Production of Nano Amorphous SiO$_2$ from Malatya Pyrophyllite

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Abstract. Pyrophyllite (Al$_4$Si$_8$O$_{20}$(OH)$_4$) is an important industrial clay mineral. In this paper, highly pure nano silica powder was synthesized by alkaline treatment method from the local pyrophyllite deposit which is in Malatya, Turkey. The morphologies, structures and properties of the raw pyrophyllite and the obtained nano amorphous SiO$_2$ were determined by XRF, XRD, ATR, SEM and EDX. The results showed that the nano silica can be produced with a high purity (98%) and nano size (< 50 nm).

1. Introduction
Nano silica powder is widely used in many industrial applications such as cement production, ceramics, chromatography, catalytic application, production of many advanced materials (e.g. SiC, Si$_3$N$_4$, elemental Si and Mg$_2$Si) and also waste water treatment [1 - 4]. The nano silica is produced by various methods such as sol–gel method [5] and precipitation method [6] (using highly pure chemicals to obtain high purity SiO$_2$. The main drawback about these synthesis methods is the cost depending on the chemicals’ price and the high synthesis temperature.

In the literature, recently low-temperature alkali extraction method has been focused on the synthesis of nano silica from fly ash [7], rice-husk ash [8], biomass [9] and local silica rich ore [10]. This way is simple and effective as well as an eco-friendly method, due to the decreasing the solid waste to transform them into nano silica. In addition, narrow nano SiO$_2$ particle size with high surface area and meso-porosity can be obtained by this method.

The aim of the present study is to produce nano silica powder from Malatya-Turkey pyrophyllite ore by alkaline treatment method.

2. Materials and methods
Pyrophyllite ore as a nano silica source was taken from Malatya, Turkey. The ore crushed and ground to 80–85 mass % passing 180 μm in a ball mill. NaOH, H$_2$SO$_4$ and HCl (from Merck) were used as chemicals.

The experimental procedure was based on the study conducted by Mourhly et al., [10] with some modifications. In their work, nano silica was synthesized from pumice rock by alkaline treatment method. The pyrophyllite ore used in this study has higher SiO$_2$ and Al$_2$O$_3$ content than the pumice ore. Especially, iron, calcium and other alkali metal content are too low in the used ore. Our preliminary test results showed that it is not necessary to keep the pyrophyllite in the alkaline leaching system too long. All experiments were duplicated. 5 gr of pyrophyllite was mixed with 300 ml of 3 molarities NaOH in a 500 ml 3 neck flask equipped with a reflux condenser. The system was put into a
magnetic stirrer with heating mantle and heated at 100 °C for 14 hours to dissolve the silica and produce sodium silicate. After that the solid and liquid were separated by centrifuge and filtration. The liquid was titrated with H₂SO₄ (5M) while being stirred vigorously until obtaining a silica gel which was occurred at pH 7. The silica gel was kept at room temperature for 24 hours and then filtrated and washed several times to remove the sulphate salt and the solid was heated at 80°C for 24 hours. The soluble minerals Al and K were removed with a solution of hydrochloric acid HCl (1M) at 110°C for three hours. Then the solid and liquid were separated by centrifuge and the solid was washed several times and dried at 110°C overnight and then heated at 800 °C for two hours.

Characterization and chemical structure of the pyrophyllite and the obtained SiO₂ were done by Spectro XEPOS, Rigaku Miniflex 600 with Cu Kα (40 kV, 15 mA, λ=1.5405 Å) XRD, Perkin Elmer Spectrum One FTIR-ATR and Leo Evo-40x VP Electron Microscope (Inonu University, Central Research Lab).

3. Results and discussions
The crystallinity and chemical structure of the raw pyrophyllite and nano silica were determined by XRD and the diffractions are given in figure 1. The patterns of the raw pyrophyllite match well with the powder diffraction data reported in the literature [11, 12] and show crystalline structure. Comparing to the XRD patterns indicated that the pyrophyllite was decomposed into amorphous SiO₂, since no peaks were recorded for nano silica sample and just the strong broad hump was detected between 15 and 30° at 20 values [10, 12].

![Figure 1. XRD patterns of the pyrophyllite and nano SiO₂](image)

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The IR spectra of the raw pyrophyllite and nano silica are presented in figure 2. The sharp and narrow bands with low intensities at 3650 cm\(^{-1}\) and 3500 cm\(^{-1}\) which were observed at IR spectra of pyrophyllite are attributed to stretching vibrations of Al\(_2\)OH and O-H vibration, respectively [13]. In addition, three clear bands were detected at 1012 cm\(^{-1}\), associated with the asymmetric stretching-vibrations of siloxane \(\nu_{as}(\text{Si-O-Si})\), 946 cm\(^{-1}\) associated with Si-OH groups and 826 cm\(^{-1}\) associated with symmetric siloxane groups \(\nu_{s}(\text{Si-O-Si})\) [10]. The sharp and intensive peaks belonging to nano silica at 1035 cm\(^{-1}\) and 789 cm\(^{-1}\) represented the stretching-vibrations of Si-O-Si. The wide peak recorded between 3600 and 3450 cm\(^{-1}\) indicated the silanol groups (Si-OH) on the nano silica surface [14].

![IR spectra of the raw pyrophyllite and extracted nano silica](image)

**Figure 2.** IR spectra of the raw pyrophyllite and extracted nano silica

In order to support the XRD and IR explanation, the elemental composition of pyrophyllite and extracted nano silica were given in Table 1. It can be concluded that the silicon of pyrophyllite is extracted by low temperature alkaline treatment with high purity. In the literature, amorphous SiO\(_2\) with mullite was obtained at 1100 °C. Comparing the results with literature data indicate that amorphous SiO\(_2\) can be obtained easily and cheaply by the alkaline method.

| Element | SiO\(_2\) | Al\(_2\)O\(_3\) | Fe\(_2\)O\(_3\) | TiO\(_2\) | CaO | MgO | Na\(_2\)O | K\(_2\)O |
|---------|-----------|----------------|----------------|----------|-----|-----|---------|---------|
| %       | 59.53     | 30.14          | 0.64           | 0.71     | 0.24| 0.16| 0.65    | 1.89    |
| %       | 98.68     | 0.08           | n/a            | n/a      | n/a | n/a | 0.210   | 0.1     |

**Table 1.** Elemental compositions of the raw pyrophyllite ore and nano silica.

The XRD, IR and XRF results indicated that the amorphous and highly pure SiO\(_2\) could be produced from the local pyrophyllite ore. In order to check the size, morphology and the purity, SEM and EDX investigation were done. The SEM image of the raw pyrophyllite indicated the laminated structure and irregular shaped particles and large size distribution (Figure 3a). The particle size of the amorphous and highly pure SiO\(_2\) was tried to identified using SEM (not have TEM options), showing that the particle sizes were smaller than 50 nm and agglomeration was seen due to the low resolution (figure 3b). It could be seen that the particle sizes of extracted amorphous and highly pure silica are of a nanometre scale. The purity also was checked EDX (Figure 3c, d) and SEM mapping (figure 4) options and the results supported the XRF, XRD and FTIR results.
Figure 3. SEM images and EDX results belonging to the raw pyrophyllite (a, c) and nano SiO$_2$ (b, d)

Figure 4. SEM image and mapping of nano SiO$_2$
4. Conclusions
Highly pure amorphous nano silica as a powder form can be extracted by an alkaline treatment method from the local silica rich pyrophyllite ore. The overall results revealed that obtaining amorphous SiO2 having 98 % purity with a nano size is possible and it might be a good candidate for catalytic applications, ceramics and adsorption purposes.

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