

## Two-step rapid synthesis of mesoporous silica for green tire

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(Received 21 January 2012 • accepted 17 April 2012)

**Abstract**—We report a two-step rapid route of synthesizing inexpensive mesoporous silica using the waste material (hexafluorosilicic acid,  $\text{H}_2\text{SiF}_6$ ) of phosphate fertilizer industry and sodium silicate ( $\text{Na}_2\text{O}\cdot\text{SiO}_2$ ). The reaction was performed in a newly innovated manufacturing apparatus. This apparatus produces mesoporous silica with uniform properties through controlled mixing of source materials at predetermined equivalent ratio. The precursors are rapidly mixed within the nozzles to enable uniform control of physical properties of the final product. The obtained mesoporous silica was characterized using  $\text{N}_2$  physisorption studies, scanning electron microscope (SEM), and EDS. The final product was found to have superior properties that are suitable for green tire (environmentally friendly tire) as inorganic filler. The process reported in this study may significantly reduce the release of hazardous materials into the environment and it might confer economic benefits to the responsible industries. A project on innovative industrial application of our products for the tire industry is in progress.

Key words: Mesoporous Silica, Hexafluorosilicic Acid, Sodium Silicate, Green Tire

### INTRODUCTION

The fertilizer industries are the major producers of a large amount of hexafluorosilicic acid ( $\text{H}_2\text{SiF}_6$ ) as a by-product from phosphate fertilizer [1]. Hexafluorosilicic acid is a major environmental pollutant that also causes economical challenge: end-of-pipe waste treatment. Studies have been reported on the merits of hexafluorosilicic acid when reacted with sodium silicate or several other reagents [2-4] to produce materials such as silica and sodium fluoride, both of which are useful for various applications [5,6]. The major drawbacks of the previous studies, including our former work [7], are the nature of the manufacturing apparatus and the precursors that are normally used and the limited scope of the final product for the large scale production [6-9].

Introduced in the 1990s, silica is one of the key ingredients in energy-saving tires (green tires). According to Rhodia, until now, the best silicas have made it possible to reduce rolling resistance by approximately 25%, bringing about a reduction in fuel consumption and vehicle  $\text{CO}_2$  emissions by an estimated 5%. Moreover, the company claims that its new Zeosil® Premium range enables rolling resistance to be further reduced by almost 10%, making silica ‘the most environmentally friendly filler option’ for tire tread [10]. Studies conducted demonstrate that the impact of the tire on health and the environment is very largely due to the fuel consumption caused by rolling resistance. It was reported that, after 40,000 km a tire containing silica in its tread gives a gain of five eco-points, or 11%, in comparison with one that contains only carbon black. This gain is equivalent to the total environmental impact of the tire produc-

tion and the raw materials from which it is made [10].

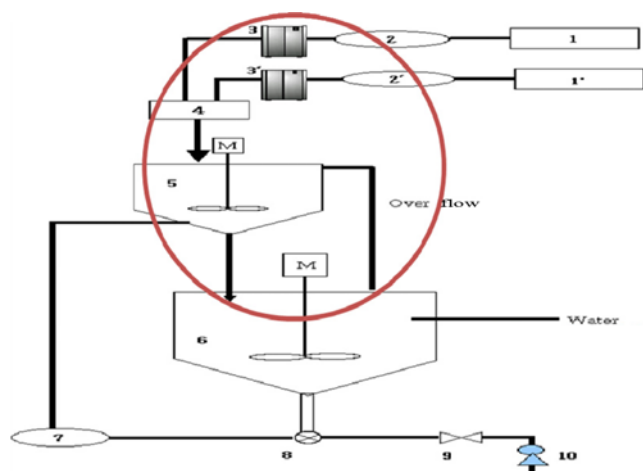
In our present study we are reporting a versatile method of recovering mesoporous silica (MPS) from hexafluorosilicic acid. We anticipate that our new mesoporous silica will compete with other commercial products such as the Rhodia’s Zeosil® Premium due to its superior properties and for being inexpensive. The reaction was performed in a newly innovated manufacturing apparatus designed by the researchers of E&B Nanotech Co. Ltd., Republic of Korea in collaboration with the Hanyang University, South Korea. The hexafluorosilicic acid was reacted with sodium silicate while the pH of the slurry in the precipitator was controlled within a desired range. The silica recovery process was done at various aging time while the concentration ratio of the initial reactants ( $\text{H}_2\text{SiF}_6$  and  $\text{Na}_2\text{O}\cdot\text{SiO}_2$ ) and pH was fixed at predetermined values. A versatile method of recovering pure mesoporous silica was inverted by optimizing the concentration ratio of the initial compounds as we have reported in our previous work [7,8]. The physical (surface and pore structure) and textural properties of the obtained mesoporous silica are reported. The final product was also tested for real industrial application as reinforcing filler for the green tire.

### EXPERIMENTAL PROCEDURES

#### 1. Experimental Steps of Recovery of Mesoporous Silica

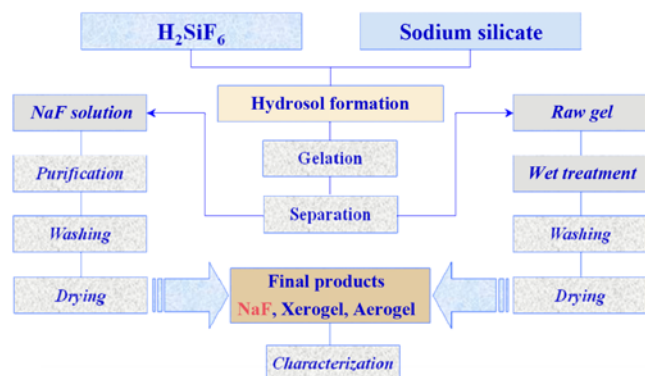
Sodium silicate (purchased from DUKSON Chem. Co. Ltd.) and hexafluorosilicic acid (by-product of Namhae Chemicals Fertilizer Plant of Yoechun Industrial Complex located in Yosu City, South Korea) were used to produce mesoporous silica and sodium fluoride. The concentration of hexafluorosilicic acid solution collected from the fertilizer plant wastes was adjusted to 25 wt%. For the present experiment, 50 ml of 25 wt% hexafluorosilicic acid and 18 wt%

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**Fig. 1.** A diagram showing a new innovative apparatus developed by the Hanyang University and E&B Nanotech Co. Ltd., Republic of Korea, for the production of mesoporous silica from hexafluorosilicic acid.

- |                    |                             |
|--------------------|-----------------------------|
| 1. Precursor       | 5. High speed reaction tank |
| 2. Precision pump  | 6. Low speed reaction tank  |
| 3. Air chamber     | 7, 8, 9, 10. Valves         |
| 4. Reaction nozzle |                             |



**Fig. 2.** A flow chart of the experimental procedures for the production of highly pure mesoporous silica from hexafluorosilicic acid as a waste material of phosphate fertilizer industry.

of sodium silicate were used to prepare mesoporous silica. Double distilled water was used to prepare the desired concentrations of hexafluorosilicic acid and sodium silicate. The reaction was carried out in a newly innovated reaction apparatus (Fig. 1) and the simplified experimental steps are summarized in Fig. 2. The apparatus reported in this work (Fig. 1) produces mesoporous silica with uniform properties by rapidly mixing the source materials at a predetermined equivalent ratio. It is comprised of high-speed and low-speed reaction tanks with the capacity of 2 liters and 4 liters, respectively. The precursors were rapidly mixed within the nozzles before being released into the high-speed reaction tank (then to the low-speed reaction tank) at the flow rate of 60 ml/min.

Furthermore, to investigate the influence of the aging time on textural properties of the final product (mesoporous silica), the silica recovery processes were done at various aging times (1 to 5 hours) at a predetermined pH of 7. In each of these processes, 900 ml of

water was added in order to obtain slurry; and the reaction temperature was raised from the room temperature to 100 °C. After 3 hours, the solution was cooled to room temperature. The resultant slurry was then filtered to separate NaF which was treated according to the previously reported procedures [7]. The filtrate was aged for a desired period (1 to 5 hours) in 400 ml of water at 80 °C. Eventually, the mesoporous silica was filtered, washed with distilled water and dried at 150 °C for 2 hours in an oven and the final product was characterized. The final products were labeled depending on the aging time: MPS-1 (aged for 1 hour), MPS-2 (aged for 2 hours), MPS-3 (aged for 3 hours), MPS-4 (aged for 4 hours), and MPS-5 (aged for 5 hours).

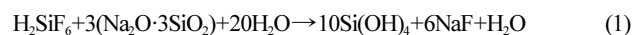
## 2. Characterization Methods

The specific surface area and pore size distributions (PSDs) of the final product were analyzed by using Brunauer Emmet and Teller (BET) and BJH nitrogen gas adsorption and desorption method (ASAP 2020, Micromeritics, USA). BET analysis from the amount of N<sub>2</sub> gas adsorbed at various partial pressures (five points  $0.05 < p/p_0 < 0.3$ , nitrogen molecular cross sectional area = 0.162 nm<sup>2</sup>) was used to determine the surface area, and a single condensation point ( $p/p_0 = 0.99$ ) was used to determine the pore volume. Before N<sub>2</sub> adsorption, the sample was degassed at 200 °C. Pore size distributions were calculated from the desorption isotherms. Microstructure studies of the final product were carried out by scanning electron microscope (FE-SEM, JSM 6700 F microscope, JEOL). The atomic percentage of residual impurities in the obtained silica was investigated by energy dispersive X-ray spectroscopy (EDS).

## RESULTS AND DISCUSSION

### 1. EDS Results

The mesoporous silica with superior property was successfully recovered by the aforementioned method, that is, by using the newly innovated apparatus. The mechanism of formation of mesoporous silica via the proposed procedure (reaction of H<sub>2</sub>SiF<sub>6</sub> and Na<sub>2</sub>O·SiO<sub>2</sub>) is briefly described using the chemical reactions presented in Eqs. (1) and (2). Generally, hexafluorosilicic acid reacts with sodium silicate to form unstable monomeric silicic acid. Then the latter undergoes condensation and polymerization to develop siloxane links. Silanol contained in monomers or weakly branched oligomers are most likely to be protonated. As a result, silica clusters aggregate to form a three-dimensional porous silica network. The following chemical reactions are expected to take place when H<sub>2</sub>SiF<sub>6</sub> reacts with Na<sub>2</sub>O·SiO<sub>2</sub>:



From our previous study [7] we realized that at 25 wt% hexafluorosilicic acid and 18 wt% of sodium silicate there was no fluoride contamination in the recovered silica samples. But when the wt% of the initial compounds was varied the final product had admixtures. Thus, the result presented in this work is for the final product obtained at 25 wt% hexafluorosilicic acid and 18 wt% of sodium silicate at various aging time (1 to 5 hours). The EDS spectra in Fig. 3(a) do not show the presence of NaF in mesoporous silica. It only shows and therefore confirms the presence of the expected ele-

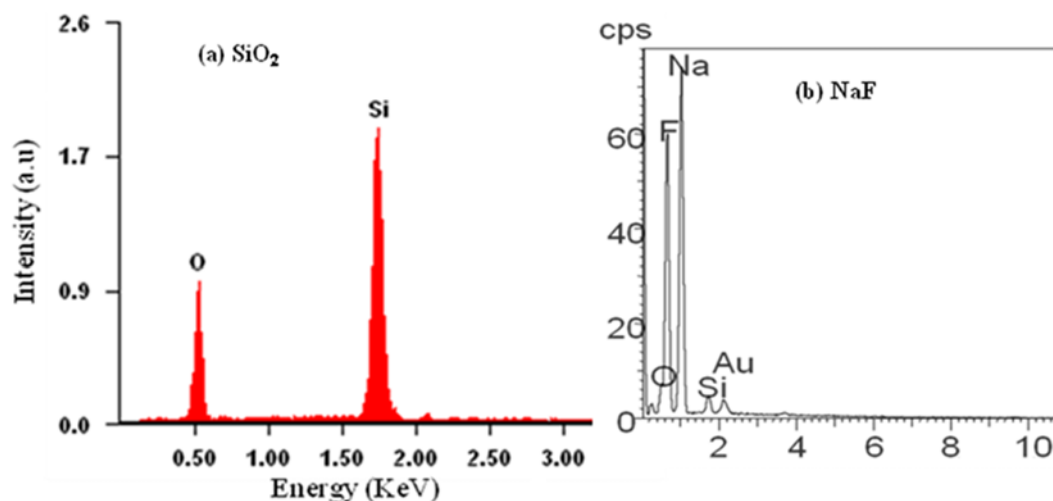


Fig. 3. EDS spectra of (a) mesoporous silica and (b) sodium fluoride.

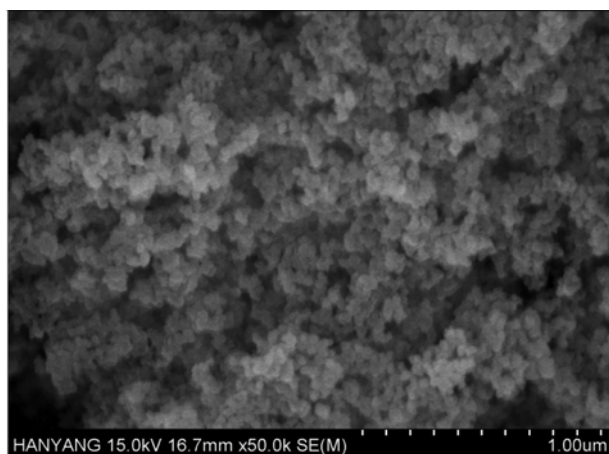


Fig. 4. FE-SEM image of mesoporous silica.

ments in pure silica, namely, Si, and O; while in Fig. 3(b) Na and F were the major existing elements. Thus, the purity of the final product (mesoporous silica) obtained in the present study was empirically substantiated.

## 2. SEM Result

The SEM image for mesoporous silica (Fig. 4) illustrates particles (less than 50 nm) of irregular shape which tend to form larger

accumulations (the so-called aggregates and agglomerates). No larger primary particles attributed to the presence of other compounds (contaminants, such as NaF) can be seen. The previous study [7] reported that the SEM image of NaF has conspicuous primary particles with an average diameter of 400 nm.

## 3. Nitrogen Physisorption Studies as Summarized in Table 1

The porosity of the obtained mesoporous silica products was examined by using N<sub>2</sub> adsorption/desorption physisorption technique. The results obtained are summarized in Table 1. The average pore diameter resides in the range of 2.24–2.95 nm, which confirms that the obtained silica is mesoporous. The BET surface area and pore volume range from 123–237 m<sup>2</sup>/g and 0.51–1.4 cm<sup>3</sup>/g, respectively. A desired final product for tire fillers was obtained at the aging time of 5 hours (MPS-5: BET 123 and pore size 2.24 nm). Silica with BET surface area below 175 m<sup>2</sup>/g was reported to be highly dispersible in tire [11]. Thus, the MPS-5 product demonstrates highly dispersible properties similar to that of the commercial product as summarized in Table 1.

## 4. Test of Mesoporous Silica for Application as Filler in Tire

Five samples of mesoporous silica were sent to NEXEN Tire Co. Ltd., South Korea for comparative analysis. The performance of our samples was compared with the commercialized product that is currently available in the market of silica for tire. Generally, most of the properties of the commercial product were found to be similar

Table 1. Comparison of the properties of mesoporous silica (MPS) with the commercial product (from Rhodia)

| Item                                   | Commercial (Zeosil®) | MPS-1 | MPS-2 | MPS-3 | MPS-4 | MPS-5 |
|--|----------------------|-------|-------|-------|-------|-------|
| BET SA (m <sup>2</sup> /g)             | 116                  | 237   | 224   | 206   | 217   | 123   |
| Pore vol. (cm <sup>3</sup> /g)         | 0.47                 | 1.33  | 1.40  | 1.19  | 1.11  | 0.51  |
| Pore size (Å)                          | 203                  | 277   | 295   | 274   | 257   | 224   |
| Oil adsorption (cm <sup>3</sup> /100g) | 118                  | 218   | 243   | 266   | 247   | 134   |
| HARD'S (index)                         | 64                   | 79    | 74    | 77    | 76    | 76    |
| Abrasion resistance (%)                | 100                  | 109   | 111   | 114   | 121   | 140   |
| Tensile strength (kg/cm <sup>2</sup> ) | 263                  | 200   | 228   | 242   | 228   | 187   |
| Relative dispersity (index*)           | A                    | C     | A     | A     | A     | A     |

\*A - Very good, B - Good, C - Poor. These tests were conducted by the NEXEN Tire Co., Ltd., South Korea

to the products developed in this study, while the latter has an added economic advantage for being inexpensive, since it is recovered from the waste materials (hexafluorosilicic acid). The dispersion index of mesoporous silica is very good (class A, as shown in Table 1), except MPS-1 which had unexpectedly poor dispersion. Most of the products developed in this study have very good dispersion, high tensile strength, optimum HARD'S index, high abrasion resistance, and high oil absorption comparable to their BET surface area. Detailed explanation of the test method employed, species of rubber, loading of silica, and other test reported in Table 1 is beyond the scope of this article. The main thrust of this work is the "synthesis" rather than the application. Nevertheless, since the application results are very important as a starting point for further improvement of rubber fillers, the samples were sent to a tire company to compare the performance of our product with the commercial product (Rhodia's Zeosil® Premium).

### CONCLUSIONS

The recovery of mesoporous silica from hexafluorosilicic acid (waste material of phosphate fertilizer industry) using sodium silicate is reported in this study. The reaction was performed in a newly innovated manufacturing apparatus. Mesoporous silica that was obtained as a final product was found to have superior properties that are suitable for green tire as inorganic filler. It is highly pure as confirmed by various characterization techniques, particularly through EDS. Also, it has a desired BET surface area and improves various aspects of the green tire. The process of recovering mesoporous silica from the waste products may significantly reduce the release of hazardous materials into the environment and it might confer economic benefits to the responsible industries.

### ACKNOWLEDGEMENTS

This work was supported by the research fund of Hanyang University (HY-2010-N).

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