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Influences of Catalyst Amount in Xerogels Precursors on the Structure and Property of Silicon Carbide with Taixi Coal as Carbon Source

Kangli He, Aonan Fan, Jianping Jia, Wanyi Liu [#], Bing Li

1School of Chemistry and Chemical Engineering, Ningxia University, Yinchuan 750021, China

[#]Email: liuwy@nxu.edu.cn

Abstract

A simple and cost effective method was reported for the synthesis of silicon carbide by the sol-gel and carbothermal reduction method, in which Taixi coal and Na_2SiO_3 9H2O were respectively employed as carbon and silica precursors, Fe $(NO_3)_3$ $9H_2O$ as the catalyst. XRD, BET and SEM were used to characterize the SiC samples. The results show that the amount of the catalyst has important influences on the stacking fault density, average crystallite size, surface area and morphology of the SiC products. What's more, when the molar ratio of iron and silicon is 0.01, the silicon carbide sample is β-SiC nanoparticles without other morphologies and the size of SiC particles are in the range of 40-70 nm.

Keywords: Silicon Carbide; Catalyst Amount; Control; Taixi Coal

1 INTRODUCTION

Silicon carbide (SiC) is a refractory material with outstanding thermal, chemical and mechanical properties. It has high mechanical strength, high thermal conductivity, low thermal expansion coefficient, large band gap, low density, high hardness and excellent corrosion resistances [1-3]. Many processes have been proposed for the preparation of SiC nanostructures, such as catalyzed autoclave synthesis [4], carbon nanotube-confined growth [5] and catalyst-assisted polymeric precursor pyrolysis method [6], etc. However, most of these synthetic approaches involved complex processes and manipulation. Among them, metal catalysis has been known as a simple and economical method for SiC preparation. However, the structure and sroperty of SiC should be controlled by the amount of catalyst in xerogels precursors. On the other hand, the choice of carbon is one of the crucial factors for SiC production. Currently, the carbon source is limited to carbon black, coke, phenolic resin and other materials. Therefore, an alternative carbon source is required to develop an efficient and economical process to synthesise SiC. Taixi coal which rich reserves in Ningxia can be a potential carbon material employed for synthetizing SiC due to their ultra-low ash, high mechanical strength and flexible polycyclic carbon nanosheets [7]. This paper reports a simple and cost effective method for the synthesis of β-SiC from controlling the catalyst amount in xerogels precursors with Taixi coal as carbon source.

2 EXPERIMENTAL

2.1 Materials

All the reagents were of A. R. and used as received without further purification. Coal in this work was obtained from Ningxia Taixi Coal Industry Group Co., Ltd. and was further purified to ultra-clean coal resources by muriatic acid (HCl) and hydrofluoric acid (HF) to eliminate the ash by intermittent ultrasound for 8 h. The SiC samples were analyzed by scanning electron microscopy (SEM, KY-100) at 25 kV and 20 mA. The X-ray diffraction (XRD) was performed by a Philips instrument operating with Cu-Ka radiation (k = 1.5406 Å) at 40 kV/40 mA. The specific

surface areas of the samples were measured by nitrogen adsorption at 77 K, using a Micromeritics Tristar 3000 analyzer.

2.2 Preparation of β-SiC

A mixture of Na_2SiO_3 9H_2O and Taixi coal was prepared by sol-gel method, in which different amount of Fe $(NO_3)_3$ 9H_2O was used as additive. The mixture was heated under argon flow to 1000 ^oC at a rate of 8 ^oC /min, then heated to 1450 ^oC at a rate of 2 ^oC /min and maintained at this temperature for 5 h. After the furnace was cooled down to room temperature, the raw products contained SiC were collected. The raw products were heated in air at 700 ℃ for 3 h to remove the residual carbon in an air flowing and subsequently treated by muriatic acid (HCl) and hydrofluoric acid (HF) to eliminate the unreacted silica and other impurities.

3 RESULTS AND DISCUSSION

3.1 XRD analysis

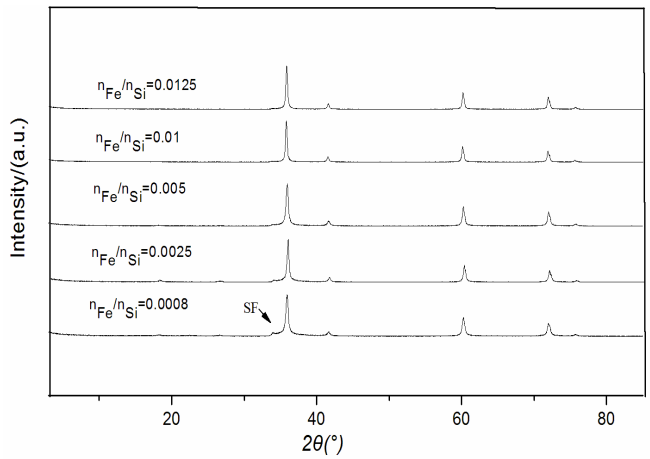

FIG.1. XRD PATTERNS OF THE SIC SAMPLES

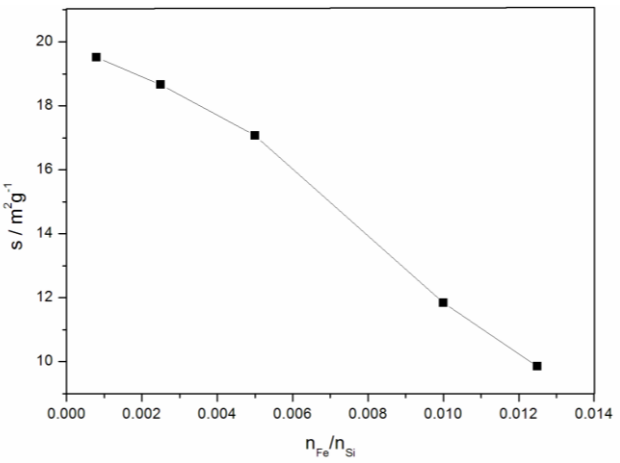

FIG.2. BET PATTERN OF THE SIC SAMPLES

The XRD patterns of the samples are shown in Fig.1. The sample content of the XRD measurement is almost the same for all samples. From the patterns, a total of five main strong peaks at 35.7 °, 41.4 °, 60.0 °, 72.0 ° and 75.6 ° are attributing to the (111), (200), (220), (311) and (222) planes, which indicates all samples are cubic typed β-SiC. The peak denoted as'SF'is due to stacking faults in SiC structure [8]. Besides these peaks, no other impurities are found in the XRD patterns. However, the intensity ratio of the peaks at 33.6° and 41.4° (2θ) (I 33.6° / I 41.4°) in samples are different. The ratio of the two peaks can be used to evaluate the stacking faults density, and the large ratio indicates a high density of the stacking faults in the SiC crystal [9-10].

3.2 BET analysis

As shown in Table 1, with the increase of Fe $(NO_3)_3$ 9H_2O, the stacking faults of SiC decreases obviously, and the average crystallite size of SiC increases. As shown in Fig.2, with the increase of Fe $(NO_3)_3$ 9H_2O, the surface area of SiC decreases. And the maximum and minimum surface area of SiC is ranging from 19.8 m^2g^{-1} to 9.6 m^2g^{-1}. This is associated with the growth mechanism of β-SiC. Because all samples were prepared from almost the same experimental conditions except the amount of additive, it is reasonable to suppose that the decrease of the stacking faults in samples is due to the increase of $Fe(NO_3)_3$ 9H_2O during the sol-gel process. The reaction of sol-gel and carbothermal reduction of β-SiC is quite complicated. The growth mechanism may follow the "vapor-liquid-solid" mechanism [11]. The process of synthesis silicon carbide may be as follows:

$$xSiO_2(s) + yFe(s) + 2xC(s) \rightarrow Fe_ySi_x(l) + 2xCO(g), \quad (1)$$

$$Fe_ySi_x(l) + xC(s) \rightarrow xSiC(s) + yFe(s), \quad (2)$$

The formation of β-SiC may go through the "melt-reaction-precipitation " process from the reaction of (2), which

refer to the carbon first need to dissolve in the eutectic solution, and then carbon react with Si in the eutectic solution to form β-SiC. Finally, the β-SiC segregated from the eutectic solution. The eutectic solution provided favorable conditions for the migration and rearrangement of SiC. With the increase of Fe(NO3)3•9H2O, more eutectic solution formed which lead to stacking faults in β-SiC samples decrease.

TABLE 1 INFLUENCES OF THE AMOUNT O F CATALYST ON THE STACKING FAULTS DENSITY (X) AND AVERAGECRYSTALLITE SIZE (D) OF THE SIC SAMPLES

nFe /nSi	0.0008	0.0025	0.005	0.01	0.0125
X	0.870	0.556	0.440	0.153	0.139
D/nm	24.9	26.1	25.3	28.4	28.9

3.3 SEM characterization

It can be seen from Fig.3a, The sample is consist of linear whiskers and particles with a small amount particles. While in Fig.3b, The SiC with nanoparticle silicon is much more than sample A. It can be seen from Fig.3c that sample C mainly composed by nanoparticle silicon with different sizes, and the linear whiskers in sample C is fewer than B. As show in Fig.3d, It is interesting to note that the sample is consist of nanoparticle silicon, there are no linear whiskers in sample D, and the size of SiC particles was in the range of 40-70 nm. It can be seen from Fig.3e, the SiC nanoparticles are almost as same as D, but the surface area is smaller than D (As shown in Fig.2). This is relate to the formation mechanism of SiC, because Fe $(NO_3)_3$ $9H_2O$ is insufficient for forming the eutectic solution; there are not many eutectic solutions to form SiC. The process of synthesis silicon carbide with linear whiskers may be as follows [12]:

$$SiO_2 + C(s) \rightarrow SiO(g) + CO(g), (3)$$
$$SiO_2(s) + CO(g) \rightarrow SiO(g) + CO_2, (4)$$
$$CO_2(g) + C(s) \rightarrow 2CO(g), (5)$$
$$SiO(g) + 2C(s) \rightarrow SiC(s) + CO(g), (6)$$
$$SiO(g) + 3CO(g) \rightarrow SiC(s) + 2CO_2(g), (7)$$

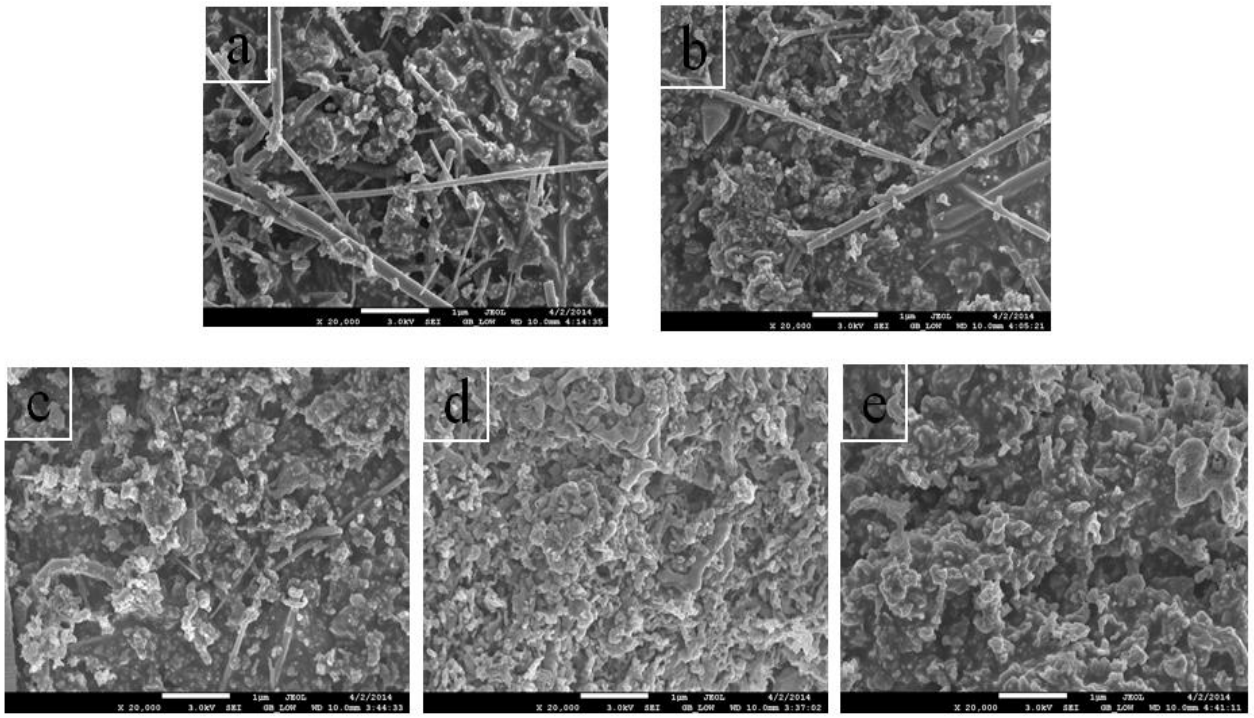

FIG. 3. SEM IMAGES OF THE IRREGULAR SIC PARTICLES OBTAINED WITH DIFFERENT AMOUNT OF FE CATALYST (A, B, C, D, E)A: N_{FE}/N_{Si}=0.0008; B: N_{FE}/N_{Si}=0.0025; C: N_{FE}/N_{Si}=0.005; D: N_{FE}/N_{Si}=0.01; E: N_{FE}/N_{Si}=0.0125;

As reaction (7) was carried out continuously, a gaseous chemical reaction between SiO and CO took place quickly to form SiC crystals with linear whiskers. However, with the increase of Fe$(NO_3)_3$ $9H_2O$, SiC with linear whiskers

decrease obviously. According to reaction (1)，as the amount of $Fe(NO_3)_3$ $9H_2O$ is adequate, so the eutectic solution from (1) is expected to react with C to produce SiC particles. So the SiC sample is consist of particles, when the molar ratio of iron and silicon $\geq$ 0.01.

4 CONCLUSIONS

In summary, SiC samples were successfully prepared by the sol-gel and carbothermal reduction method with Taixi coal as carbon source, in which Fe (NO3)3 9H2O was used as the catalyst. From our preliminary study, it appears that the SiC samples can be obtained by carefully controlling the catalyst amount. The SiC sample is consist of particles, when the molar ratio of iron and silicon $\geq$ 0.01, and the size of SiC particles was in the range of 40-70 nm. What's more, the amount of the catalyst has important influences on the stacking fault density, average crystallite size, surface area, and morphology of the SiC products.

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AUTHORS

Kangli He. She was born in Ningxia province, on February 13th, 1989. She received her BS in 2012 and will get MS in 2015 from Ningxia University. Since September 2012, she follows with Prof. Wanyi Liu and her current research focuses on the synthesis of carbon-based nanostructures using the sol-gel method.

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