The Study on hydrothermal synthesis of ZrO_2 nanofibers under different conditions

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Abstract. Nano-ZrO_2 has a high atomic active surface and is used as catalyst carrier. The traditional method of preparing ZrO_2 nanofibers is electrostatic spinning, which has the problems of high cost and high equipment requirements. In order to solve the shortcomings of traditional preparation methods and prepare excellent ZrO_2 nanofibers, a series of ZrO_2 nanofibers were prepared based on hydrothermal method by changing the types of reactants, the ratio of reactants to organic additives, solvents, reaction time and other relevant parameters, to explore the growth mechanism of ZrO_2 nanofibers, providing a new idea for the preparation of ZrO_2 nanofibers on the active surface of altiplano.

1 Introduction

ZrO_2 (Zirconia) is a white, odorless, tasteless, inorganic, non-metallic material with excellent physical and chemical properties, usually used as a structural and functional material[1]. Meanwhile，ZrO_2 is the only metal oxide which own acidity, alkalinity, reducibility and oxidizability at the same time. Nano-ZrO_2 has a high atomic activity surface, which is very suitable to be used as catalyst and catalyst carrier[2-4]. As a transition metal oxide, ZrO_2 has both basic and acidic sites on the surface, with many oxygen vacancies on the surface and good ion exchange performance. Therefore, it can be used as a catalyst with excellent performance and also as a carrier of the catalyst. Nano-ZrO_2 has a small size and a large specific surface area, providing a large space for catalytic reaction.

The traditional way preparing ZrO_2 nanofibers was electrostatic spinning technique, which has a high cost and high equipment requirements[5, 6]. The hydrothermal method is characterized by low cost, easy operation and adjusting various parameters[7-10]. If ZrO_2 nanofibers prepared by hydrothermal methodare with good morphology,,it will provide a new idea for the preparation of ZrO_2 nanofibers. Therefore, in this paper, ZrO_2 nanofibers were prepared by hydrothermal method, their morphology was observed by SEM, and their formation mechanism was analyzed.

2 Experiment process and plan

The 0.32g $ZrOCl_2 \cdot 8H_2O$ solid (calculated by 0.025mol/L) was dissolved in 35ml alcohol, and the solution was put on a magnetic heating agitator and stirred evenly. Slowly add 5 ml of ethylene diamine to $ZrOCl_2$ solution while stirring. After stirring for 20min, pour the solution into the reactor and put it into a drying oven. Set the reaction temperature at 180℃. Take out the reactor after 36h, 48h and 60h.The reactor was centrifuged at 800r/min for 5 minutes using a high-speed centrifuge. After repeated cleaning with alcohol and distilled water for three times, the nano-ZrO_2 powder was dried, and its morphology was observed subsequently.

3 Results and Discussion

3.1 Effects of different reactants on the morphology of nano-ZrO_2

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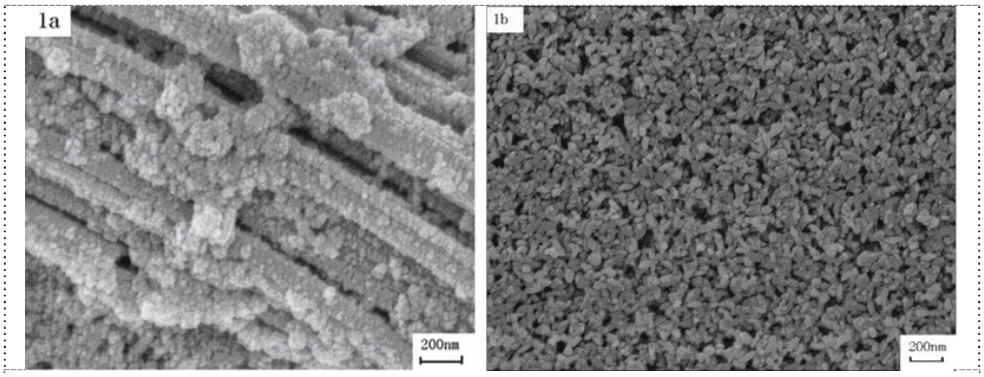

Fig 1. The SEM images of sample ZrO_2 prepared by different reactants

The morphology of nano-ZrO_2 prepared with $ZrOCl_2$and nano-ZrO_2 prepared with Zr $(NO_3)_4$as the reactant were shown in figure 1 a, b. It can be seen that bundles of nanofibers composed of nanorods can be obtained by adding ethylenediamine at 180 ℃ for 36 h and using $ZrOCl_2$ as the reactant. The nanofibers have poor dispersion, owning many nanoparticles on the rough surface. The maximum length and aspect ratio of the nanofibers can be measured as 2400 nm with a length to diameter ratio 29:1. Zr $(NO_3)_4$ was used as the reactant for hydrothermal reaction to obtain ZrO_2 nanoparticles. Infigure 1 b, these nanoparticles were in the shape of a short rod with a diameter of only 10 nm, which they were small and uniform in size, with good dispersibility and no agglomeration.

3.2 Effect of reaction time on the morphology of nano-ZrO_2

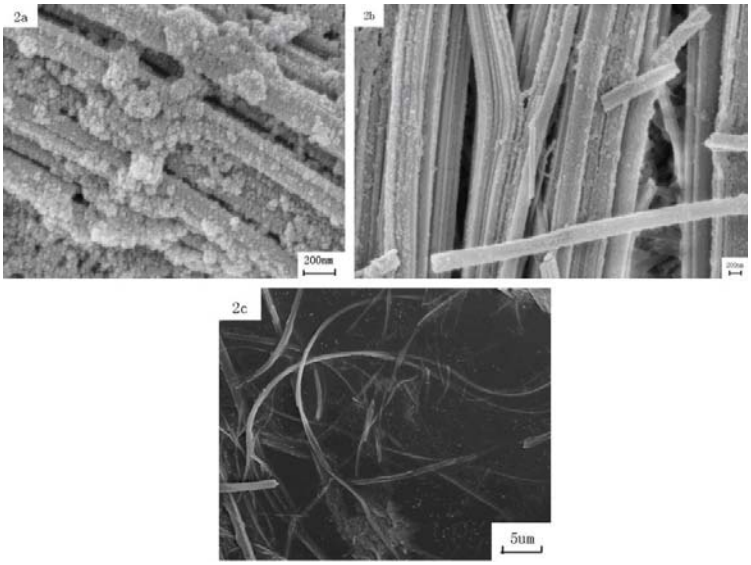

Fig 2. The SEM images of sample ZrO2 prepared in different response time

In Fig.2, the morphology of nano-ZrO_2 varies greatly with different hydrothermal reaction times. When the hydrothermal reaction time is 36 h, the ZrO_2 nanofibers are formed into bundles of nanorods, with obvious nanoparticles attached to the surface. When the reaction time was 48 hours, it could be seen that the surface of the fiber was much smoother than that of the fiber in Fig. 2 a, and the surface adhesion of nanoparticles was significantly reduced. The cross section of the fiber was rectangular, and the most obvious feature was that the bunched nanofibers tended to decompose into dispersed fibers. Within the scanning observable field, the fiber length of hydrothermal reaction for 48 h can reach 23 μm, and the aspect ratio can reach 77:1. When the hydrothermal reaction time was extended to 60 h, it could be seen from figure 2 c that there were no nanoparticles and only nanofibers existed. Moreover, ZrO_2 nanofibers had better dispersion condition with uniform diameter of the fibers and a tendency of cracking from the fibers into multiple bundles of new fibers. Within the scanning observable field, the fiber length and aspect ratio of 60 h after hydrothermal reaction can reach 72 μm and 161:1.

Above all, with the increase of hydrothermal reaction time, ZrO_2 nanoparticles gradually decreased. When the reaction time was 60 h, ZrO_2 nanoparticles completely disappeared, and the surface roughness of fibers gradually decreased. As the hydrothermal reaction time increased, the nanorods composed of bundles of nanofibers gradually

cracked to form dispersed nanofibers. By the time of reaction of 60h, they had been completely dispersed and tended to decompose into finer fibers.

3.3 Influence of solvent on the morphology of nano-ZrO_2

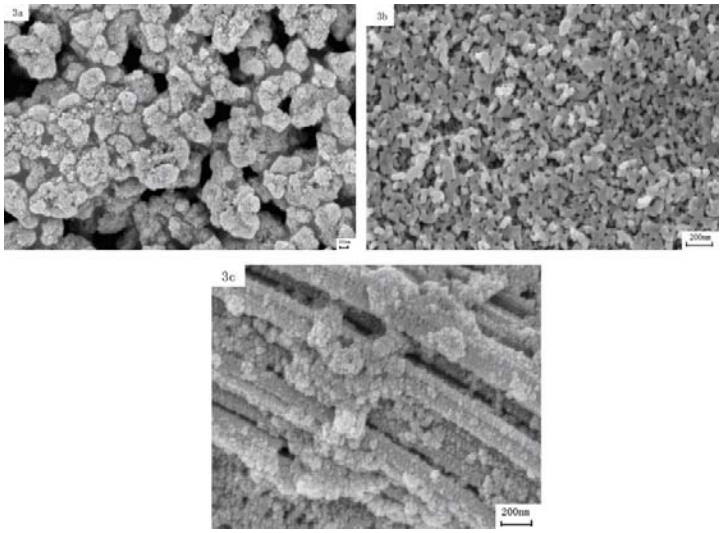

Fig 3. The SEM images of sample ZrO_2 prepared in different solvents

It can be seen from figure 3 that different solvents have a great impact on the morphology of ZrO_2. In Fig.3a, the ZrO_2 nanoparticles wereobtained with irregularshape, narrowsize distribution, rough surface and serious agglomeration. In Fig.3 b, the dispersibility of the nanoparticles obtained by using pure water is much better than that obtained by using pure water, with narrow particle size distribution and stable shape. Within the scanning observable field, the measured particle size is about 10 nm. When ethanol was used as a solvent and hydrolyzed for 48h at 180 ℃, the morphology of ZrO_2 was as shown in Fig.3 c. In the Fig.3 c, when the alcohol content increases, ZrO_2 transforms from nanoparticles to bundles of nanofibers composed of nanorods. As described in Fig.2 b, nanorods tend to be cracked into dispersed nanofibers. Besides, comparing Fig.3 a and b, it can be concluded that the addition of alcohol is conducive to improving the dispersibility of nanoparticles, reducing the agglomeration of particles, and increasing the surface area.

4 Conclusion

By changing the types of reactants, the ratio of reactants and organic additives, solvents, reaction time and other relevant parameters, this paper observed the influence on the morphology of ZrO_2 nano fibers, and explored the growth mechanism of ZrO_2 nano fibers. The results showed that the nanorods with an aspect ratio of 29:1 were obtained by using zirconium oxychloride as the reactant, ethylenediamine as the organic additive and alcohol as the solvent. When zirconium nitrate is used as the reactant under the other conditions equal, ZrO_2 nanoparticles with good dispersion are obtained. With the prolonged reaction time, the combination of ethylenediamine and alcohol, ZrO_2 nanoparticles firstly self-assemble along a grain direction and grow into nanorods, then nanorods were cracked into dispersed nanofibers. Finally, nanofibers were cracked into new thinner and longer nanofibers, with increased fiber length, aspect ratio, and better dispersion.

Acknowledgments

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