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A new preparation method for nano-sized Ce–Zr–Ba mixed oxide with high surface area

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Abstract

In this paper, an optimal way to prepare a new material of nano-sized Ce–Zr–Ba mixed oxide powder is firstly reported. It was found that macromolecule surface modified and azeotropy distill treatment are key factors for controlling particle size and increasing surface area. This new preparation method has the advantages of convenience and inexpensive. Under the optimized preparation conditions, the particle size and surface area of obtained powder are 30–50 nm and 119.0 m^2/g, respectively. The new material of Ce–Zr–Ba mixed oxide offers certain advantages in the use of TWC catalyst. The physical and chemistry properties, crystalline structure, particle sizes, and thermostability are characterized by using XRD, TEM, BET and TGA–DTA techniques. As a comparison, the sample prepared by sol–gel method is also discussed.

Keywords: Preparation method; Ce–Zr–Ba; High surface area; Nano-sized

1. Introduction

Recently, it has been paid more and more interests in the nanometer technology in the fields of catalyst design, for they are considerable interest for electronics, optics, and magnetic storage, especially in the catalysis. Different techniques have been used to prepare nano-sized particles, such as sol–gel method, precipitation-stripping method, and solid-state reaction method [1–5]. But all these methods have the shortcoming of low surface area and the sample is easily agglomeration after high-temperature treatment. Cerium–zirconium mixed oxide is an important kinds of catalyst, which is efficiently used in three-way catalysis (TWC) to treat the automotive exhaust gas [6–8]. The use of cerium–zirconium mixed oxide catalysts in the automotive three-way catalytic converter is mainly as an oxygen storage medium and thermal stabilizer. Despite there are many reports about the application of CeO_2 and Ce–Zr mixed oxide as supporter or additive to some reaction, only a few studies have been paid in the effect of preparation method, particle size, and the character of Ba added into the Ce–Zr mixed oxide. Also, there has been limited work on Ce–Zr mixed oxide in nano-particles.

This paper deals with the preparation of the nano-sized $Ce_{0.7}Zr_{0.3}Ba_{0.1}O_{2.1}$ mixed oxide catalyst by using two different preparation methods. The results reveal that the new preparation method, macromolecule surface modified method, exhibits the following advantage: (1) inexpensive precursors; (2) a nano-sized powder with the particles of 30–50 nm; (3) high surface area of 119.0 m^2/g at the treatment of 650 °C for 4 h; (4) the particle size still at the range of 50–80 nm even treatment by 1000 °C. Moreover, it is noteworthy that this nano-sized $Ce_{0.7}Zr_{0.3}Ba_{0.1}O_{2.1}$ mixed oxide shows novel CO oxidation activity compared with general ceria–zirconium mixed oxide [9]. However, the synthesis of $Ce_{0.7}Zr_{0.3}Ba_{0.1}O_{2.1}$ powder using macromolecule surface modified method has not been reported previously.

The thermal decomposition process of $Ce_{0.7}Zr_{0.3}Ba_{0.1}O_{2.1}$ mixed oxide was investigated by DTA–TGA measurement. The structure character of the sample was studied by using XRD and TEM techniques and the surface area was detected by BET method.

2. Experimental

2.1. Catalysts preparation

Samples A and B were prepared by two different methods such as macromolecule surface modified method and sol–gel method.

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2.1.1. Macromolecule surface modified method

The solutions of $Ce(NO_3)_3{\cdot}6H_2O$, $Zr(NO_3)_3{\cdot}4H_2O$, and $Ba(NO_3)_2{\cdot}6H_2O$ were respectively added to a beaker by a given amount, which was dependent on the designed composition of the mixed oxide. Then the mixed solutions were added into a 5 wt.% polyethylene glycol-20000, the resultant mixture was continuously stirred at room temperature using a magnetic agitator. The gel was put into the refrigerator at the temperature of below 0 °C for 24 h, then adding *n*-butyl alcohol to azeotropy distill. After washing many times, the sample was dried at 120 °C overnight and calcined at 600 °C for 4 h. The sample is denoted as sample A.

2.1.2. Sol–gel method

Analytical grade zirconium nitrate, cerium nitrate, barium nitrate, citric acid, and ethylene diamine tetraacetic acid (EDTA) were used as raw materials to prepare $Ce_{0.7}Zr_{0.3}Ba_{0.1}O_{2.1}$ mixed oxide. The appropriate amounts of metal nitrates and citric acid were dissolved in a certain distilled water. The molar ratio of nitrates to citric acid was 1:1. A small amount of ammonia was added to the solution to adjust the pH to 6. Then, the mixed solution was poured into a beaker and heated at 120 °C for 24 h, the dried gel burnt in a self-propagating combustion manner until all the gels were brunt out completely to form a loose powder and then calcined at 600 °C for 4 h. The sample is denoted as sample B.

2.2. Characterization

The phase identification of the $Ce_{0.7}Zr_{0.3}Ba_{0.1}O_{2.1}$ mixed oxide was performed using X-ray diffraction (XRD) with Cu Kα radiation. Transmission electron microscope (TEM) examination of the synthesized powder was performed using a JEM-200CX electron microscope. Surface area of the samples were measured by BET method, using a OMNISORP 100CX instrument (Carlo Erba). Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) measurement of the precursor gel were carried out at a heating rate of 20 °C/min in N_2 atmosphere.

3. Results and discussion

3.1. Structure character

Fig. 1 gives the X-ray diffraction patterns of $Ce_{0.7}Zr_{0.3}Ba_{0.1}O_{2.1}$ mixed oxide with different preparation methods at 600 °C calcination temperature. All the samples suggest mainly phases as the Ce–Zr solid solution, consisting of three diffraction lines ($d = 3.09$, 1.89, and 1.61). There are no any typical lines of zirconium oxide, cerium oxide, and barium oxide. The unit cell parameters of $Ce_{0.75}Zr_{0.25}O_2$ mixed oxide can be calculated as $a = 5.349$ Å and BaO $a = 5.335$ Å, both are consistent with the isomorphic compounds [10].

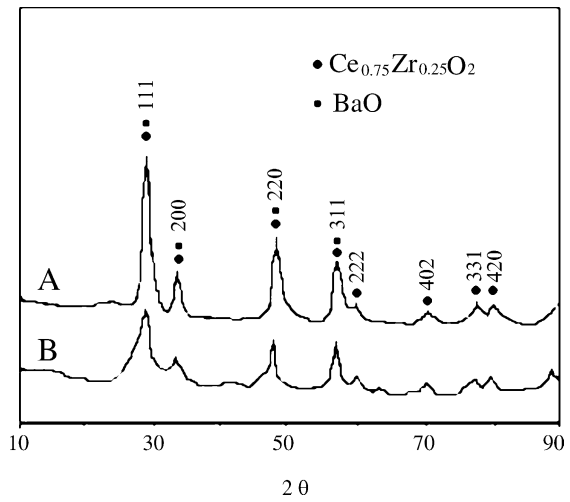

Fig. 1. XRD patterns of $Ce_{0.7}Zr_{0.3}Ba_{0.1}O_{2.1}$ mixed oxide with different preparation method: (A) macromolecule surface modified method; (B) sol–gel method.

Contrast the crystalline with the JCPDS [11], it can detect the diffraction peaks corresponding to $Ce_{0.75}Zr_{0.25}O_2$ and BaO crystal. It is worth to note that the planes (1 1 1), (2 0 0), (2 2 0) and (3 1 1) are superimposed peaks. This indicates that the two phases ($Ce_{0.75}Zr_{0.25}O_2$ and BaO) are too close to be superposition in the crystal. The typical crystal superposition in structure may be favorableness for the dispersion of Ce–Zr and Ba^{2+}, which are optimum for enhancing the surface area. Meanwhile, the typical $Ce_{0.75}Zr_{0.25}O_2$ and BaO crystal line in sample A look stronger than in sample B.

3.2. CO oxidation activity

The comparison of CO oxidation activity of sample A and sample B is shown in Fig. 2. All the samples are calcined at 600 °C for 4 h. Sample A shows apparent novel catalytic activity of CO conversion to 98% at the temperature of 280 °C, it decreases about 200 °C below compared with general ceria–zirconium mixed oxide as reported. Sample A also shows higher catalytic activity compared with sample B. The difference is mainly due to the macromolecule surface modified preparation method, having good function for

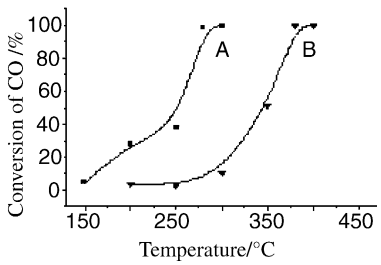

Fig. 2. CO oxidation activity of $Ce_{0.7}Zr_{0.3}Ba_{0.1}O_{2.1}$ mixed oxide with different preparation method: (A) macromolecule surface modified method; (B) sol–gel method.

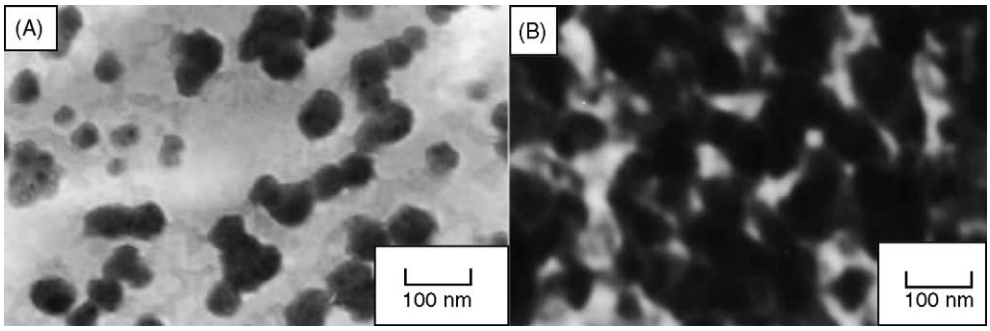

Fig. 3. TEM micrographs of $Ce_{0.7}Zr_{0.3}Ba_{0.1}$ mixed oxide with different preparation method: (A) macromolecule surface modified method; (B) sol–gel method.

controlling distribution of particle size and increasing surface area, then resulting novel catalytic activity. Another key factor of enhance CO oxidation activity can be demonstrated by barium modification ceria–zirconium mixed oxide.

3.3. Particle size

The TEM micrographs of Fig. 3 indicate that the nano-sized particles are formed in sample A and sample B which are calcined at 600 °C for 4 h. The average particle size of sample A is in the range of 30–50 nm and its distribution presents roundness, uniform and agglomeration without. Compared with sample A, there is some particle agglomeration in sample B.

Fig. 4 gives the TEM photographs of sample A calcined at various temperatures. Obviously, it can be viewed that after 800 °C treatment for 4 h, the powder still keep in particles at 50–80 nm in diameter (Fig. 4A). The shape of the particles shows no evident change after treatment at 1000 °C for 4 h (Fig. 4B). This phenomenon indicates that the macromolecule surface modified method treatment results advantage both in good distribution of the particle size and novel resistance to high-temperature treatment.

Table 1 lists the surface areas data of sample A and sample B. The specific surface area of sample A is three times larger than sample B. It indicates that the surface area is also associated with the preparation conditions. After 800 °C temperature treatment, sample A still shows high surface area of 87.4 m^2/g. In another way, the results suggest that the surface area of $Ce_{0.7}Zr_{0.3}Ba_{0.1}O_{2.1}$ mixed oxide increased greatly comparing with Ce–Zr mixed oxide (usually below 30 m^2/g).

Table 1
BET surface area of $Ce_{0.7}Zr_{0.3}Ba_{0.1}$ mixed oxide at different temperature treatment

Catalyst	Surface area (m^2/g)		
	600 °C calcination	800 °C calcination	1000 °C calcination
Sample A	119.0	87.4	23.3
Sample B	38.6	16.8	4.0

3.4. TGA–DTA

Fig. 5 is the DTA–TGA profiles of the dried gel of $Ce_{0.7}Zr_{0.3}Ba_{0.1}O_{2.1}$ mixed oxide with two different preparation methods. It can be seen from Fig. 5 that the decomposition reaction is strong in sample B, in which the weight loss of decomposition water is approximately 50%. The peak at about 320 °C in DTA curve, indicating the decomposition reaction of the EDTA at sample B. Correspondingly, there is below 10% weight loss in sample A, which indicates that the preparation process of the dry water both in the surface and interstitial position of sample can be controlled by azeotropy distilling of *n*-butyl alcohol effectively.

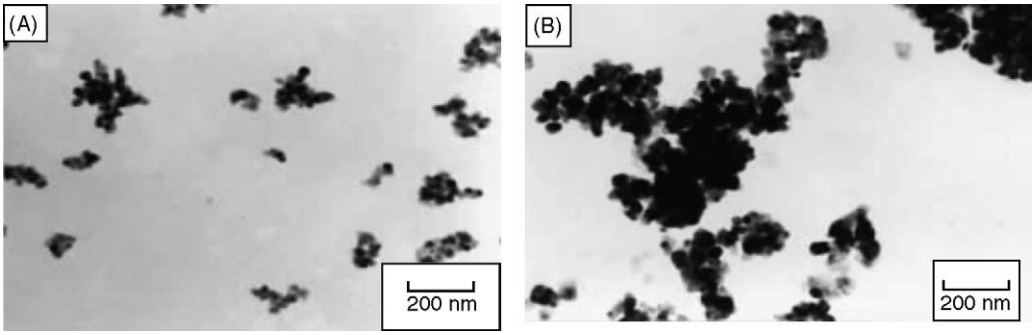

Fig. 4. TEM micrographs of sample A at different calcination temperature: (A) 800 °C for 6 h; (B) 1000 °C for 6 h.

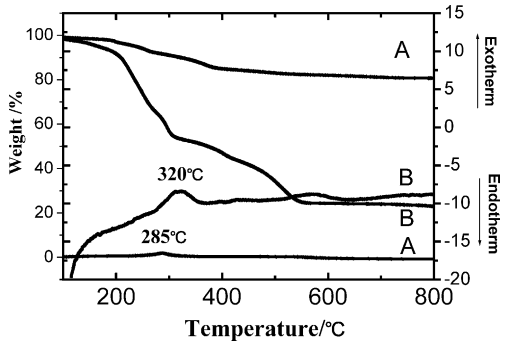

Fig. 5. TGA–DTA profile of $Ce_{0.7}Zr_{0.3}Ba_{0.1}$ mixed oxide with different preparation method: (A) macromolecule surface modified method; (B) sol–gel method.

4. Conclusion

In this paper, a new nano-sized $Ce_{0.3}Zr_{0.7}Ba_{0.1}O_{2.1}$ mixed oxide is attempted using a macromolecule surface modified method. Concluding the above experimental results, it can be seen that the macromolecule surface modified method is a good method to synthesize high surface area, novel catalytic activity and thermal stability of $Ce_{0.7}Zr_{0.3}Ba_{0.1}O_{2.1}$ powder with nano-size. The preparation method is easy to performance and it neither requires expensive nor special equipment like method such as supercritical fluid drying method.

However, much investigation should be conducted in order to further reveal the novel synthesis mechanism.

References

[1] A. Gotoh, K. Kamiya, F. Ikazaki, J. Mater. Sci. Lett. 19 (2000) 217.
[2] H.-Y. Dang, Y.-L. Zhang, J.-K. Liang, S.-S. Xie, J. Mater. Sci. 28 (1993) 5176.
[3] J. Dianzeng, Y. Jianqun, X. Xi, Chin. Sci. Bull. 43 (1998) 571.
[4] A. Piras, A. Trovarelli, G. Dolcetti, Appl. Catal. B 28 (2000) 77.
[5] P. Fornasiero, G. Balducci, J. kaspar, S. Meriani, R. di Monte, M. Graiani, Catal. Today 29 (1996) 47.
[6] J.R. González-Velasco, M.A. Gutiérrez-Ortiz, J.-L. Marc, et al., Appl. Catal. B 33 (2001) 303.
[7] K.C. Taylor, Catal. Rev. Sci. Eng. 35 (1993) 457.
[8] P. Fornasiero, P. Di Monte, G. Ranga Rao, et al., J. Catal. 151 (1995) 168.
[9] E.-G. Wang, S.-Y. Chen, J. Chin. Rare Earth Soc. 19 (2001) 17.
[10] Y.-T. Qian, Introduction to Crystal Chemistry, University of Science and Technology of China Press, 1999.
[11] R.W. Cheary, A.A. Coelho, J. Appl. Cryst. 25 (1992) 109.