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Synthesis and characterization of high surface area silicon carbide by dynamic vacuum carbothermal reduction

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Abstract Silicon carbide (SiC) precursor was obtained by sol–gel used tetraethoxysilane as silicon source and saccharose as carbon source, and then the precursor was used to prepare SiC by carbothermal reduction under dynamic vacuum condition. The samples were characterized by X-ray diffraction, scanning electron microscope, and low-temperature nitrogen adsorption–desorption measurement. The results showed that the carbothermal temperature for synthesizing SiC needed to be at 1,100 °C under dynamic vacuum. At this temperature, the obtained sample is composed of agglomerated regular grains with size ranging from 20 to 40 nm and has a high surface area of 167 m^2/g and the main pore size center at 5.3 nm.

Introduction

Silicon carbide (SiC) is a kind of material with outstanding properties such as excellent mechanical strength, chemical inertness, and high-thermal conductivity [1–3]. Recently, as a catalyst support, SiC has great applications in several important chemical reactions such as isomerization of linear saturated hydrocarbons [4], catalysis oxidize [5], selective oxidation of hydrogen sulfide into elemental sulfur [6], photocatalyst reaction [7]. Its performance is apparently better than conventional support at the condition of hyperthermia and strong acid. However, surface area is thought to be an important consideration in the function of SiC as a catalyst support for these reactions. Therefore, preparing high surface area SiC becomes a significant research. Considerable attention has been focused on developing various methods for preparing high surface area SiC. Moene et al. [8, 9] produced SiC of surface areas ranging from 30 to 80 m^2/g and a pore volume of 0.2 cm^3/g by reacting activated carbon with tetrachlorosilane and hydrogen in the presence of Ni. Ledoux et al. [10] and Nicolas et al. [11] developed a shape-memory synthesis method to prepare high surface area SiC in which the porous SiC materials are synthesized by the reaction of activated carbon or coke with gaseous silicon monoxide at the temperature of 1,200–1,500 °C. Jin and Guo [12] prepared SiC with surface area of 112 m^2/g at temperature of 1,250 °C by sol–gel using tetraethoxysilane (TEOS) as silicon source and self-prepared phenolic-resin as carbon source for preparing SiC precursor, and nickel nitrate was employed in the sol–gel process as a pore-adjusting reagent. These preparation methods mentioned above mainly investigate diversity carbon source and silicon source, while there are very few reports available on the change of the process of carbothermal reaction. In this paper, SiC precursor was obtained via the sol–gel method, and the process of precursor carbothermal reaction under dynamic vacuum was studied. We could judge directly the lowest temperature of carbothermal reaction according to the relationship between furnace pressure and temperature, optimizing the conditions for the synthesis, preparing mesporous SiC with high surface area.

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Experimental

Preparation of the carbonaceous silicon xerogel

An aliquot of 30 g saccharose was dissolved in the mixed solution of 50 mL absolute ethanol and 20 mL deionized water by magnetic stirring. Then, 50 mL TEOS and 10 mL (3.5 wt.%) oxalic acid solution were added slowly to the solution to promote the hydrolysis of TEOS [13], and the solution was stirred at a temperature of 50 °C until the gel was formed. Then the gel was dried at 120 °C in an oven for 24 h to remove the excess water and other solvents. Finally, the xerogel was obtained.

Carbothermal reduction of the carbonaceous silicon xerogel under vacuum

An aliquot of 20 g xerogel was placed into a vacuum graphite oven; vacuum was created when the atmospheric pressure was reduced to 10^{-2} Pa. The xerogel was heated at a rate of 20 °C/min under dynamic vacuum, and the change of gas pressure in the furnace was recorded as a function of temperature. We named the recorded data as a thermobarogram. From this thermobarogram, the lowest temperature of carbothermal reduction for preparing SiC would be directly determined. When the lowest temperature was determined, the vacuum furnace was kept at the determined temperature for carbothermal reduction until the gas pressure below 10^{-2} Pa. After cooling, the SiC sample was heated at 650 °C in air for 2 h to remove excess carbon, and immersed in the hydrofluoric acid solution (40 wt.%) for 12 h to remove residual silica.

Characterization

Structural analysis of the samples was carried out on a German Bruker-D8 Advance X-Pert powder diffractometer with Cu Kα radiation (40 kV, 40 mA) and Ni filtering. The sample morphology was observed by a Netherlandish XL30ESEM scanning electron microscope (SEM). Texture analysis of SiC was carried out on an American NOVA win4200 gas adsorption analyzer. Brunauer–Emmett–Teller (BET) [14] and Barrett–Joyner–Halenda (BJH) [15] analyses were used to determine the specific surface area and mesopore size distribution.

Result and discussion

Determination of carbothermal reduction temperature

The high-temperature solid-phase carbothermal reduction reaction which takes place in the vacuum furnace may be written as follows [16]:

$$\mathrm{SiO_2\,(s) + 3C\,(s) \rightarrow SiC\,(s) + 2CO\,(g).}$$

In this reaction, CO gas released. We could judge whether the SiC has been generated or not from the change of the barometric pressure with the reaction temperature in the vacuum furnace. Keller and colleagues [11] and Puneet et al. [17] have obtained SiC through carbothermal reduction reaction in vacuum. They all carried out the carbothermal reduction reaction at high temperature (1,300–1,600 °C) directly, but did not notice the changes of gas pressure in the vacuum furnace. We redesigned the traditional vacuum furnace and measured the changes of the pressure in the furnace as a function of temperature. From this kind of thermobarogram, we have analyzed how to determine the lowest reaction temperature for preparing SiC in our experimental conditions. In addition, during this solid-phase reaction, the reaction rate was controlled by the partial pressure of CO. If we could separate CO product continuously from reaction system, the reaction rate would be accelerated, and the whole reaction time would be reduced.

Figure 1 shows the relationship between pressure and temperature in vacuum furnace during the carbothermal reduction of SiC precursor. During the carbothermal reduction process, the gas pressure increased dramatically at about 150–200, 350–600, and 1,100–1,400 °C, the results showed that the gas has been generated in these three temperature regions under dynamic vacuum. The pressure change in two former temperature regions may be due to the pyrolysis of the precursor. When the temperature was raised above 800 °C, the pyrolysis of xerogel would be completed [18], and the mixture of pure C and SiO_2 was formed. According to the overall carbothermal reduction, the increase in the gas pressure at the last temperature region may due to the generation of the CO product. Therefore, the SiC and CO were formed from the reaction between C and SiO_2 at the temperature of 1,100 °C. In

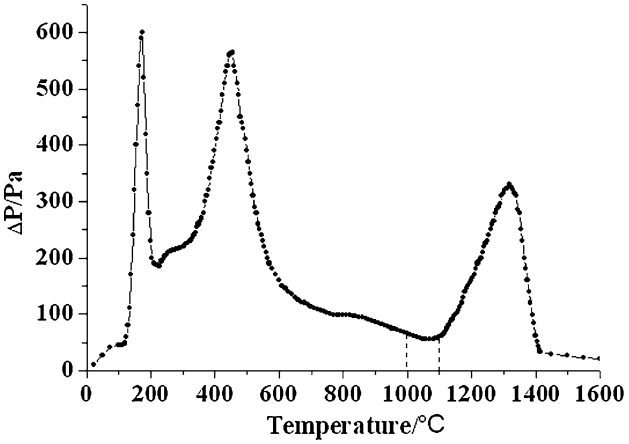

Fig. 1 The thermobarogram of the sample

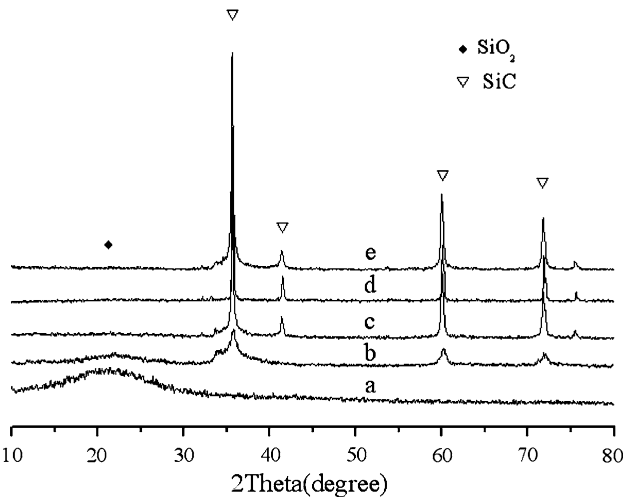

Fig. 2 The XRD profiles of binary aerogel precursor heat-treated samples at (a) 1,000 °C (b) 1,050 °C (c) 1,100 °C (d) 1,200 °C (e) 1,300 °C

other words, 1,100 °C is the lowest reaction temperature of preparing SiC in our experimental conditions. In order to further confirm the minimum reaction temperature, we analyzed the phases of the samples prepared at different temperature by the X-ray diffraction (XRD). The results are shown in Fig. 2.

Figure 2 shows the XRD patterns within the range 10–80° of the synthesized samples at different temperature. That only amorphous silica appeared in the XRD profiles showed carbothermal reduction did not take place at 1,000 °C, it means no reaction of SiO_2 occurred at this temperature. Distinct changes were presented in the pattern of the samples synthesized at 1,050–1,300 °C, implying the carbothermal reduction of SiO_2 took place at this temperature region. Although three peaks in the XRD profile at $2\theta = 35.6, 60.2,$ and $72.1°$ indicate that β-SiC has obtained when the product was heated to 1,050 °C, the amorphous silica was still appeared, which indicated the translation of SiO_2 not completed. However, all of the samples treated at 1,100–1,300 °C only displays five peaks at $2\theta = 35.6, 41.2, 60.2, 72.1,$ and $75.5°$, which correspond to the (111), (200), (220), (311), and (222) planes of the β-SiC, respectively,[1] indicating 1,100 °C was enough for translating carbonaceous silicon xerogel to β-SiC under dynamic vacuum. As is known, the partial pressure of CO gas products would affect the rate of solid–solid reaction according to the principle of chemical kinetics. Obviously, when the temperature achieved a suitable degree, the lower partial pressure of CO would be beneficial to the rate of carbothermal reduction reaction. Conversely, if CO maintains in the system, it was necessary to enhance the reaction temperature for preparing SiC. In our experimental conditions, the gaseous product was continuously evacuated from the reaction system. It would maintain the relatively lower pressure of CO in the system and make the rate of carbothermal reduction steady. Therefore, the temperature at 1,100 °C was enough for preparing large-scale SiC. We marked the samples that obtained from carbothermal reduction reaction at 1,100, 1,200, and 1,300 °C as SiC-1100, SiC-1200, and SiC-1300, respectively. Then, the microstructure of samples would be researched.

Morphology characteristics

SEM was employed to determine the morphology of SiC samples synthesized at different temperature. From SEM images (Fig. 3), SiC-1100 consists of regular sphere particles with sizes from 20 to 40 nm. The samples' particle sizes increase with increasing reaction temperature. The resulting particles are agglomerated at 1,200 °C, and further sintered at 1,300 °C. The particle size of SiC-1300 generally exceeds 150 nm. It indicated that the high reaction temperature had great influence on the growing of crystal grain. We could prepare homogeneous SiC nanoparticle through controlling the reaction temperature.

BET characterization

Figure 4 (left) shows the low-temperature nitrogen adsorption–desorption isotherms of the samples synthesized at different temperature, which gives a clear IV type adsorptive isothermal curves, the adsorptive capacity rise sharply when the relative pressure is in the range from 0.6 to 0.9, and the hysteresis loop existed at the desorption process. As we known, the shapes of the isotherms and the hysteresis loop suggest that the sample possesses a mesoporous structure. Additionally, above the relative pressure of 0.9, the isotherm still rise, indicating the sample also possesses some macroporous structures [12]. The BET method was employed to calculate the surface area of the samples, with the increase in the synthesized temperature, the BET surface areas of the samples gradually decrease, especially for the samples synthesized at 1,300 °C. The BET surface areas of the samples synthesized are 167, 88, 47 m^2/g at 1,100, 1,200, 1,300 °C, respectively. The desorption curve was selected and the BJH method was employed to calculate the pore size distributions of the samples, and the results are shown in Fig. 4 (right). The pore size distribution of SiC-1100 ranged from 3 to 40 nm, and the main pore size of the mesoporous SiC center at 5.3 nm, and its pore volume was 0.45 mL/g. The SiC-1100 was mesoporous material, which had high surface area and possessed homogeneous pores. The pore distribution becomes irregular with increasing reaction temperature. For example, the sample of SiC-1300 had a disorder pore size distribution. These results were in agreement with that from the SEM

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[1] Powder Diffraction File JCPDS 1601 Park Lane, Swarthmore, PA 19081-2389, USA, 2001.

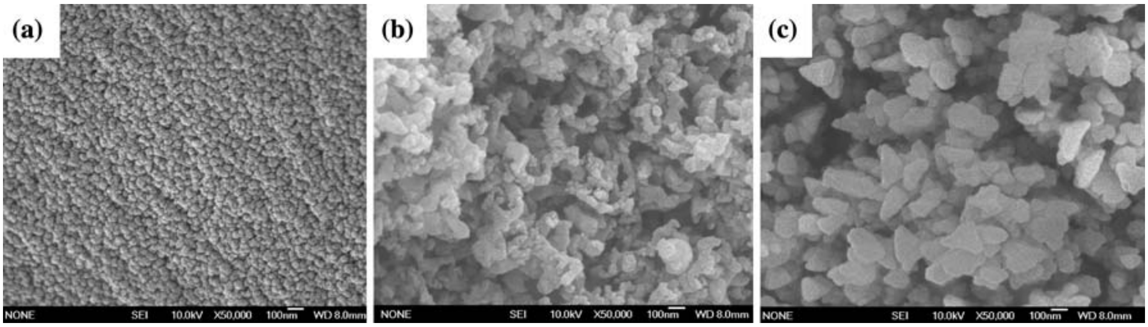

Fig. 3 The SEM image of the samples synthesized at different temperature (a) SiC-1100; (b) SiC-1200; (c) SiC-1300

Fig. 4 Nitrogen adsorption and desorption isotherm (left) and the corresponding pore size distribution (right) calculated by BJH method of the samples synthesized at different temperature (**a**) SiC-1100; (**b**) SiC-1200; (**c**) SiC-1300

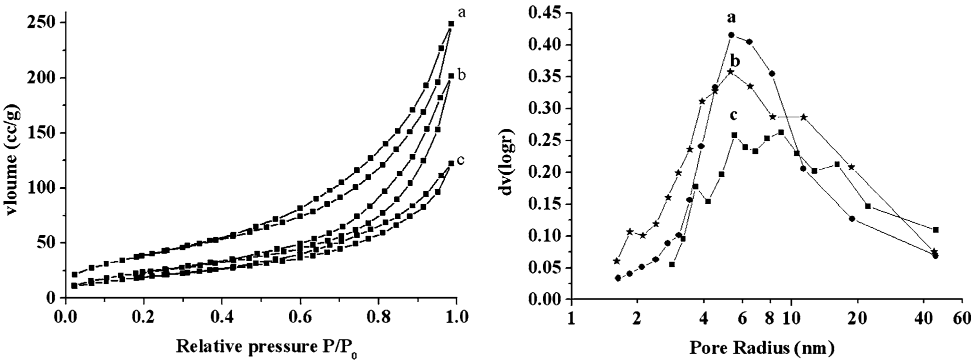

image. It indicated that the temperature was a disadvantage factor on synthesizing high surface area of SiC, and it would affect the pore distribution of the obtained sample.

In the previous research [19], SiC was obtained through carbothermal reduction of carbonaceous silicon precursor in inert atmosphere, which the conversion temperature was 1,450 °C, and the sample has a surface area of 140 m^2/g. While the sample of SiC obtained by carbothermal reduction reaction under vacuum has a surface area of 167 m^2/g, and the conversion temperature was only 1,100 °C, and the obtained SiC particle has lower glomeration extent. The possible reasons may be explained as follows: on the one hand, the temperature for carbothermal reduction was lower in the vacuum than that in the inert atmosphere. It would reduce the particles sinter-roasting extent of the obtained sample, which would be beneficial for preparing high surface area SiC; however, on the other hand, the reaction rate in vacuum was faster than that in inert atmosphere, which would result in large SiC particles, and would be unbeneficial for preparing high surface area SiC. Therefore, we can conclude that the temperature factor would play an important role in preparing high surface area SiC under dynamic vacuum.

Conclusions

A sol–gel route for the preparation of the carbonaceous silicon xerogel was presented in this paper. Then, the xerogel was used to prepare a kind of homogeneous mesoporous SiC by carbothermal reduction under dynamic vacuum at 1,100 °C, which had a high surface area of 167 m^2/g and the main pore size of the mesoporous SiC center at 5.3 nm.

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