₂ sample

Furthermore, not only the structural, morphology, and elemental analysis of sample but the purity of this SiO₂ particle was also observed. The purity of sample was examined by the XRF analysis. Table 1 shows the mass percentage of elements in sodium silicate as a precursor and the sample of crystalline silica. The purity of SiO₂ with sodium silicate as a raw precursor was about 60.5 % and the second highest is Na of about 38.6 % followed by other components as shown in table 1. On the other hand, the crystalline SiO₂ prepared by simple solution method has a high purity of SiO₂ of about 93.1 % with traces in a very less percentage (for each component).

Table 1. The mass percentage of elements in sodium silicate precursor and sample of crystalline silica prepared.

| Component | Precursor (Mass%) | SiO₂ Particles (Mass%) |
|-----------|------------------|------------------------|
| SiO₂      | 60.5             | 93.1                   |
| Na        | 38.6             | 1.13                   |
| ZrO₂      | 0.38             | 1.13                   |
| Al        | 0.34             | 0.41                   |
| TiO₂      | 0.04             | 1.18                   |
| Cl        | 0.04             | -                      |
| S         | 0.03             | -                      |
| Ca        | 0.025            | 0.63                   |
| Fe        | 0.012            | 0.43                   |
| K         | 0.0103           | 1.55                   |
| Cu        | 0.0011           | -                      |
| ZnO       | 0.0007           | 1.07                   |
4. Conclusions

Crystalline silica has been successfully prepared by using simple solution method and economic raw materials (Na$_2$SiO$_3$). The FTIR and EDX results confirmed the presence of silica in the form of silicon dioxide. The XRD showed that the silica prepared has characteristics crystalline phase with an average crystallite size of about 28 nm. This silica showed micro-flakes and irregular rod-shaped morphology with agglomeration as confirmed by SEM analysis. The XRF characterization displayed the purity of SiO$_2$ to be about 93.1%. In general, these characteristics can be used as an initial reference on the mass production of crystalline silica powder from an economic raw material for industrial and wide-scale applications.

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