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# Fabrication and properties of amorphous silica particles by fluorination of zircon using ammonium bifluoride

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#### **Graphical abstract**



#### Highlights

- The fluorination of zircon using NH<sub>4</sub>HF<sub>2</sub> as reagent at 230°C was analyzed.
- The fluorination of silica and the sublimation behavior of  $(NH_4)_2SF_6$  were investigated using TGA.
- The effect of hydrolysis temperature on the size of silica particles was comparably investigated.
- Amorphous silica particles produced at 45°C contained 99.96 wt% SiO<sub>2</sub> and the recovery ratio of SiO<sub>2</sub> reaches ~94.57%.

• Amorphous silica particles obtained at 45°C exhibited high purity, narrow size distribution, high specific surface, high DBP-absorption and low density.

#### Abstract

A method to prepare amorphous silica particles from zircon has been developed using the fluorination method through a three-step process: the fluorination of zircon using ammonium bifluoride at 230 °C, the sublimation of (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> at 300 °C and the hydrolysis of (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub>. During above progress, the composition and phases of materials produced during fluorination of zircon were analyzed; the chemical reaction of silica with ammonium bifluoride, the sublimation behavior of  $(NH_4)_2SiF_6$  and its composition were determined; the effect of hydrolysis temperature (30 °C, 45 °C and 60 °C) on the hydrolysis ratio of Si and the size of silica particles were investigated. The results indicated that (NH<sub>4</sub>)<sub>3</sub>ZrF<sub>7</sub> and (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> formed after the fluorination of zircon at 230 °C for 5 hr. (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> started to sublimate at 175 °C, but the sublimation dominated at 280 °C and ended at 300 °C. The hydrolysis results indicated that uni-modal silica particles in micrometer size range were produced at 45 °C, while bi-modal particles in a variety of sizes ranging from nanometer to micrometer were produced at 30 °C and 60 °C. The amorphous silica particles obtained at 45 °C exhibited high purity above 99.96 wt.%, narrow size distribution (average: 254±17 nm), high specific surface (136.8 m<sup>2</sup>/g), high dibutyl phthalate (DBP)-absorption (2.7 cm<sup>3</sup>/g), low density  $(0.532 \text{ g/cm}^2)$  and pH (5.7). Therefore, the amorphous silica obtained has potential application as

filler in plastic and rubber compounding. After the hydrolysis process, ammonium bifluoride can be recycled through the evaporation of NH4F solution. Thus, this work provides a novel strategy for processing zircon by ammonium bifluoride to produce amorphous silica particles and recycle of ammonium bifluoride.

Keywords: Zircon; Ammonium bifluoride; Fluorination; Sublimation; Amorphous silica article

#### **1. Introduction**

Zircon (ZrSiO<sub>4</sub>) is notoriously difficult to process because it is chemically inert and insoluble in most conventional acids under normal conditions. Hafnium is always present in zircon in concentrations of 1-3 wt. % [1]. Current processing involves digestion of zircon in large quantities of sodium hydroxide at temperatures above 600 °C [2,3], or by conversion to zirconium tetrachloride via a carbo-chlorination process above 800 °C [4-6]. Both of these methods require vast amounts of energy and/or generate large liquid waste streams. effective A more cost and environmentally-friendly process would therefore be a huge advantage. In order to develop a more efficient, cost-effective, and environmentally-friendly process for the use of zircon reserves, different fluorination routes are under investigation such as using fluorine gas (F<sub>2</sub>) [7-9], hydrogen fluoride gas (HF) [8-10], aqueous hydrofluoric acid (HF) [11], ammonium fluoride (NH<sub>4</sub>F) [12-16], ammonium bifluoride (NH<sub>4</sub>HF<sub>2</sub>) [17-25] or ammonium acid fluoride (NH<sub>4</sub>F•xHF, x>1) [26-30]. Of these, fluorine and hydrogen fluoride are corrosive and poisonous gases and thus are difficult to handle. Moreover, there remains a possibility of unreacted oxide remaining in the product [31].

Aqueous hydrofluoric acid is again highly corrosive. NH<sub>4</sub>F is highly hygroscopic and there is a possibility for oxygen contamination due to the pyrohydrolysis of fluoride [19, 32, 33]. To prepare a pure fluoride product without oxide contamination, it is necessary to use a large quantity of NH<sub>4</sub>F. Therefore, the use of NH<sub>4</sub>HF<sub>2</sub> as fluorination agent is considered as an appropriate method for obtaining oxygen-free fluoride. The fusion temperature of ammonium bifluoride is 126.8 °C, and its decomposition temperature is 238.8 °C. At room temperature NH<sub>4</sub>HF<sub>2</sub> does not represent any significant environmental danger, since it is a solid with a very low partial pressure, whereas, when heated, it becomes a powerful fluorinating reagent.

Zircon can easily reacted with ammonium bifluoride (NH<sub>4</sub>HF<sub>2</sub>) in an autoclave at 300 °C under 45 atm [34]. With the help of microwave, zircon can also completely react with ammonium acid fluoride (NH<sub>4</sub>F•xHF, x>1) at 240 °C[26, 27]. Zircon can also be made chemically more tractable by dissociation in a plasma flame at >1700 °C[35-37]. This product is called plasma dissociated zircon (PDZ, ZrO<sub>2</sub>•SiO<sub>2</sub>). Under this case, the reaction temperature of PDZ with ammonium acid fluoride (NH<sub>4</sub>F•xHF, x>1) was further decreased [28, 29]. Above results suggested that zircon should be treated at high pressure/high temperature or under microwave in order to enhance the chemical-reaction-activity. However, there is no report about the fluorination of raw zircon without treatment with NH<sub>4</sub>HF<sub>2</sub> below its decomposition temperature.

It is assumed that the reaction between zircon and ammonium bifluoride above 200 °C proceeds according to the fellow reaction [34]:

$$2ZrSiO_4 + 13NH_4HF_2 = 2(NH_4)_3ZrF_7 + 2(NH_4)_2SiF_6 + 3NH_3\uparrow + 8H_2O\uparrow$$
(1)

According to the equation (1), the calculated mass ration of NH<sub>4</sub>HF<sub>2</sub> to ZrSiO<sub>4</sub> is 2.0213:1. During fluorination, NH<sub>3</sub> and H<sub>2</sub>O formed as gas, but (NH<sub>4</sub>)<sub>3</sub>ZrF<sub>7</sub> and (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> formed in solid. NH<sub>3</sub> and H<sub>2</sub>O gas can be absorbed by water to form ammonia solution, which can be used in silica production. (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> is stable until 100 °C, at higher temperature, it loses weight (0.2% per hour) and, then sublimate above 180 °C [38] and full sublimation can be observed at 280-330 °C [20-22, 38-43]. It causes serious environmental pollution as well as being an expensive form of waste. To prepare amorphous silica particles using (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> can not only solve the problem of environmental pollution, but also create social wealth [20, 21, 41-43] because amorphous silica particles have many important applications [41-45] such as catalysts support, pigments, chromatographic adsorbent, chemo-mechanical polishing, hybridcomposite materials, humidity sensors and thermal insulators due to their many outstanding properties, including high melting point, rigidity thermal stability, low density, high surface area and good dispersibility.

A great many methods have been reported for the preparation of amorphous silica particles including sol–gel processing [46, 47], chemical precipitation [48] and other technique requiring specific equipment with large investment such as plasma synthesis [49], chemical vapor deposition (CVD) [50], combustion synthesis [51, 52] and pressurized carbonation [53]. Fumed silica is manufactured by a high temperature vapor process in which silicon tetrachloride is hydrolyzed in a flame of hydrogen-oxygen at 2000 °C. Thus silica particles with low density, large surface area and smooth nonporous surface produced and can be used as fillers in the production of thermal insulation materials [54]. Precipitated silica is manufactured by wet procedure by treating sodium silicate with inorganic acid in the course of precipitation [55, 56]. The size and size distribution might be easily affected by some factors due to aggregation because silica particles have more silanol groups (Si-OH)

groups on the surface. The sol-gel process is the common technique for the synthesis of silica particles with size of 0.2-2  $\mu$ m because of the ease in controlling the particle size and shape by systematically tailoring the synthesis conditions [16, 20, 21, 41-43] according to the following reaction:

$$(NH_4)_2SiF_6 + 4NH_3 \cdot H_2O = SiO_2\downarrow + 6NH_4 F + 2H_2O$$
(2)

Previous investigation [20, 21, 41-43] further indicated that the use of  $(NH_4)_2SiF_6$  solutions less than 10 wt.% is not useful for obtaining amorphous silica because it is very difficult to filter SiO<sub>2</sub> gel at such concentrations. Furthermore, the optimum hydrolysis temperature is 30-60 °C because higher temperatures above 80 °C increases the pollution and temperatures lower than 25 °C yield a product with poor quality. Keeping of the suspension for 0.5-2.5 hr promotes the stabilization of the final product and a considerable improvement of its filterability.

After the hydrolysis, NH<sub>4</sub>HF<sub>2</sub> was regenerated by evaporation of aqueous solution of NH<sub>4</sub>F according to the follow reaction [16, 20, 21, 41-43]:

$$2\mathbf{N}\mathbf{H}_{4}\mathbf{F} = \mathbf{N}\mathbf{H}_{4}\mathbf{H}\mathbf{F}_{2} + \mathbf{N}\mathbf{H}_{3}\uparrow\tag{3}$$

During this progress,  $NH_3$  can be recycled and used as ammonia to produce amorphous silica (reaction (2)).

Compared with others process, this process has a higher production and ammonium bifluoride can be recovered with no solid, liquid, or gaseous waste [20, 21, 41-43]. Therefore, it can solve the problem of environmental pollution of  $(NH_4)_2SiF_6$ .

The present works investigates the reaction of zircon with ammonium bifluoride at 230 °C, the reaction of silica with ammonium bifluoride and the sublimation behavior of (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub>. Moreover, the effect of hydrolysis temperature (30 °C, 45 °C and 60 °C) on the hydrolysis rate of Si and the size of silica particles was investigated, with the aim to investigate the optimal temperature for obtaining high purity silica. The properties of silica particles produced at optimal temperature was further analyzed.

#### 2. Experimental

#### **2.1 Materials**

The zircon used in this study was obtained from Australia Eucla Basin. Commercially available analytical reagents ammonium bifluoride (Sinopharm Group, > 99.5 wt.%) was used as fluorination reagent. Distilled water and aqueous ammonia (NH<sub>4</sub>OH, 24%) were used during the dissolution and hydrolysis of (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub>. The silica for thermal gravimetric analysis (TGA) was also analytical grade (Sinopharm Group, > 99.8 wt.%).

#### 2.2 Equipment

The fluorination and sublimation were conducted in a modified tubular furnace consisting of a reactor for the heating of zircon and ammonium bifluoride and a two-zone condenser for trapping and collecting the volatile products during the heating progress. The working zone of reactor and condenser were made from nickel (NP-2 grade). The tail gas was absorbed in a Teflon vessel filled with water. In order to collect all the volatile product and absorb all the tail gas, N<sub>2</sub> (purity>99%) gas was fed into the furnace during heating.

Thermalgravimetric analysis (TGA)-derivative thermogravimetry (DTG) for mixture of silica and NH<sub>4</sub>HF<sub>2</sub> were carried out from 25 °C to 600 °C on a Pyris 1 TGA.

The synthesis of amorphous silica was carried out in a three necked plastic flask. The regeneration of ammonium bifluoride occurred in a laboratory-size evaporator/crystallizer system.

#### **2.3 Experimental procedure**

The experimental procedure had three major steps: the fluorination of zircon with ammonium bifluoride, the sublimation and condensation of  $(NH_4)_2SiF_6$  and the hydrolysis of  $(NH_4)_2SiF_6$ .

The fluorination process conducted in the reactor. Firstly, certain zircon was carefully mixed with ammonium bifluoride at the mass ratio of NH<sub>4</sub>HF<sub>2</sub> to zircon of 2.5 in a agate mortar. Then the mixture was moved into a nickel crucible in the tubular furnace. Under a steady flow of N<sub>2</sub> (high purity: 99%), the mixtures were heated up to 230 °C at a heating rate of 10 °C/min, kept at 230 °C for 5 hr and then cooled down to room temperature at 10 °C/min. During the fluorination process, the temperature of condenser was kept at 100 °C-150 °C in order to condensate the volatile product. The mass in the crucible and sublimate collected in the condenser were weight after fluorination. In order to investigate the interaction of silica with ammonium bifluoride, and the sublimation behavior of (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub>, the thermalgravimetric analysis (TGA)-derivative thermogravimetry (DTG) for mixture of silica and NH<sub>4</sub>HF<sub>2</sub> were carried out from 25 °C to 600 °C on a Pyris 1 TGA. The mixture of NH<sub>4</sub>HF<sub>2</sub> with silica about 1000-1200 mg (mass ratio of NH<sub>4</sub>HF<sub>2</sub>: silica=3:1) was set in platinum crucible under N<sub>2</sub> flow rate of 150 cm<sup>3</sup>/min with a heating rate of 10 °C/min. During TGA-DTG, the mixture was kept at 175 °C for 30 min in order to convert all silica into (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> and also analyze its sublimation behavior at 175 °C.

After fluorination at 230 °C for 5hr, the mixture was further heated up to 300 °C and kept at 300 °C for different time, and then cooled down to room temperature at 10 °C/min under the flow of N<sub>2</sub>. During this progress,  $(NH_4)_2SiF_6$  sublimates from the mixture in the reactor and condensates at the two-zone condenser with the temperature controlled at 100 °C- 150 °C.

The hydrolysis and amorphous silica production experiments were performed in a 250 ml three necked plastic flask employed with a stirrer, pH meter and reflux condenser. Firstly, 10 wt. % (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> solution was prepared and added into the three-necked plastic flask, and then heated to the target reaction temperature in a thermostatical water bath. To investigate the effect of hydrolysis temperature on the properties of amorphous silica particles, the temperature was varied from 30 °C to 60 °C (30 °C, 45 °C and 60 °C). After using 24% ammonia solution to adjust the pH to 9, the mixture was stirred at 200 rpm for 1.5 hr and aged for 1 hr. Finally, the mixture was filtered and washed with distilled water and drying at 120 °C for 2 hr. The regeneration of ammonium bifluoride could be circularly utilized by evaporation and crystallization of the filtrate.

#### 2.4 Characterization

The chemical compositions of zircon raw materials and produced amorphous silica particles were analyzed by X-ray fluoroscopy (XRF, Axios mAX Holand PANalytical Co.Ltd). Before and after the fluorination/sublimation, the mass measurements were conducted using a balance with 0.01 mg sensitivity. The phase of samples was characterized using D/Max-2500 pc type X-ray diffraction (XRD) with Cu Kα radiation at 40 kV and 160 mA with a scan speed of 3°/min from 10° to 90° in 20. The morphology and chemical composition of zircon, (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> sublimate and amorphous silica particles produced were examined using Camscan MX2600FE type-scanning electron microscopy

with energy dispersive X-ray spectroscopy (SEM/EDS) (Oxford Instruments, INCA) under the accelerating voltage of 20 kV. The morphology of the amorphous silica particles was further characterized using TECNAI-20 type transmission electron microscope (TEM) operated at 200 kV.

For the determination of surface area, nitrogen adsorption/desorption isotherm measurements were exploited at 77 K with Micrometrics TriStar II 3020 equipment. All samples were degassed at 200 °C and 10<sup>-6</sup> Torr for 10 hr prior to analysis. Specific surface areas of the produced silica particles were calculated with the Brunauer–Emmett–Teller (BET) equation by using isotherm adsorption data for relative pressure p/p<sub>0</sub> from 0.05 to 0.3. To measure the tapping density, a container of known volume was filled with silica powders and gently tapped until no further powders could be added. The powders were then weighed to obtain the tapping density <sup>[57, 58]</sup>. This is a non-standard technique but gives reproducible results. The DBP-absorption and pH value of the produced amorphous silica particles was measured according to China National Standards HG/T3072-2008 and HG/T3067-2008, respectively. Measurements were performed five times for each sample, and then the average value was calculated.

#### 3. Results and discussion

#### **3.1 Properties of zircon**

SEM image and the corresponding EDS of original zircon powders is shown in Fig. S1 (in Supplementary Material). Clearly, the zircon particles exhibited cylinder morphology with diameter 30-35  $\mu$ m and length 60-70  $\mu$ m. Zircon always contains ZrSiO<sub>4</sub> and other oxides such as HfO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, etc. However, EDS results in Fig. S1c indicated that only Zr, Si and O were detected due to low content of other oxides and detection limit. The atom ration of Zr to Si is close to 1:1. XRD

results in Fig. 1a indicated that only  $ZrSiO_4$  observed. Above results suggests that the content of other oxides is very low. In order to know the content of other oxides in zircon, XRF analysis of the chemical composition of zircon is conducted and the result is listed in Table 1. It indicated that the  $ZrO_2$ ,  $HfO_2$ ,  $SiO_2$ ,  $Al_2O_3$ ,  $TiO_2$ ,  $P_2O_5$  and  $Y_2O_3$  contents are 66.647 wt.%, 1.421 wt.%, 32.267 wt.%, 0.269 wt.%, 0.353 wt.%, 0.258 wt.% and 0.307 wt.%, respectively.

#### 3.2 Fluorination of zircon with NH4HF2 at 230 °C

Fig. 1b shows the XRD pattern of zircon after fluorination at 230 °C for 5 hr. Clearly, the fluorides of zircon were composed of (NH<sub>4</sub>)<sub>3</sub>ZrF<sub>7</sub>, (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> and minor unreacted NH<sub>4</sub>HF<sub>2</sub> agent. No ZrSiO<sub>4</sub> is observed suggesting that the fluorination of ZrSiO<sub>4</sub> is complete or the content of un-reacted ZrSiO<sub>4</sub> is lower than the detection limit. Fig. 2 shows the SEM image and the corresponding EDS of zircon after fluorination at 230 °C for 5 hr. Clearly, coarser zircon particles disappeared, and finer particles formed, as seen in Fig. 2a. EDS results in Fig. 2c indicated that the finer particles were composed of Zr, Si and F without N due to lower atomic weight. At high magnification, coarser particles of  $\sim 20 \,\mu m$  with smooth surface occasionally observed in some areas, as seen in Fig. 2b. EDS results in Fig. 2d indicated that these particles contained high O content and minor Ni. The existence of O suggested that some zircon particles were not completely fluorinated. The existence of Ni is due to the corrosion of nickel crucible. The change of particles morphologies is caused by fluorination, it can be concluded that the finer particles were fluorides of (NH<sub>4</sub>)<sub>3</sub>ZrF<sub>7</sub> and (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub>. Based on the chemical reaction (1), if no (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> and NH<sub>4</sub>HF<sub>2</sub> sublimate, the mass loss after fluorination should be -15.20%; if all residue of NH<sub>4</sub>HF<sub>2</sub> (without reaction with zircon) sublimate but  $(NH_4)_2SiF_6$  does not sublimate, the mass loss should be -28.87%. However, the

real mass loss is -49.2% (larger than -28.87%), suggesting that the sublimation and condensation of some fluorides occurred during fluorination at 230 °C After fluorination at 230 °C for 5 hr, some white materials were collected in the condenser. The XRD pattern of white materials collected in the condenser is shown in Fig. S2. Clearly, it composes of major (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> and minor NH<sub>4</sub>HF<sub>2</sub>. The results suggested that both (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> and NH<sub>4</sub>HF<sub>2</sub> sublimate during fluorination at 230 °C, especially the former. SEM and the corresponding EDS of the white materials collected in the condenser are shown in Fig. S3. Clearly, faceted-grain particles with smaller spherical particles on the surface observed, as seen in Fig.S3a. EDS in Fig. S3b indicated that the faceted-grain particles composed of Si and F. However, lower Si and higher F contents were observed on the spherical particles. Based on XRD and SEM results, it can be concluded that the faceted-grain is (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> while smaller spherical particles without any faceted is NH<sub>4</sub>HF<sub>2</sub> due to lower melting point.

#### 3.3 TGA-DTG of the reaction of silica with NH4HF2

In order to investigate the interaction of silica with NH<sub>4</sub>HF<sub>2</sub>, and the sublimation behavior of (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub>, TGA-DTG for mixture of silica+NH<sub>4</sub>HF<sub>2</sub> were carried out from 25 °C to 600 °C with the mass ratio of NH<sub>4</sub>HF<sub>2</sub>: silica=3:1, as seen in Fig. 3. Clearly, there existed three mass loss peak at 126.8 °C, 175 °C and 280 °C, respectively. On TGA-DTG curves, from 25 °C-126.8 °C, the chemical reaction between silica and NH<sub>4</sub>HF<sub>2</sub> occurred with minor mass loss, as addressed below:

$$\operatorname{SiO}_2 + 3\operatorname{NH}_4\operatorname{HF}_2 = (\operatorname{NH}_4)_2\operatorname{SiF}_6 + 2\operatorname{H}_2\operatorname{O}^{+}\operatorname{NH}_3^{\uparrow}$$
(4)

At 126. 8 °C, the melting of  $NH_4HF_2$  occurred and the fluorination of silica has the highest rate with significant mass loss; at 150 °C the mass loss is of -15.2%, and corresponds to the departure of water

following reaction (4), in fair agreement with the calculated value of -14.98%; from 150-175 °C, the loss of -6.9% is due to the ammonia removal (reaction (4)), in agreement with the calculated value of -7.08% [20]. Based on above chemical equation (4), the fluorination of 1g silica consumed 2.8453g NH<sub>4</sub>HF<sub>2</sub>. Thus, in this study, 3.87% NH<sub>4</sub>HF<sub>2</sub> without reaction with zircon stayed as residue after fluorination of silica. During the keeping at 175 °C, a further 16.688% mass loss occurred, as seen in Fig. 3. Clearly, the value is larger than the sublimation of NH<sub>4</sub>HF<sub>2</sub> residue (3.87%). The results suggested that the loss of -16.688% during the keeping at 175 °C is mainly due to the sublimation of (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub>; from 175-280 °C, the loss of -58.343% is due to the sublimation of (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub>. After 300 °C, the residue without sublimation is of -1.79%, suggesting that almost all the (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> has been sublimated. Based on above results, several observations can be made: 1) the fluorination of silica starts at the time of mixing of silica with NH<sub>4</sub>HF<sub>2</sub> and dominates at 126.8 °C with the departure of water; 2) the removal of ammonia is between 150-175 °C, 3) (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> starts to sublimate at 175 °C, dominate at 280 °C and end at 300 °C

#### 3.4 Sublimation of (NH4)2SiF6 at 300 °C

In order to enrich  $(NH_4)_3ZrF_7$  for further treatment,  $(NH_4)_2SiF_6$  should be sublimated and removed completely. Above TGA-DTG results indicated that  $(NH_4)_2SiF_6$  sublimated between 175 °C-300 °C, especially dominated at 280 °C. Thus in this section, the mixture of zircon after fluorination at 230 °C for 5 hr was further heated up to 300 °Cand kept at 300 °C for different time under the flow of N<sub>2</sub>. During this progress,  $(NH_4)_2SiF_6$  sublimates and condenses in the two-zone condenser with the temperature controlled at 100 °C-150 °C. Fig. 4 shows XRD patterns of  $(NH_4)_2SiF_6$  collected in the condenser during keeping at 300 °C for different time. Clearly, two type

phases of  $(NH_4)_2SiF_6$  observed:  $\beta$ - $(NH_4)_2SiF_6$  (#44-1424) and  $\alpha$ - $(NH_4)_2SiF_6$  (#07-0013). Furthermore, the peak intensity of  $\beta$ - $(NH_4)_2SiF_6$  (#44-1424) decreased with the increment of time. After 7 hr,  $\beta$ - $(NH_4)_2SiF_6$  (#44-1424) disappeared and only  $\alpha$ - $(NH_4)_2SiF_6$  (#07-0013) observed, suggesting  $\beta$ - $(NH_4)_2SiF_6$  (#44-1424) transformed into  $\alpha$ - $(NH_4)_2SiF_6$  (#07-0013) during the heating progress [38].

Fig. 5 shows the SEM images and the corresponding EDS of  $(NH_4)_2SiF_6$  collected in the condenser during sublimation at 300 °C for different time. Clearly, faceted-grain particles with needle-plate like particle on the surface observed, as seen in Fig. 5a [43]. With the increment of time, the quantity of needle-plate like particles gradually decreased and disappeared after 7 hr, as seen in Fig. 5c and Fig. 5e. EDS in Fig. 5b, Fig. 5d and Fig. 5f indicated that the materials collected only composed of Si, F and N. Based on XRD and SEM results, it can be concluded that the faceted-grain particle is  $\alpha$ -(NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> (#07-0013) and the needle-plate like particle is  $\beta$ -(NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> (#44-1424). The chemical analysis indicated that (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> collected in the condenser still contained minor impurity of Al, Ti, Fe, Na, and K under N<sub>2</sub> gas. The (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> thus obtained was further purified by sublimation at temperatures to 300 °C again. The (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> obtained as a result of sublimation again is of high purity. This is confirmed from the chemical analysis. The content of the metallic impurities (Al, Ti, Fe, Na and K) does not exceed 10<sup>-3</sup>-10<sup>-5</sup> %. This is because during sublimation the impurity compounds of Al, Ti, Na, and K form simple fluorides,which remain in the nonvolatile residue at 300 °C [20, 21, 43].

#### 3.5 Hydrolysis of (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> solution

Fig. 6 is the macroscopic morphology of amorphous SiO<sub>2</sub> produced by hydrolysis of

 $(NH_4)_2SiF_6$  at different hydrolysis temperature. Clearly, similar white powders observed without significant difference. Fig. 7 shows the XRD patterns of silica particles produced at different hydrolysis temperature, which clearly indicated that no crystalline phases exist, as only a single broad peak between  $15^\circ$  and  $30^\circ$  (2 $\theta$ ) is observed. The peak width shows that particles of prepared silica are of nano-size dimension. The results suggest that the silica particles have an amorphous nature. Previous studies [20, 21, 41-43] have also confirmed the amorphous nature of silica particles derived from the hydrolysis of (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub>.

The effect of temperature on the hydrolysis of Si-bearing filtrate is shown in Fig. 8 as the hydrolysis pH is kept at 9.0. The results show that the hydrolysis ratio of Si increases from 94.25% to 98.65% as the hydrolysis temperature increases from 30 °C to 45 °C, then the hydrolysis ratio of Si decreases with the further increase of hydrolysis temperature due to the volatilization of  $NH_3$  and pollution [20, 21, 41-43].

Fig. 9 shows the SEM images of amorphous silica particles produced by hydrolysis of  $(NH_4)_2SiF_6$  at different temperature. Clearly, the particles produced at 45 °C are spherical in nature with a narrow size distribution, as seen in Fig. 9b, suggesting uni-modal silica particles occurred. However, at 30 °C and 60 °C the presence of silica particles at two different sizes can clearly be seen from Fig. 9a and Fig. 9c. The result suggests that bi-modal distribution of silica particles was produced [56]. To understand the morphology of silica particles clearly, high magnification images were conducted using TEM and the results are presented in Fig. 10. Clearly, the silica particles produced at 30 °C and 60 °C exhibited two different sizes with spherical morphology. The average particle sizes of two different distributions at 30 °C and 60 °C were:  $386\pm 26$  nm (Fig. 10a),  $20\pm 2.6$  nm (Fig. 10b) and  $374\pm 34$  nm (Fig. 10e),  $25\pm 2.4$  nm (Fig. 10f), respectively. For comparison, TEM

images of the amorphous silica particles produced at 45 °C are shown in Fig. 10c and Fig. 10d. Clearly, only one-modal distribution of silica particles with spherical morphology was observed. The average diameter of silica particles produced at 45 °C is 254±17 nm, which is consistent with SEM image in Fig. 9b. Previous results [56] indicated that the concentration has a direct effect on the particle size. The average particle size increased continuously with the increasing of the concentration. Besides the concentration, the temperature also play a critical role in the morphology and size of particles by affecting the rate of nucleation, the nucleation period, and the growth rate. The nucleation rate and the growth rate increases with the increasing of temperature while the nucleation period decreases. Thus, at different temperature, different morphology and size of particles occurred. In this paper, at low (  $30^{\circ}$ C) or high ( $60^{\circ}$ C) temperature, some nucleus formed at the latter stage could not grow into large particles due to different effects and bi-modal distribution of silica particles occurred, which need further investigation. Based above on results, the optimal temperature is 45 °C in order to obtain finer uniform silica particles. The chemical composition of amorphous silica particles produced at 45 °C is further analyzed using XRF and the result is listed in Table 2. Clearly, the SiO<sub>2</sub> content is ~99.96 wt.% with 0.024 wt.% TiO<sub>2</sub> and PPM scale of Fe, Ni, F, Al, Na and K. The total recovery ratio of SiO<sub>2</sub> reaches ~94.57%. The impurities contents meet the requirements of white carbon.

The BET surface was analyzed using N<sub>2</sub> adsorption isotherms, as seen in Fig. 11. The isotherm is essentially type-IV curve. The estimates of BET surface is high values of up to 136.8 m<sup>2</sup>/g, as listed in Table 3. The DBP, tapping density and pH of amorphous silica particles produced at 45°C are further analyzed and the results are also listed in Table 3. From Table 3, the amorphous silica particles obtained at 45 °C exhibited narrow size distribution (average:  $254\pm17$  nm), high specific

surface (136.8 m<sup>2</sup>/g), high DBP-absorption (2.7 cm<sup>3</sup>/g), low density (0.532 g/cm<sup>2</sup>) and appropriate pH (5.7). Thus, amorphous silica particles obtained under the optimal temperature has potential application as filler in plastics and rubber compounding. The high purity amorphous silica has large BET surface area, which might be useful as an adsorbent or catalyst support in fine chemical synthesis.

Amorphous silica remains amorphous up to 900 °C during thermal treatment and devitrification occurs after this temperature [59]. The XRD patterns of amorphous silica particles produced at 45 °C before and after calcination at 900 °C for 5 hr is shown in Fig. S4 shows. Clearly, the produced silica particles still keep its amorphous structure without devitrification even after calcination at 900 °C for 5 hr. Furthermore, after calcination treatment, ~4.5 wt. % mass loss was observed due to the removal of fluoride, ammonium, remnant ammonium oxofluosilicate,  $(NH_4)_2SiF_6$  and absorbed H<sub>2</sub>O [20, 41, 43]. SEM image and the corresponding EDS of silica particles after calcination at 900 °C for 5 hr are shown in Fig. S5. Clearly, the silica particles are spherical in nature with average diameter of  $261\pm12$  nm, as seen in Fig. S5a and Fig. S5b. The value is consistent with the results ( $254\pm17$  nm) before calcination. EDS results in Fig. S5c further indicated that the particles were composed of O and Si with the atom ration of O to Si of 2, suggesting it is pure silica.

After filtration of silica, the solution was heated and some white materials formed. XRD result in Fig. S6 indicates that it is NH<sub>4</sub>F. By evaporation of aqueous solution of NH<sub>4</sub>F in a laboratory-size evaporator/crystallizer system, NH<sub>4</sub>HF<sub>2</sub> was regenerated and recycled [16, 20, 21, 41-43].

#### 4. Conclusions

A method to prepare amorphous silica particles from zircon using the fluorination method

through a three-step process including fluorination, sublimation and hydrolyzing progress has been developed and proven feasible. The following conclusions were drawn:

1)  $(NH_4)_3 ZrF_7$  and  $(NH_4)_2 SiF_6$  formed after the fluorination at 230 °C for 5 hr.

2)  $(NH_4)_2SiF_6$  started to sublimate at 175 °C, dominated at 280 °C and ended at 300 °C.

3) Amorphous silica particles produced at 45 °C exhibited uni-modal in micrometer size range,

while bi-modal amorphous particles in a variety of sizes ranging from nanometer to micrometer were

produced at 30 °C and 60 °C.

4) Amorphous silica particles obtained at 45 °C exhibited high purity, narrow size distribution,

high specific surface, high DBP-absorption and low density.

5) Ammonium bifluoride can be recycled through the evaporation of NH4F solution.

#### Conflict of Interest

We wish to confirm that there are no known conflicts of interests associated with this publication and there has been no significant financial support for this work that could have influenced its outcome.

We confirm that the manuscript has been read and approved by all named authors and that there are no other persons who satisfied the criteria for authorship but are not listed. We further confirm that the order of authors listed in the manuscript has been approved by all of us.

We confirm that we have given due consideration to the protection of intellectual property associated with this work and that there are no impediments to publication, including the timing of publication, with respect to intellectual property. In so doing we confirm that we have followed the regulations of our institutions concerning intellectual property.

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#### **Declaration of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data

also forms part of an ongoing study

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#### **Figure Captions**

Fig.1 XRD patterns of zircon (a) before and (b) after fluorination at 230 °C for 5 hr

Fig.2 (a) (b) SEM images and (c) the corresponding EDS of zircon after fluorination at 230  $^{\circ}\text{C}$  for 5 hr

Fig.3 TGA-DTG results of NH<sub>4</sub>HF<sub>2</sub> with SiO<sub>2</sub>: (3 ABF to 1 SiO<sub>2</sub>)

Fig.4 XRD patterns of  $(NH_4)_2SiF_6$  condensates at 100-150 °C for different time during 300 °C sublimation: (a) 3 hr; (b) 5 hr; (c) 7 hr

Fig.5 (a) (c) (e) SEM images and (b) (d) (f) the corresponding EDS of  $(NH_4)_2SiF_6$  collected in the condenser at 100-150 °C for different time during sublimation at 300 °C: (a) (b) 3 hr; (c) (d) 5 hr and (e) (f) 7 hr

Fig.6 Macroscopic morphology of SiO<sub>2</sub> particles produced by hydrolysis of  $(NH_4)_2SiF_6$  at different temperature + drying at 120 °C for 2 hr: (a) 30 °C; (b) 45 °C and (c) 60 °C

Fig.7 XRD patterns of amorphous SiO<sub>2</sub> particles produced by hydrolysis of  $(NH_4)_2SiF_6$  at different temperature + drying at 120 °C for 2 hr: (a) 30 °C; (b) 45 °C and (c) 60 °C

Fig.8 Effect of hydrolysis temperature on the hydrolysis rate of Si in Si-bearing solution

Fig.9 SEM images of amorphous SiO<sub>2</sub> particles produced by hydrolysis of  $(NH_4)_2SiF_6$  at different temperature + drying at 120 °C for 2 hr: (a) 30 °C; (b) 45 °C and (c) 60 °C

Fig.10 TEM images of amorphous SiO<sub>2</sub> particles produced by hydrolysis of  $(NH_4)_2SiF_6$  at different temperature + drying at 120 °C for 2 hr: (a) (b) 30 °C; (c) (d) 45 °C and (e) (f) 60 °C

Fig.11 Nitrogen adsorption isotherms for amorphous  $SiO_2$  particles produced by hydrolysis of  $(NH_4)_2SiF_6$  at 45 °C + drying at 120 °C for 2 hr



Fig.1



Fig.2



Fig.3





Fig.5



Fig. 6



Fig. 7





Fig.9



Fig.10



Fig.11

Table 1 XRF results of chemical composition of zircon (wt. %)

ZrO <sub>2</sub>	HfO <sub>2</sub>	SiO <sub>2</sub>	$Al_2O_3$	$Fe_2O_3$	TiO <sub>2</sub>	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	$Cr_2O_3$	$P_2O_5$	$Y_2O_3$
64.647	1.421	32.267	0.269	0.096	0.353	0.088	0.006	0.014	0.014	0.258	0.307

Table 2 XRF results of chemical composition of a morphous SiO\_2 particles (wt. %) produced at  $45\,^\circ\!\mathrm{C}$ 

SiO <sub>2</sub>	TiO <sub>2</sub>	Ni/ppm	F/ppm	Al/ppm	Na/ppm	K/ppm
99.96	0.024	35	25	45	28	27

Table 3 Average particle size, BET surface area, DBP, tapping density and pH of amorphous silica particles prepared at 45°C

Avaraga partiala siza	BET Surface area	Tapping density	DBP	, all	
Average particle size	(m <sup>2</sup> /g)	$(g/cm^3)$	(ml/g)	рп	
254±17 nm	136.8	0.532	2.7	5.7	