



Recovery of high surface area mesoporous silica from waste hexafluorosilicic acid (H_2SiF_6) of fertilizer industry

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ABSTRACT

In this article we report recovery of mesoporous silica from the waste material (hexafluorosilicic acid) of phosphate fertilizer industry. The process involves the reaction of hexafluorosilicic acid (50 ml, 24 wt% H_2SiF_6) and 100 ml, 0.297 M Na_2CO_3 to generate the alkaline aqueous slurry. Silica was separated from the slurry by filtration and the sodium fluoride was extracted from the aqueous solution by evaporation method. The obtained mesoporous silica was characterized by N_2 absorption/desorption (BET), thermogravimetric analysis (TGA), X-ray diffraction (XRD), scanning electron microscope (SEM), and EDS. The results confirm that the separation of silica and NaF was successful and the final products have high purity. The silica product was found to have an average pore diameter of 4.14 nm and a high surface area (up to 800 m^2/g). 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.

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1. Introduction

A huge amount of hexafluorosilicic acid is generated annually as a by-product from phosphate fertilizer industries [1]. The collection of H_2SiF_6 is normally carried out via the absorption process of gaseous silicon tetrafluoride (SiF_4) in the water scrubber. Generally, being one of the wastes released from industrial production of phosphate fertilizer, hexafluorosilicic acid is a major environmental (hazardous) and economical (end-of-pipe waste treatment) challenge. This by-product of phosphate fertilizer industry could be converted to non-hazardous materials such as silica and sodium fluoride, both of which are useful for various applications [2–5]. Sodium fluoride can be recovered from the aqueous solution (by evaporation or extraction) and used *per se* or reacted with sulfuric acid to produce hydrogen fluoride.

Although various modes of silica recovery and general utilization of hexafluorosilicic acid have been reported [3,6–13], a mesoporous silica with high surface area (recovered from Fertilizer Industries wastes) is not yet reported. Moreover, the recovery processes suggested were tedious and non-economical for large scale production. For instance, Dragicevic and Hraste [7] described a process whereby fluosilicic acid is neutralized with ammonia to generate ammonium fluoride and silica. Afterward, silica was separated by filtration and the NH_4F was concentrated to a molten state and subsequently treated with sulfuric acid to produce hydrogen

fluoride. The Ammonia remains in the sulfuric acid and is sent to a phosphate acidulation unit. The chief drawbacks of the process are the necessity of recycling the ammonia and the failure to remove P_2O_5 impurity from the final product.

In this study, we are reporting a versatile method of recovering high surface area mesoporous silica from hexafluorosilicic acid wastes. The latter was reacted with sodium carbonate while the pH of the slurry in the precipitator was controlled within a desired range. The silica recovery processes were done at various concentration ratios of the initial reactants (H_2SiF_6 and Na_2CO_3) and at a predetermined pH in order to investigate the influence of the reaction pH on the BET surface area of the final product (mesoporous silica). The process of removing sodium fluoride (and its utilization in production of hydrofluoric acid) from the silica slurry is described in detail. In fact, the removal of the sodium fluoride from the silica slurry is tedious due to its high solubility in silica solution. Thus, through several attempts, a versatile method of recovering high surface area pure silica was inverted by optimizing the concentration ratios of the initial compounds. The physical (surface and pore structure) and textural properties of the obtained mesoporous silica and sodium fluoride are reported.

2. Experimental procedures

2.1. Experimental steps of recovery of mesoporous silica

In this study, sodium carbonate (purchased from DUKSON Chem. Co. Ltd.) and hexafluorosilicic acid (by-product of Namhae Chemicals Fertilizer Plant of Yoechun Industrial Complex located

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Fig. 1. A photograph of the reflux glass vessel for the production of high purity mesoporous silica from hexafluorosilicic acid as a waste material of phosphate fertilizer industry.

in Yosu city, South Korea) were used to produce high surface area mesoporous silica and sodium fluoride. The concentration of hexafluorosilicic acid solution collected from the Fertilizer Plant wastes was determined and found to be 27.5 wt%. For the present experiment, 50 ml of 24 wt% hexafluorosilicic acid and 100 ml of 0.297 M sodium carbonate were used to prepare mesoporous silica. Double distilled water was used to prepare the desired concentrations of hexafluorosilicic acid and sodium carbonate. The reaction was carried out in reflux glass vessel (Fig. 1) and the simplified experimental steps are summarized in Fig. 2.

Furthermore, in order to investigate the influence of the reaction pH on the BET surface area of the final product (mesoporous silica), the silica recovery processes were done at various concentration ratios of the initial reactants (H_2SiF_6 and Na_2CO_3) at a predetermined pH. In each of these processes, 900 ml of water was added in order to obtain slurry; and the reaction temperature was raised to 100°C while the pH was controlled at a predetermined value (ranging from pH 1 to pH 10). After 3 h, the solution was cooled to room temperature. The resultant slurry was then filtered and aged for 8 h in 400 ml of water at 80°C . Eventually, the precipitated amorphous silica was filtered, washed with distilled water and dried at 150°C for 2 h in an oven. On the other hand, the filtrate (the remaining aqueous solution containing sodium fluoride) was evaporated and thoroughly washed with water to remove admixtures; and finally it was spray dried to obtain solid sodium fluoride.

As it was pointed out in the introduction part, the obtained sodium fluoride can be used per se or reacted with sulfuric acid to produce hydrogen fluoride. In the present study, a simple procedure of preparing the hydrogen fluoride is proposed. In this case, 40 g of the obtained solid sodium fluoride were heated to a desired temperature (160°C) in a reactor (Fig. 3) under a constant supply of nitrogen gas. The latter was passed from storage tank through a flowmeter into the reactor to remove oxygen (to avoid corrosion). The reactor was embedded in a heating mantle to maintain the desired reaction temperature. After flushing the reactor with nitrogen gas, the sulphuric acid (contained in a burette connected to the reactor) was quickly introduced. The product gas was passed through a condenser and collected by a Teflon-made beaker. After the reaction, the nitrogen gas was flushed again through the reactor; this assisted in carrying HF gas from the reactor.

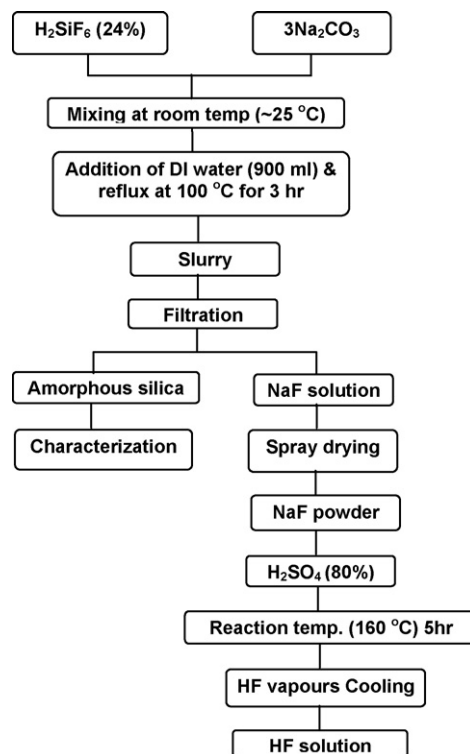


Fig. 2. A flow chart of the experimental procedures for the production of high purity mesoporous silica from hexafluorosilicic acid as a waste material of phosphate fertilizer industry.

2.2. Characterization methods

The products obtained were characterized using XRD, BET, TGA, SEM, and EDS. X-ray diffraction data were collected with a XRD-6000 Shimadzu Diffractometer employing $\text{CuK}\alpha$ radiation. The specific surface area and pore size distributions (PSDs) of the final product were analyzed using Brunauer Emmet and Teller (BET) and BJH nitrogen gas adsorption and desorption method (ASAP 2000, Micromeritics, USA). BET analysis from the amount of N_2 gas adsorbed at various partial pressures (five points $0.05 < p/p_0 < 0.3$, nitrogen molecular cross-sectional area = 0.162 nm^2) was used to determine the surface area, and a single condensation point

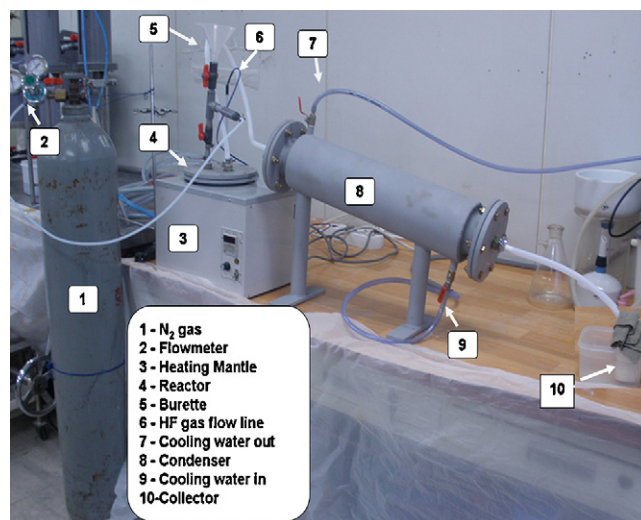


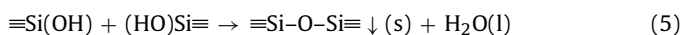
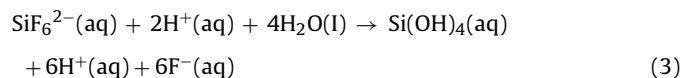
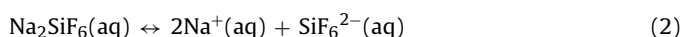
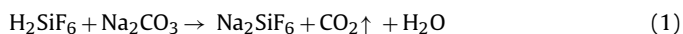
Fig. 3. A photograph of equipment used for preparation of hydrofluoric acid from sodium fluoride.

($p/p_0 = 0.99$) was used to determine the pore volume. Before N_2 adsorption, the sample was degassed at 200°C . Pore size distributions were calculated from the desorption isotherms [14,15]. In order to study the thermal stability of the mesoporous silica, the samples were examined by the thermo gravimetric and differential thermal analysis (TG–DTA). 6 mg of the hydrophobic mesoporous silica were heat-treated in air, from room temperature (25°C) up to 1000°C with controlled heating rate of $1.5^\circ\text{C min}^{-1}$ using a microprocessor-based Parr temperature controller (Model 4846) connected to a muffle furnace (A.H.JEON Industrial Co. Ltd., Korea). 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).

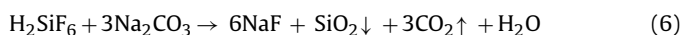
3. Results and discussion

3.1. XRD and EDS results

The main challenge encountered in this study was to recover sodium fluoride (due to its solubility in silica) from the developed slurry. Thus, when solution which contains sodium fluoride is evaporated, some silica may be admixed and this would be extremely difficult, if not impossible, to separate; as disclosed by Sikdar and Moore [4]. However, in the present study, mesoporous silica was successfully recovered by the gradual dropping of a diluted sodium carbonate solution into a diluted hexafluorosilicic acid solution. The mechanism of formation of mesoporous silica via the proposed procedure (reaction of H_2SiF_6 and Na_2CO_3) can be explained by considering the chemical reactions presented in Eqs. (1)–(6). Generally, hexafluorosilicic acid reacts with sodium carbonate to form unstable monomeric silicic acid. Then the latter undergo condensation and polymerization to develop siloxane links. Also it is known that the condensation rate can be enhanced using acidic catalyst [16]. The protonation of the silanol makes the silicon more electrophilic and consequently more susceptible to the nucleophilic attack. The most basic silanol species (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_2SiF_6 reacts with Na_2CO_3 :



The silicic acid monomers obtained in Eq. (3) polymerize to form small silica particles chains: Monomer \rightarrow Oligomer \rightarrow Polymer (Eq. (5)); and consequently a silica network (mesoporous silica) is developed. Therefore, the complete/overall reaction equation for the synthesis of silica and sodium fluoride from hexafluorosilicic acid and sodium carbonate can be summarized as follows:



In the present work we realized that, at a concentration ratio of 1:3 ($\text{H}_2\text{SiF}_6:\text{Na}_2\text{CO}_3$) there was no fluoride contamination in the recovered silica samples. But when the molar ratios of the initial compounds were varied (above or below 1:3) the final product had

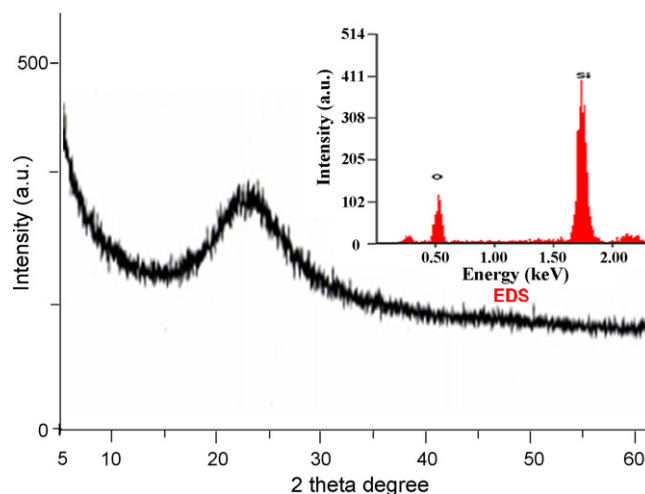


Fig. 4. X-ray diffraction patterns and EDS spectra of mesoporous silica.

admixtures. Thus, the result presented in this work is for the final product obtained at ratio 1:3. The broad X-ray diffraction pattern in Fig. 4 indicates the formation of amorphous silica. No trace of NaF was observed. Fig. 5 shows the X-ray diffraction pattern for recovered sodium fluoride from hexafluorosilicic acid. The three prominent sharp peaks located at 20° , 39° , and 56° matches with the expected NaF standard XRD peaks [17]. No other crystalline phases detectable by XRD were found indicating the purity of NaF, as also substantiated through EDS study (Figs. 4 and 5). The EDS result in Fig. 4 (inset) confirms the presence of the expected elements in pure silica, namely, Si, O; while in Fig. 5 Na and F were the only existing elements. Thus, the purity of the final products (silica and sodium fluoride) obtained in the present study was empirically confirmed.

3.2. SEM result

The SEM image for mesoporous silica (Fig. 6(a)) illustrates precipitated 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. On the other hand, the SEM image for sodium fluoride (Fig. 6(b)) illustrates the conspicuous primary particles with an average diameter

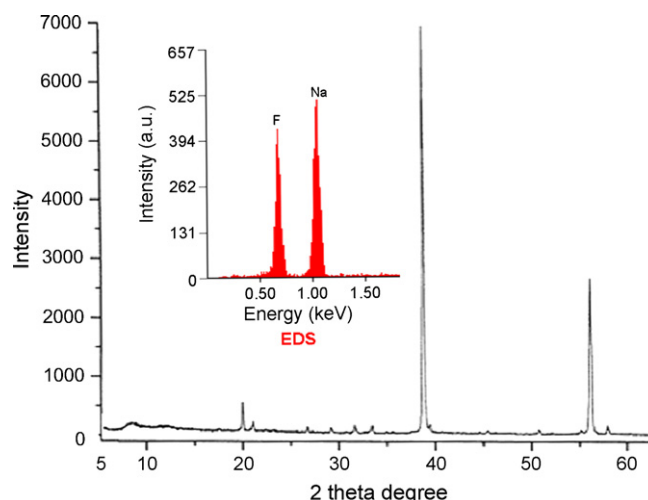


Fig. 5. X-ray diffraction patterns and EDS spectra of sodium fluoride.

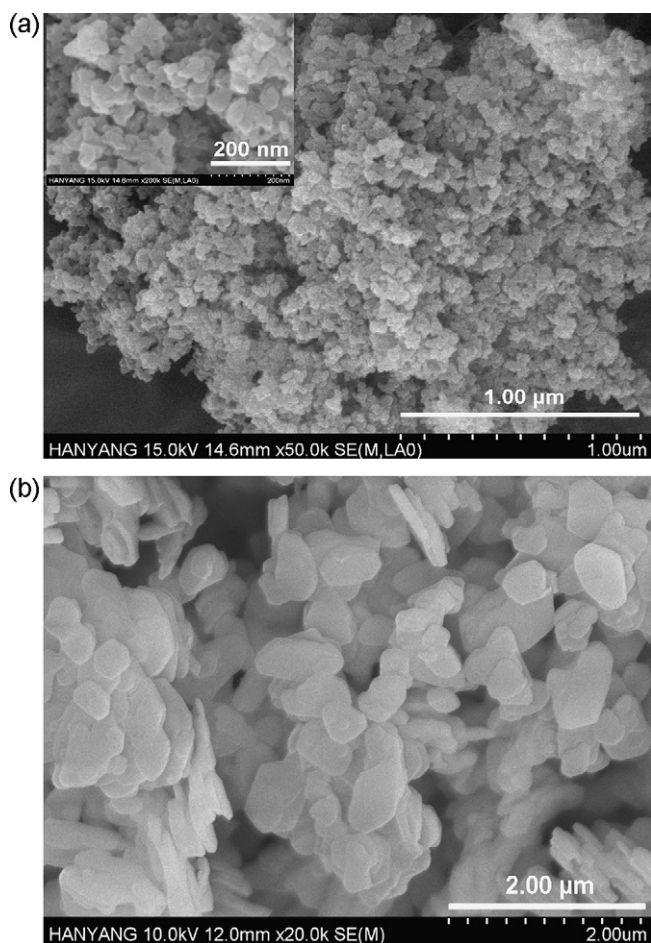


Fig. 6. FE-SEM images of the (a) mesoporous silica and (b) sodium fluoride.

of 400 nm. No small particles that could be attributed to the presence of silica are evident, indicating the purity of NaF.

3.3. TGA/DTA curves

Fig. 7 depicts the TG–DTA curves of the obtained mesoporous silica in the temperature range of 25–800 °C. Significant weight losses were observed at 150 °C and at the range of 400–800 °C. The former weight loss is attributed to the loss of water from the

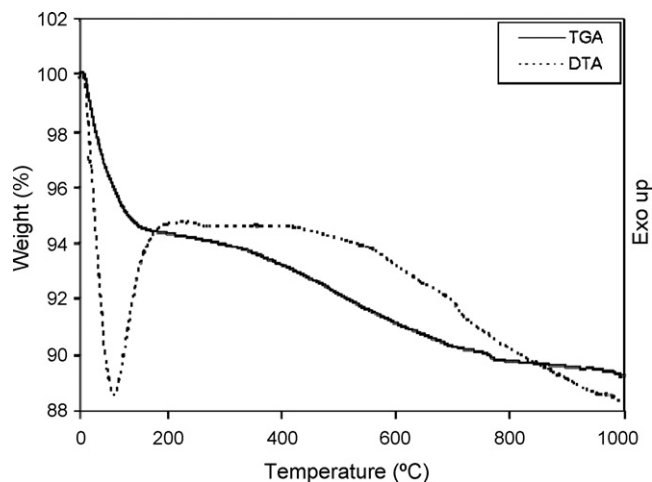


Fig. 7. Thermogravimetric and differential thermal analysis (TG–DTA) curve for the mesoporous silica.

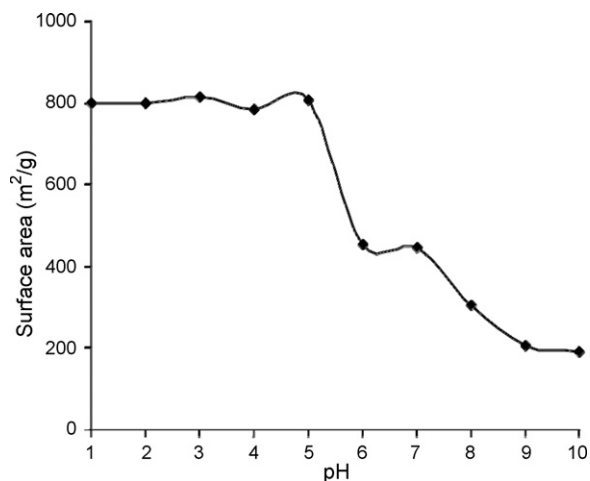


Fig. 8. Variation of mesoporous silica surface area with change in reaction pH.

sample (as it is also demonstrated by the endothermic peak in the DTA curve) while the latter is attributed to the dehydration of the silanol groups. The sample weight remained constant at the range of 800–1000 °C. Thus, it is clearly evident from Fig. 7 that a significant silica weight loss occurs at elevated heat-treatment (up to 800 °C). This implies that the product obtained via the present method has a high thermal stability.

3.4. Effect of the reaction pH on surface area of silica

Fig. 8 shows the effects of the pH on the specific surface area of the recovered mesoporous silica. It is generally recognized that silica surface area is inversely proportional to the size of the primary particles formed on gelation. Thus, at pH 1 the primary particles of polymeric silicic acid were relatively small and correspondingly large at pH 10. Now, in the present study, as it can clearly be seen in Fig. 8, the surface area of the obtained mesoporous silica decreases with the increase in pH. For instance, at pH 1 the surface area of silica was found to be 800 m²/g while the minimum value is observed at pH 10.

3.5. Nitrogen physisorption studies

Physisorption of the obtained mesoporous silica powders were explored by obtaining the N₂ adsorption/desorption isotherms and pore size distributions. Fig. 9 depicts N₂ adsorption and desorp-

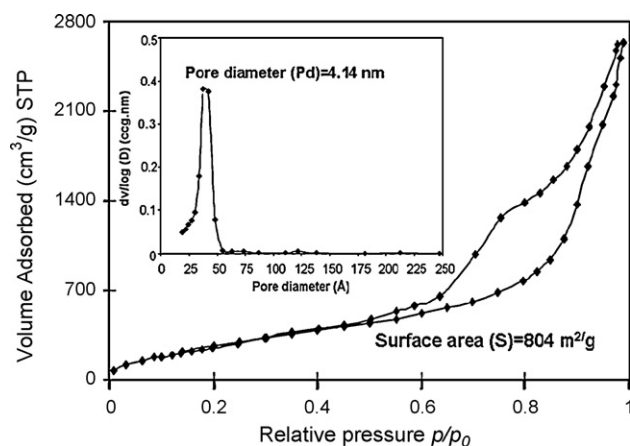


Fig. 9. N₂ adsorption/desorption isotherms and pore size distribution (PSD) of the mesoporous silica.

tion isotherms. The physisorption isotherms exhibited hysteresis loop with type IV isotherms which are generally observed for the mesoporous materials due to capillary condensation in the mesopores [18–20]. Fig. 9 (inset) depicts the pore size distributions of the recovered silica. The peak pore diameter resides at the range of 2.5–5 nm; this confirms that the obtained silica is mesoporous.

4. Conclusions

The recovery of mesoporous silica and sodium fluoride from hexafluorosilicic acid (waste material of phosphate fertilizer industry) using sodium carbonate is reported in this study. The final products have high purity as confirmed by various characterization techniques, particularly through EDS. The separation of silica and NaF was successful. Mesoporosity of silica was substantiated via nitrogen physisorption studies in which the material was found to have an average pore diameter of 4.14 nm. The silica obtained has a high surface area (up to 800 m²/g). Nevertheless, the surface area decreases with the increase in reaction pH. Therefore, in this study, we have demonstrated that high surface area mesoporous silica and sodium fluoride can be obtained from hexafluorosilicic acid wastes of the fertilizer industry by using a simple and economical procedure. This process may significantly reduce the release of hazardous materials into the environment and it might confer economic benefits to the responsible industries.

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References

- [1] H.S. Yu, K.I. Rhee, C.K. Lee, D.H. Yang, Two-step ammoniation of by-product fluosilicic acid to produce high quality amorphous silica, *Korean J. Chem. Eng.* 17 (4) (2000) 401–408.
- [2] A. Krysztalkiewicz, Use of highly dispersed, precipitated carbonate–silicate powders as fillers for elastomers, *Powder Technol.* 63 (1) (1990) 1–11.
- [3] A. Krysztalkiewicz, B. Rager, M. Maik, Silica recovery from waste obtained in hydrofluoric acid and aluminum fluoride production from fluosilicic acid, *J. Hazard. Mater.* 48 (1996) 31–49.
- [4] S.K. Sikdar, J.H. Moore, Process for producing fluorine compounds and amorphous silica, US Pat. 4,308,244 (1981).
- [5] S.K. Sikdar, J.H. Moore, Recovery of hydrofluoric acid from fluosilicic acid with high pH hydrolysis, US Pat. 4,213,951 (1980).
- [6] R. Spijker, Process for the preparation of pure silicon dioxide, European Patent 94,139 (1983).
- [7] T. Dragicevic, M. Hraste, Surface area of silica produced by neutralization of fluosilicic acid, *Chem. Biochem. Eng.* 8 (3) (1994) 141–143.
- [8] L. Zorya, V. Krot, Method of high-purity silica production from hexafluorosilicic acid, *React. Kinet. Catal. Lett.* 50 (1–2) (1993) 349–354.
- [9] V.V. Krot, L.N. Zoryal, O.D. Orlova, G.P. Panasyuk, V.B. Lazarev, E.E. Vinogradov, G.N. Tarasova, I.M. Karataeva, L.N. Nikolaeva, Preparation of amorphous silicon dioxide from hexafluorosilicic acid, *Zhurnal Neorganicheskoy Khimii* 37 (6) (1992) 608–610.
- [10] S.Y. Jeong, J.K. Suh, J.M. Lee, O.Y. Kwon, Preparation of silica-based mesoporous materials from fluorosilicon compounds: gelation of H₂SiF₆ in ammonia surfactant solution, *Colloid Interface Sci.* 192 (1997) 156–161.
- [11] C. Barber, C. James, Recovery of fluorine from waste gases, US Pat. 4,613,494 (1986).
- [12] O.Y. Kwon, S.W. Kim, S.W. Choi, Synthesis of mesoporous molecular sieves: hydrolysis of H₂SiF₆ by a non-ionic polyethyleneoxide surfactant template microporous, *Mesopor. Mater.* 27 (2–3) (1999) 255–259.
- [13] S.K. Sikdar, et al., Preparation of calcium fluoride from fluosilicic acid solutions, US Pat. 4,264,563 (1980).
- [14] C.J. Brinker, S.W. Sherere, *Sol–Gel Science: The physics and Chemistry of Sol–Gel Processing*, Academic Press, San Diego, 1990, p. 662.
- [15] D.S. Kim, C.K. Lee, Surface modification of precipitated calcium carbonate using aqueous fluosilicic acid, *Appl. Surf. Sci.* 202 (1–2) (2002) 15–23.
- [16] D.J. O' Connor, B.A. Sexton, R.C. St Smart (Eds.), *Surface Analysis Method in Materials Science*, Springer, 2003, p. 23.
- [17] T. Cardinal, O.M. Efimov, H.G. Francois-Saint-Cyr, L.B. Glebov, L.N. Glebova, V.I. Smirnov, Comparative study of photo-induced variations of X-ray diffraction and refractive index in photo-thermo-refractive glass, *J. Non-Cryst. Solids* 325 (1–3) (2003) 275–281.
- [18] J.L. Mohanan, S.L. Brock, Influence of synthetic and processing parameters on the surface area, speciation, and particle formation in copper oxide/silica aerogel composites, *Langmuir* 15 (13) (2003) 2567–2576.
- [19] W.C. Li, A.H. Lu, S.C. Guo, Control of mesoporous structure of aerogels derived from cresol–formaldehyde, *J. Colloid Interface Sci.* 254 (1) (2002) 153–157.
- [20] A.C. Pierre, E. Elaloui, G.M. Pajonk, Comparison of the structure and porous texture of alumina gels synthesized by different methods, *Langmuir* 14 (1) (1998) 66–73.