SHORT COMMUNICATION

Preparation of CeO$_2$-ZrO$_2$ mixed oxide with high surface area and high thermal stability

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Abstract−Ceria-zirconia solid particles have been recognized as a key material of the automotive exhaust catalysts since they can release and uptake oxygen owing to the rapid reversible oxidation states of cerium between Ce^{3+} and Ce^{4+}. Several methods have recently been described to prepare the CeO$_2$-ZrO$_2$ solid particles used in the catalysts. In this paper, a new coprecipitation method is used to prepare the CeO$_2$-ZrO$_2$ solid particles. The Ce-Zr alcogel is dried and calcined in flowing N$_2$ not in flowing air under atmospheric pressure. The results show that the ceria-zirconia sample calcined at 650 °C has high surface area over 90 m^{2}g^{-1}, which drops to 40 m^{2}g^{-1} following treatment at 900 °C.

Key words: Ceria-zirconia Solid Particles, High Surface Area, Thermal Stability, A New Co-precipitation Method

INTRODUCTION

Cerium oxide, as a non-stoichiometric rare-earth oxide, has been extensively used in heterogeneous catalysis [1], especially in eliminating pollutants (NO$_x$, CO, and hydrocarbons) in automobile exhausts [2,3]. Ceria and zirconia play an integral role in providing oxygen storage, which broadens the conversion efficiency for all three pollutants during rich/lean perturbations associated with the feedback control regulating the air-to-fuel ratio used by the engine. Additionally, these components (Ce, Zr) favor noble metal dispersion, increase thermal stability, and promote water-gas shift, steam reforming, CO oxidation reactions and partial oxidation of methane or isooctane [4-8].

Several methods have been explored to synthesize CeO$_2$-ZrO$_2$ powders. Solid state reaction method shows the homogenization of the CeO$_2$-ZrO$_2$ composition [9]. However, this method gives materials with very low surface area. More homogeneous compounds are generally prepared via chemical methods, such as co-precipitation techniques [10], hydrothermal synthesis [11], spray pyrolysis [12], physical gelation [13], solution combustion [14], sol-gel [15], and the microemulsion methods [16]. The surface areas of ceria-zirconia obtained by conventional co-precipitation or sol-gel methods are typically in the range 60-90 m^{2}g^{-1} after calcination in air at 400-500 °C [17,18]. Surface areas over 100 m^{2}g^{-1} have been reported for materials obtained from CeO$_2$-ZrO$_2$ aerogels, while the supercritical drying of the precursor hydrogels is needed [19].

In the present investigation, a further modification of co-precipitation method is made to avoid the use of the high pressure of supercritical ethanol for drying the alcogel. Instead, the alcogel is processed in flowing nitrogen under atmospheric pressure. By comparison with those from co-precipitation method in air, we show that this novel processing with atmospheric nitrogen can form small CeO$_2$-ZrO$_2$ nanocrystals that are resistant to sintering up to 900 °C.

EXPERIMENTAL

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Aqueous solutions with molar concentration ratios of cerium nitrate to zirconium oxynitrate in series were used as starting materials. The molar concentration ratio of Ce to Zr ions, Zr/(Ce+Zr), in the solution changed from 0 to 100 mol% at intervals of 10 mol%. Precipitations were obtained by adjusting pH with ammonia solution with careful control of pH=10. The precipitated Ce-Zr hydrogel was left to digest in the solution for 10 h at room temperature before it was separated by filtration and washed with doubly deionized water. Half of the Ce-Zr hydrogel was taken for drying in air at 110 °C. The hydrogel was then calcined in air at 650 °C. The sample thus prepared was coded as CeO$_2$-ZrO$_2$-650air. The remaining Ce-Zr hydrogel was changed to alcogel being washed with anhydrous ethanol for several times. The alcogel was placed in a quartz tube reactor and dried/calcined at different temperatures (heating to 110 °C at a rate of 2 °C/min and then to the desired temperature at 5 °C/min) in flowing N$_2$ under atmospheric pressure. The flowing rate of N$_2$ is 50 ml/min. The sample prepared with this processing is named CexZry-T, in which x:y is the molar ratio of Ce:Zr, T is the calcined temperature.

Surface areas of the samples were measured with nitrogen adsorption at −196 °C on a thermo Finnigan Sorptomatic 1990 instrument. The samples were dehydrated with a flow of dry nitrogen at 300 °C for 5 h before the adsorption measurement.

The crystal structures of CeO$_2$-ZrO$_2$ samples were characterized with powder X-ray diffraction by using the Cu Kα source at 40 kV and 40 mA. The crystal size of CeO$_2$-ZrO$_2$ was measured from the X-ray broadening analysis by using the well-known Scherrer equation.

TEM measurement of the sample was performed on a Hitachi H-800 electron microscope.

RESULTS AND DISCUSSION

The nitrogen adsorption/desorption isotherms of Ce6Zr4-650 are shown in Fig. 1. It exhibits a typical Type IV shape. The p/p$_0$ position of the inflection point corresponds to a diameter in the mesopore range, and the BJH pore size distribution is narrow and centered at about 4 nm, indicating a uniform pore size distribution in the sam-
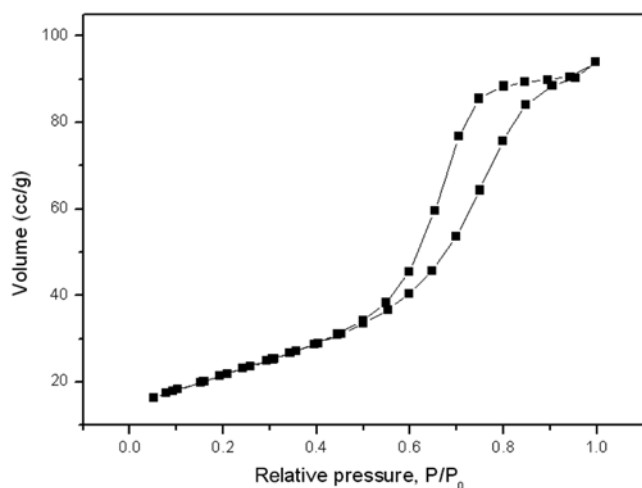
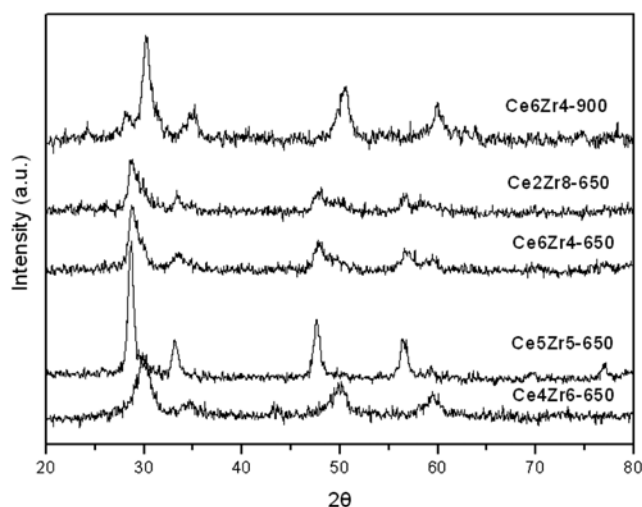**Fig. 1. Nitrogen adsorption/desorption isotherms of the Ce6Zr4-650 sample.**

Fig. 2. XRD patterns of the CeO$_2$-ZrO$_2$ samples.

Fig. 3. TEM photograph of Ce6Zr4-650.

Table 1. Surface area of the CeO$_2$-ZrO$_2$ samples

Sample	A$_{BET}$/(m^{2}g^{-1})
Ce2Zr8-650	128.89
Ce4Zr6-650	119.89
Ce5Zr5-650	109.99
Ce6Zr4-650	91.45
Ce6Zr4-650air	51.32
Ce6Zr4-900	42.99

the particles grow and the sample prepared by the N$_2$ calcination method has good high thermal stability.

The TEM photograph of CeO$_2$-ZrO$_2$ in Fig. 3 shows that the particle size is 15 nm, which is a little bigger than that obtained by the XRD spectra with the line-broadening method. The particles of the sample prepared by the method with N$_2$ atmosphere calcination are very fine and near-spherical.

Table 1 compares the properties of the calcined CeO$_2$-ZrO$_2$ products. The CeO$_2$-ZrO$_2$-650air shows a surface area of 51.32 m^{2}g^{-1}. These data are comparable with literature values of CeO$_2$-ZrO$_2$ species. On the other hand, the surface area value becomes 91.45 m^{2}g^{-1} after being dried and calcined in flowing N$_2$, which is almost two-fold higher than that of the CeO$_2$-ZrO$_2$-650air. Even after the calcination at 900 °C, a surface area of 42.99 m^{2}g^{-1} is maintained, which is only a bit smaller than that of the CeO$_2$-ZrO$_2$-650air. The results of the surface area also show that the surface area of the CeO$_2$-ZrO$_2$ increases with the increase of the Zr content, in which the Ce2Zr8-650 sample shows the highest surface area (128.89 m^2/g). This agrees with the results by Yao et al. [20]. They proved that the particle size of the CeO$_2$-ZrO$_2$ decreased with increasing zirconia loading.

The metal oxides prepared by the method of air drying and calcination are present as very large and hard aggregates, which sinters nanocrystals and reduces the surface areas [21]. In contrast, the CeO$_2$-ZrO$_2$ oxides prepared by the method of N$_2$ drying and calcinations are present as discrete nanocrystals and much less crystal aggregation, which shows excellent thermal stability and keeps a high sur-

ple. Even after calcination at 900 °C, this mesoporous structure is still maintained, which shows that these mixed oxides have good thermal stability.

Typical XRD patterns of the mixed oxides are shown in Fig. 2. The diffraction peaks accord well with that of the CeO$_2$-ZrO$_2$ solid particles. The results suggest that CeO$_2$-ZrO$_2$ preferably crystallizes into a cubic structure when the content of Ce is equal or lower than 0.6. The presence of the cubic phase only in the samples indicates that Ce and Zr are highly homogeneously distributed. On the other hand, the evidence of a tetragonal phase is found when the content of Ce reaches 0.8. It is noted that the monoclinic phase is preferable when the sample is calcined at 900 °C. The diffraction peaks of single oxide have not been observed. The diffraction peaks reinforce and the peak breadth narrows with the increase of the calcination temperature. The broad peaks are attributed to the small crystallites. The average particle size of the samples can be estimated by the line-broadening method. The average particle size of the samples calcined at 650 °C and 950 °C for 4 h is 8.5 and 12.2 nm, respectively. The results show that a high temperature treatment makes
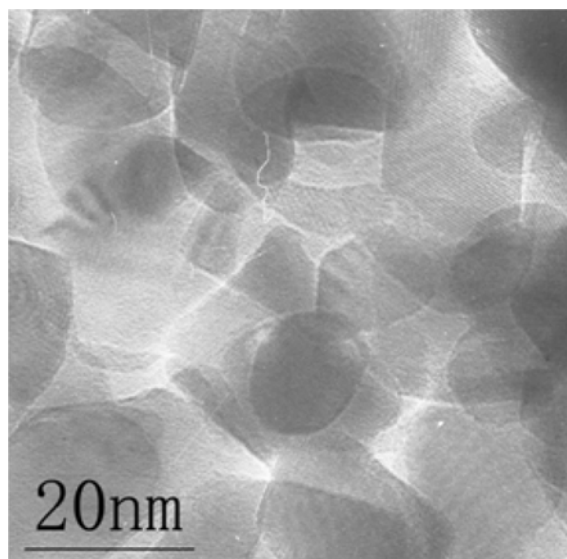
face area. The present data demonstrate that thermal processing on the hydroxide alcogel in flowing N$_2$ derived from conventional inorganic metal salt is a good method for the preparation of small nano crystallite of CeO$_2$-ZrO$_2$.

CONCLUSION

CeO$_2$-ZrO$_2$ particles with excellent thermal stability have been successfully synthesized by a co-precipitation method and calcination in flowing nitrogen, not in air. The sample calcined at 650 °C for 4 h exhibits fine nanoparticles and a high surface area. It has a high surface area even after being calcined at 900 °C and is superior to the sample prepared by normal co-precipitation method.

REFERENCES

1. A. Trovarelli, *Catal. Rev.-Science & Engineering*, **38**, 439 (1996).
2. P. Fornasiero, G. Balducci, J. Kaspar, S. Meriani, R. Di Monte and M. Graziani, *Catal. Today*, **29**, 47 (1996).
3. J. C. Summers, J. E. Sawyer and A. C. Frost, *ACS Symp. Ser.*, **495**, 98 (1992).
4. R. J. Farrauto and R. M. Heck, *Catal. Today*, **51**, 351 (1999).
5. J. Kaspar, P. Fornasiero and M. Garziani, *Catal. Today*, **50**, 285 (1999).
6. B. S. Shin, J. H. Bae, J. P. Yoo, S. J. Choung, Y. Song and G. K. Yeo, *Korean J. Chem. Eng.*, **15**, 474 (1998).
7. Z. W. Liu, H. S. Roh, K. W. Jun, S. E. Park and T. K. Song, *Korean J. Chem. Eng.*, **19**, 735 (2002).
8. Praharso, A. A. Adesina, D. L. Trimm and N. W. Cant, *Korean J. Chem. Eng.*, **20**, 468 (2003).
9. A. Suda, T. Kandori, N. Terao, Y. Ukyo, H. Sobukawa and M. Sugiura, *J. Mater. Sci. Lett.*, **17**, 89 (1998).
10. S. Rossignol, Y. Madier and D. Duprez, *Catal. Today*, **50**, 261 (1999).
11. M. P. Kapoor, A. Raj and Y. Matsumura, *Micropor. Mesopor. Mater.*, **44-45**, 565 (2001).
12. T. Yoshioka, K. Dosaka, T. Sato, A. Okuwaki, S. Tanno and T. Miura, *J. Mater. Sci. Lett.*, **11**, 51 (1992).
13. T. Settu and R. Gobinathan, *Bull. Chem. Soc. Jpn.*, **67**, 1999 (1994).
14. A. S. Prakash, A. M. A. Khadar, K. C. Patil and M. S. Hegde, *J. Mater. Synth. Process.*, **10**, 135 (2002).
15. M. F. Luo, G. L. Lu and X. M. Zheng, *J. Mater. Sci. Lett.*, **17**, 1553 (1998).
16. A. A. Martinez, G. M. Fernandez, V. Balleseros, L. M. Salamance, J. C. Conesa, C. Otero and J. Soria, *Langmuir*, **15**, 4796 (1999).
17. P. Forhasiero, G. Balducci, R. Di Monte, J. Kaspar, V. Sergo, G. Gubitosa, A. Ferrero and M. Graziani, *J. Catal.*, **164**, 173 (1996).
18. C. De Leitenburg, A. Trovarelli, G. Bini, F. Cavani and J. Llorca, *Appl. Catal. A: General*, **139**, 161 (1996).
19. Y. Sun and P. A. Sermon, *J. Mater. Chem.*, **6**, 1025 (1996).
20. M. H. Yao, R. J. Baird, F. W. Kunz and T. E. Hoost, *J. Catal.*, **166**, 67 (1997).
21. B. Q. Xu, J. M. Wei, Y. T. Yu, J. L. Li and Q. M. Zhu, *Topics Catal.*, **22**, 77 (2003).