Study on the Reproducibility of Preparation Reaction of SiO$_2$ Nanoparticles

Hongyun Zhao[1], Lixia Qin[1*], Xiangqing Li[1], Yuxiang Yang[2], Hanmin Xiao[3], Yu-Kui Huang[1], Shi-Zhao Kang[1*]

[1]*School of Chemical and Environmental Engineering, Center of Graphene Research, Shanghai Institute of Technology, 100 Haiquan Road, Shanghai 201418, China*

[2]*Department of Chemistry, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237*

[3]*Department of Porous Flow & Fluid Mechanics, Research Institute of Petroleum Exploration & Development, Petrochina, 20 Xueyuan Road, Beijing 100083, China*

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Abstract: In this paper, nano-sized SiO$_2$ particles were prepared using sodium silicate as raw material. Meanwhile, the effects of the reaction parameters, including pH, reactant initiative concentration, reaction time, and reaction temperature, on the yield were explored. Furthermore, the reproducibility was systematically studied via the calculation of the average value and coefficient of variation. The results show that the as-prepared SiO$_2$ nanoparticles are amorphous, and the particle size is in the range of 25 - 90 nm. When the pH value is 7, the initiative sodium silicate concentration is 0.7 mol/L, the reaction time is 2 h, and reaction temperature is 10 $^{\circ}$C, the reproducibility of preparation reaction is optimum. Among the above four parameters, the pH value is the most important factor in the reproducibility of preparation reaction.

1. Introduction

Nanoscale silica (denoted as nano-SiO$_2$) is a kind of inorganic powders with high specific surface area and a great number of unsaturated bonds, which has novel physical and chemical properties is widely used in many respects [1-3]. Although nano-SiO$_2$ has excellent properties, however, considering the costly silica sources and high energy consumption, the development of environmentally firendly synthesis techniques and the use of inexpensive raw materials remain a research hotspot [4]. Many reports indicate that the sodium silicate is a cheap, non-toxic material, and it is less energy-consuming and environmentally friendly in the preparation of nano-SiO$_2$. Thus, it is an ideal material for the large-scale production of nano-SiO$_2$ [5].

In this paper, the pH, sodium silicate concentration, reaction time, and reaction temperature were

selected as the experimental conditions to be investigated. Five experimental variables were set for each reaction condition, and ten parallel experiments were performed for each variable. By processing the data of ten sets of parallel experiments, we can obtain the average yield and coefficient of variation (CV) under this experimental variable. The CV can be used to indicate the degree of fluctuation of experimental data, and the smaller the coefficient of variation, the less fluctuation of data. The calculation formula of the coefficient of variation is $CV=S/\overline{X}$ (S is the standard deviation, $\overline{X}$ is the average) [6-8]. Finally, a comprehensive analysis of the average yield and coefficient of variation was performed. The best experimental conditions obtained through this method which have a high degree of confidence.

2. Experimental

Materials: Deionized water, laboratory-made; sodium metasilicate nonahydrate (AR) and hydrochloric acid (AR, 36 - 38%) were purchased from the Titan platform.

Instruments: The scanning electron microscope (SEM) image was taken with an S-3400 N Hitachi scanning electronic microscopy (Japan). The X-ray diffraction (XRD) patterns were measured with a Bruker D8-Advance X-ray diffractometer (Germany).

Methods: A certain amount of sodium metasilicate nonahydrate was configured it into 100 mL sodium silicate solution, then the dilute hydrochloric acid ($V_{HCl} : V_{H2O}=1 : 2$) was slowly added into the above solution. In a 20 ^{o}C water bath, adjust the pH value of solution is 7 and stir the reaction for 2 h. After reaction for a certain time, the precipitates were formed and separated through centrifugal machine and washed with deionized water and ethanol each for three times. The precipitates were dried in a vacuum oven at room temperature for 8.0 h, and then the dried precipitate was calcinated in a muffle furnace at 600°C for 1.5 h to form the silica powders.

3. Result and discussion

3.1 Characterization

Fig. 1 (A, B, C, D) shows the SEM images of nano-SiO_2 under the different experimental conditions, respectively. Clearly, when the sodium silicate concentration is 0.9 mol/L and the reaction temperature is 20 ^{o}C, the obtained nano-SiO_2 has an irregular structure, and the particle size is nonuniform which is in the range of about 10 ~ 70 nm (Fig. 1A). Moreover, when the sodium silicate concentration is reduced to 0.7 mol/L, and the reaction temperature is decreased to 10 ^{o}C, the average size of the produced nanoparticles exhibits a gradual decreasing trend (Fig. 1C and D).

The XRD analysis of nano-SiO_2 was performed and the results are shown in Fig. 2A. It can be found in Fig. 2 that only a large peak appears at $2\theta = 22°$, and there is no other significant crystal diffraction peak, indicating that this powder is an amorphous structure of silica [9]. As shown in Fig. 2B, the FT-IR spectra at 466 cm^{-1} corresponds to the bending vibration of the Si-O-Si bond. The bands at 809 cm^{-1} and 1089 cm^{-1} are the symmetrical stretching vibrational and anti-symmetrical stretching vibrational of Si-O-Si bonds, respectively. Also, the bands at 1636 cm^{-1} and 3443 cm^{-1} correspond to the O-H bond of water molecules. The former is the bending vibration of the H-O-H

bond related to free water (capillary water, surface physical adsorption water), and the latter is silicon hydroxyl and bonded water anti-symmetric O-H bond stretching vibration [10].
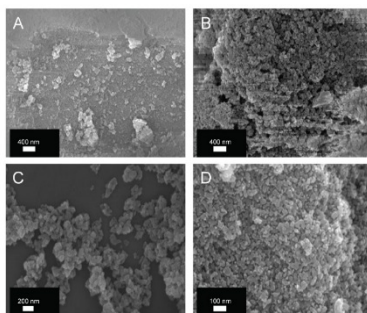

Fig. 1 SEM images of nano-SiO$_2$, A: the pH value is 7, the sodium silicate concentration is 0.9 mol/L, the reaction time is 2 h, the reaction temperature is 20 ^{o}C and the average size is ~ 50 nm; B: the pH value is 7, the sodium silicate concentration is 0.7 mol/L, the reaction time is 2 h, the reaction temperature is 20 ^{o}C and the average size is ~ 40 nm; C: the pH value is 7, the sodium silicate concentration is 0.9 mol/L, the reaction time is 2 h, the reaction temperature is 10 ^{o}C, the average size is ~ 41 nm; D: the pH value is 7, the sodium silicate concentration is 0.7 mol/L, the reaction time is 2 h, the reaction temperature is 10 ^{o}C, the average size is ~ 25 nm.
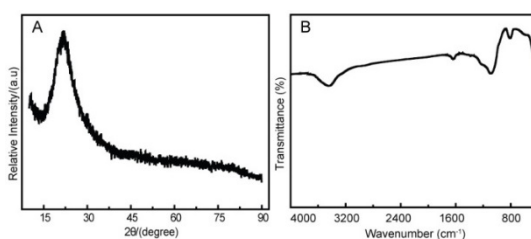

Fig. 2 (A) X-ray powder (XRD) pattern of nano-SiO$_2$; (B) FT-IR spectra nano-SiO$_2$; The reaction conditions of nano-SiO$_2$ are as follows: the pH value is 7, the sodium silicate concentration is 0.7 mol/L, the reaction time is 2 h and the reaction temperature is 10 ^{o}C.

3.2 Effect of pH value on yield and reproducibility

From Fig. 3 it can be seen that the yield is increasing at a pH value of 11 ~ 7. When the pH value was 7 ~ 5, the yield showed a decreasing trend, and also the yield showed an increasing trend when the pH value was 5 ~ 3. From the curve b, it can be seen that the reproducibility of the reaction increases when the pH value is in the range of 11 ~ 5, and the reproducibility tends to decrease at a pH value of 5 ~ 3. The reason is that with the continuous addition of hydrochloric acid, the charge in the reaction system continues to increase, and the micelle absorbs a large amount of charge. These micelles will repel each other and inhibit the progress of the positive reaction [10]. This inhibition will lead to an increase in the reproducibility of the experiment. However, when the pH value is 3, the catalytic effect of hydrochloric acid is greater than the inhibitory effect between the colloidal particles, which leads to a decrease in the reproducibility of the experiment while leading to a rise in yield. Thus, the optimum pH value of the reaction was 7.
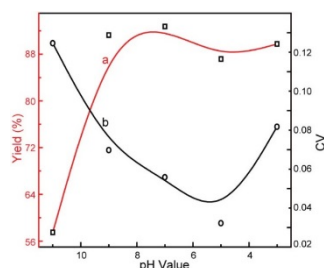
Fig. 3 The change of trend diagram of yield and CV with pH value in the range of 11 ~ 3.

3.3 Effect of sodium silicate concentration on yield and reproducibility

As can be seen in Fig. 4, the yield increases when the concentration of sodium silicate is in the range of 0.3 ~ 0.9 mol/L, and the maximum yield is stable at about 92 %. However, with the increasing concentration of sodium silicate (0.9 ~ 1.1 mol/L), the yield showed a downward trend. As can be seen from curve b, when the sodium silicate concentration is 0.3 ~ 0.9 mol/L, the experimental reproducibility first increases and then stabilizes. As the concentration of sodium silicate increases (0.9 ~ 1.1 mol/L), the reproducibility of the experiment rapidly decreased. This is because when the sodium silicate concentration is 0.3 mol/L, the product of the reaction is small, and the proportion of the washing loss is large, resulting in a low yield and reproducibility. When the sodium silicate concentration is 0.5 ~ 0.9 mol/L, the proportion of the washing loss is continuously reduced, resulting in an increase in the yield, and the reproducibility of the experiment tends to be stable. However, when the sodium silicate concentration is 1.1 mol/L, the precipitate formed by the system will produce co-precipitation, resulting in a decrease in the yield and the reproducibility. Based on above results, the optimal concentration of sodium silicate is 0.7 mol/L.
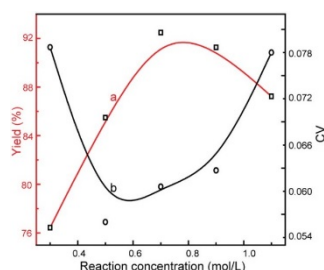

Fig. 4 The change of trend diagram of yield and CV with the concentration of sodium silicate. The range of sodium silicate concentrations varies from 0.3 mol/L to 1.1 mol/L.

3.4 Effect of reaction time on yield and reproducibility

As can be seen from Fig. 5, when the reaction time is 0 ~ 2 h, the yield presents an increasing trend. When the reaction time is 2 ~ 4 h, the yield shows a decreasing trend. When the reaction time was 0 ~ 1 h, the reproducibility of the experiment showed a rapid increase. When the reaction time was 1 ~ 4 h, the reproducibility of the experiment slightly decreased. This phenomenon is explained as follows: as the reaction time increases, the reaction degree of sodium silicate continues to proceed, so that the yield increases continuously. However, an increase in the reaction time will increase the diameter of the particles, resulting in a slight increase in the washing loss, and thus the yield will be decreased slightly [11]. When the reaction time is 0 h, the mother liquor still contains a large amount of unreacted sodium silicate. The mother liquor was separated by centrifuge, a large amount of sodium silicate will continue to react, resulting in lower reproducibility. With the

increase of time, the degree of reaction has been continuously deepened, and the reproducibility of the experiment has been increasing. When the reaction time is 1 h, the reproducibility of the experiment is maximized. When the reaction time was 1 ~ 4 h, the difference in the loss of washing resulted in a slight decrease in the reproducibility of the experiment. According to the above results, the optimal reaction time is 2 h.
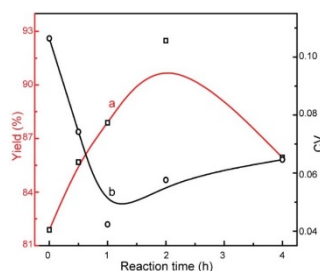

Fig. 5 The change of trend diagram of yield and CV with reaction time. The reaction time is range from 0 h to 4 h.

3.5 Effect of reaction temperature on yield and reproducibility

As shown in Fig. 6, when the reaction temperature is in the range of 10 ~ 20 ^{o}C, the yield tends to increase. When the reaction temperature is 20 ~ 50 ^{o}C, the yield tends to decrease. This is because the reaction is an exothermic reaction, and as the temperature increases, the forward progress of the reaction is inhibited, resulting in a decrease in the yield. When the reaction temperature is in the range of 10 ~ 20 ^{o}C, the yield tends to increase, because the temperature is too low to reduce the reaction rate, so that the total yield decreases when the reaction temperature is 10 ^{o}C. When the reaction temperature was 10 ~ 30 ^{o}C, the reproducibility of the experiment showed a downward trend. When the reaction temperature is 30 ~ 50 ^{o}C, the reproducibility of the experiment showed an increasing trend. The proposed explanation can be explained as follows: at the reaction temperature of 10 ~ 30 ^{o}C, the reaction rate increases with the temperature increasing, but it also suppresses the forward progress of the reaction, so the reproducibility of the experiment may be reduced. When the reaction temperature is 30 ~ 50 ^{o}C, the resulted inhibitory effect by the increasing temperature which plays a dominate role, so the orderliness of the experiment will increase. Therefore, the optimal reaction temperature is 10 ^{o}C.

4. Conclusion

In summary, nano-sized SiO_2 particles were prepared under the different conditions, and the data were processed using the coefficient of variation to analyze the effect of different experimental conditions on the yield and reproducibility. When the optimal reaction pH is 7, the sodium silicate concentration is 0.7 mol/L, the reaction time was 2 h and the reaction temperature was 10 ^{o}C, the size of the nanoparticles produced exhibits a decreasing trend. Furthermore, the greatest influence factor on the reproducibility of reaction is the pH value, then the reaction time, followed by sodium silicate concentration and the reaction temperature, respectively. Based on these, we hope that these results could provide certain experimental references in actual production of nano-SiO_2.
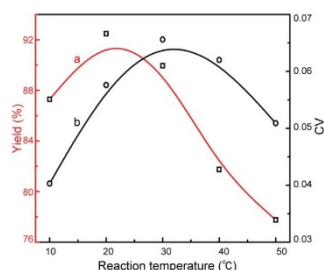
Fig. 6 The change of trend diagram of yield and variation coefficient with reaction temperature. The reaction temperature varies from 10 $^{\circ}$C to 50 $^{\circ}$C.

Acknowledgments

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