Short Note

Preparation and Catalytic Property of CeO₂ Nanoparticles/YTZ Pellet CatalystTakashi HATTORI^{1*}, Masatomo HATTORI² and Masakuni OZAWA²¹Department of Materials Science and Engineering, Graduate School of Engineering, Nagoya University,
Furo-cho, Chigusa-ku, Nagoya 464-8603, Japan.²Institute of Materials and Systems for Sustainability, Nagoya University, Furo-cho, Chigusa-ku, Nagoya 464-8603, Japan.

Received November 29, 2017; Revised February 27, 2018; Accepted March 22, 2018

ABSTRACT

This study deals with the preparation of CeO₂ nanoparticles (NPs) catalyst supported by YTZ ball ceramics, and investigations of its morphology and hydrogen oxidation property. A CeO₂ NP layer was prepared by a simple dipping process. As the results, the CeO₂ NPs maintained the high dispersion state even after heat treatment at 1000°C. According to H₂-TPR measurement, it was also found that a CeO₂ NPs-modified YTZ sample has better catalytic property than CeO₂ powder. Thus, the catalytic functionalized YTZ ball-type ceramic was provided by simple processing with the modification of CeO₂ NPs as a novel catalytic material.

KEY WORDS

CeO₂, nanoparticle, catalyst, YTZ, dispersion

1 Introduction

Metal oxide nanoparticles (NPs) have received a lot of attention owing to the novel functions that are different from those of the bulk materials¹⁾. Ceria (CeO₂) NPs are one of the important materials for a wide range of applications in fuel cell¹⁰⁾, solar cells¹¹⁾, oxygen sensors¹²⁾, and catalysts including water-gas shift reaction and automotive catalysts¹³⁾. In all these cases, the use of nanostructured CeO₂-based materials is expected to improve the properties in comparison with micrometer-sized or bulk-like materials¹⁴⁾. CeO₂ is able to release its oxygen under a reducing atmosphere and store oxygen under an oxidizing atmosphere, and therefore facilitating the maintenance of the gaseous stoichiometric condition for sustained CO and HC oxidation and simultaneous NO_x reduction^{22,23)}. The catalytic activity of CeO₂ was found to be significantly enhanced by nanometer-sized particles compared with their bulk counterparts and was attributed to their high surface area to volume ratio. However, NPs have tendency to be sintered and to grow at elevated temperature owing to their high surface energy.

In our previous study, we investigated the preparation, morphology and catalytic behavior of a CeO₂ NP layer on Al₂O₃(0001)²⁴⁾. This system exhibited smaller crystallinity of CeO₂ NPs with less than 40 nm in size which could highly dispersed on the substrate even after heat treatment at 1000°C in air. In general, the TWC system employs a ceramic monolith held subjected in the exhaust gas

stream²⁵⁾, and several works reported that the properties of CeO₂-based TWC catalyst could be improved by element doping such as, zirconium (Zr) and yttrium (Y)^{26,27)}. Recently, yttria stabilized tetragonal zirconia (YTZ) balls can be used mainly as grinding media. In this work, we prepared CeO₂ NPs catalyst supported by YTZ ball ceramics, and investigated its morphology and hydrogen oxidation property. The results showed that highly dispersed CeO₂ NPs could be maintained on YTZ balls even after heat treatment at 1000°C and exhibited better catalytic property than the CeO₂ powder.

2 Experimental methods

2.1 Synthesis of CeO₂ nanoparticles and catalyst

Starting CeO₂ was prepared by hydrothermal method in previous papers. Briefly, aqueous solutions of diammonium cerium(IV) nitrate ((NH₄)₂Ce(NO₃)₆) and potassium oleate (C₁₇H₃₃COOK), were mixed, and followed by addition of ammonia aqueous solution. The mixture was then sealed in a Teflon-lined stainless steel autoclave and heated at 200°C for 48 h, and the products were separated from the reaction solution by centrifugation^{28,29)}, washed with distilled water and dried at 90°C for 24 h in air, and then dispersed in toluene (C₆H₅CH₃), leading to stable colloid solution. Yttria-stabilized-zirconia ceramic balls (YTZ[®] ball; Nikkato CO., Japan; 1 mm diameter) were cleaned in an ethanol ultrasonic bath for 10 min, and then these were blown dry for a minute with air. These were dipped in the CeO₂ colloidal solution and dried, and then calcined at 400°C for 3 h in air, followed by heat treatment at 1000°C for 3 h in air. As a reference, a portion of the CeO₂ NPs

* Corresponding author, E-mail: hattori.takashi@h.mbox.nagoya-u.ac.jp

** The content of this article had been presented at JSPMIC2017.

were calcined at 400°C for 3 h in air, followed by heat treatment at 1000°C for 3 h in air.

2.2 Characterization

X-ray diffraction (XRD) analysis was performed on Rigaku MiniFlex II with Cu-K α radiation. The crystallite size of CeO₂ was determined by measuring the physical broadening of individual diffraction profiles using the Scherrer formula³⁰. The surface microstructure of the CeO₂ NP layer on YSZ ball was observed using a field emission scanning electron microscope (FE-SEM; Hitachi S-4800). The catalytic properties were investigated by a temperature-programmed reduction with hydrogen (H₂-TPR) measurement using a BP-1 apparatus (Hemmi Slide Rule). A reaction mixture containing 5 vol% H₂ in Ar was supplied at a flow rate of 30 mL min⁻¹. In the reaction mixture, the sample was heated from 30 to 600°C at a rate of 10°C/min. The hydrogen consumption as a function of temperature was continuously monitored by a cell of a thermal conductivity detector (TCD). For the H₂-TPR measurements, 0.1 g of CeO₂ powder and 1.3 $\times$ 10⁻³ g CeO₂ NPs loaded CeO₂-modified YSZ pellet catalyst (3.55 g) were set in the reactor made from quartz, respectively.

3 Results and discussion

3.1 Characterization of CeO₂ powder and CeO₂-modified YSZ pellet catalyst

Fig. 1 shows the XRD patterns of CeO₂ powder as-dried and heated at 1000°C. For both samples, only peaks assigned the fluorite cubic structure of CeO₂ were found, and no other impurity phase was observed. The crystallite sizes of CeO₂ powder as-dried and heated at 1000°C determined via X-ray line broadening of the (220) peaks were 5 and 52 nm, respectively. The observed crystallite growth of CeO₂ particles is a typical phenomenon between particles, followed by grain growth after the coarsening of particles. Therefore, CeO₂ powder become the larger grains and induced the surface area loss, due to sintering after heat treatment at 1000°C.

Fig. 1 XRD patterns of CeO₂ powder as-dried and heated at 1000°C for 3 h in air.

Fig. 2 shows the images of CeO₂-modified YSZ pellet catalyst. Fig. 2 (a) is the optical picture of one YSZ ball sample with a diameter of 1 mm. Figs. 2 (b) and 2 (c) compare the FE-SEM images of bare YSZ ball surface and the surface of the CeO₂ NPs supported on YSZ ball, after heat treatment at 1000°C, respectively. In comparison with the smooth surface of bare YSZ ball, the granular microstructure of the CeO₂ NPs layer on YSZ ball appeared. Fig. 2 (d) shows the cross-sectional FE-SEM image of CeO₂ NPs layer on YSZ ball. The film thickness from the image

Fig. 2 (a) Optical picture of YSZ ball, surface FE-SEM images of (b) bare YSZ ball, and (c) CeO₂ NP layer on YSZ ball after heat treatment at 1000°C and (d) cross-sectional FE-SEM image of CeO₂ NP layer on YSZ ball after heat treatment at 1000°C.

was ca. 150 nm. The CeO₂ NPs composed of small grains with sizes below several tens of nanometers. Also it was observed that the CeO₂ NP layer contained the pores between particles, indicating the high dispersion and porous state of CeO₂ NPs even after heat treatment at 1000°C. In our previous paper²⁴⁾, the substrate showed the similar effect on maintaining the less contacted state of CeO₂ NPs in the system of CeO₂ and the Al₂O₃ substrate. It was concluded that the migration and coarsening of CeO₂ NPs and further sintering were inhibited on the Al₂O₃ substrate. It is suggested that the interaction between CeO₂ NPs on YTZ ball substrate hinders the sintering of the CeO₂ NPs.

3.2 Catalytic properties

Fig. 3 (a) shows the H₂-TPR profiles of the CeO₂ powder heated at 1000°C for 3 h in air. The TCD signal (the y-axis) means the gaseous hydrogen consumption on catalysts with oxygen gas content (H₂/Ar). Since the reaction system contains no gaseous oxygen, all the hydrogen consumption corresponds to the oxidation of gaseous hydrogen into H₂O, which is attributed to active oxygen by the reduction of CeO₂ according to the following total reaction^{31,32)}:

CeO₂ powder shows the hydrogen consumption starting at approximately 400°C and exhibited the maximum reaction rate at approximately 620°C (out of range in Fig. 3 (a)). In general, the hydrogen consumption of CeO₂ was started by the reduction of the surface capping oxygen (e.g. adatoms or activated oxygen adsorbed) at low temperatures¹⁵⁾. Yao et al. reported that the main hydrogen consumption phenomena were followed at higher temperature region and attributed to reduction in surface and deep bulk region of CeO₂ at around 600°C. This means the oxygen storage capacity of CeO₂ by release of lattice oxygen for reaction with reactant (hydrogen). On the other hand, Fig. 3 (b) shows the H₂-TPR profiles of YTZ balls (dashed line) and the CeO₂ NPs-modified YTZ ball catalyst (solid line) heated at 1000°C. The CeO₂ NPs-modified YTZ ball catalyst shows the two hydrogen consumption peaks in the temperature region of 400–600°C (below 600°C), attributing to the H₂ consumption with different kind of surface oxygen species. It is assumed that the peak amplitude ratio of surface oxygen (low temperature peak) to lattice oxygen (high temperature peak) for CeO₂ NPs, as discussed in our previous paper. In the system of CeO₂ supported on YTZ ball, a high surface-to-volume ratio of CeO₂ is expected by the morphology of the dispersed (less-connected) NPs on the substrate. The TPR result indicates that a CeO₂ NPs-modified YTZ sample shows more active for a reaction (1) than that of CeO₂ powder because the maximum oxidation rate of H₂ over a ball catalyst is found to move to low temperature region (at around 480°C). Since the dispersed CeO₂ NPs are successfully deposited on YTZ ball, even after heat treatment at 1000°C in air, NPs will bring better oxygen storage capacity at lower temperatures. It suggests better fundamental properties for various reactions as catalyst by dispersing of NPs on the present substrate. Thus, the catalytic functionalized YTZ ball-type ceramic was provided by a simple processing with the modification of CeO₂ NPs as a novel catalytic material.

4 Conclusions

We investigated the preparation, morphology and catalytic property of a CeO₂ NPs-modified YTZ ball catalyst. The CeO₂ NP layer on YTZ ball was composed of dispersed particles with sizes below several tens of nanometers. The CeO₂ NPs maintained the high dispersion state even after heat treatment at 1000°C. According to H₂-TPR measurement, the prepared YTZ ball showed better catalytic property than CeO₂ powder. It was concluded that the YTZ ball catalyst in this work was useful as the functionalized support material with CeO₂ NPs.

Acknowledgment

This work was financially supported by the Project of Creation of Life Innovation Materials for Interdisciplinary and International

Fig. 3 H₂-TPR profiles of (a) CeO₂ powder heated at 1000°C and (b) YTZ balls (dashed line) and CeO₂ NPs/YTZ catalyst (solid line) heated at 1000°C. Hydrogen consumption corresponds to the oxidation of gaseous hydrogen to H₂O by CeO₂; $\text{CeO}_2 + x\text{H}_2 \rightarrow \text{CeO}_{2-x} + x\text{H}_2\text{O}$.

Researcher Development of the Ministry of Education, Culture, Sports, Science and Technology, Japan, and by Grant-in-Aid for Scientific Research No. 17H03100 from the Japan Society for the Promotion of Science.

- (1) We prepared the CeO₂ (NPs) catalyst supported by YSZ ball ceramics by a simple dipping process.
- (2) The CeO₂ NPs supported on YSZ ball maintained the high dispersion state even after heat treatment at 1000°C, and has better catalytic property than CeO₂ powder.
- (3) We found that the catalytic functionalized YSZ ball-type ceramic was provided by a simple processing with the modification of CeO₂ NPs as a novel catalytic material.

References

- 1) J. Dai, M. L. Bruening: *Nano Lett.*, **2** (2002) 497-501.
- 2) P. K. Sudeep, B. I. Ipe, K. G. Thomas, M. V. George, S. Barazzouk, S. Hotchandani, P. V. Kamat: *Nano Lett.*, **2** (2002) 29-35.
- 3) M. Merschdorf, W. Pfeiffer, A. Thon, S. Voll, G. Gerber: *Appl. Phys. A*, **71** (2000) 547-552.
- 4) C. J. Zhong, M. M. Maye: *Adv. Mater.*, **13** (2001) 1507-1511.
- 5) B. C. Gates: *Chem. Rev.*, **95** (1995) 511-522.
- 6) Y. Kim, R. C. Johnson, J. T. Hupp: *Nano Lett.*, **1** (2001) 165-167.
- 7) A. Ruiz, J. Arbiol, A. Cirera, A. Cornet, J. R. Morante: *Mater. Sci. Eng. C*, **19** (2002) 105-109.
- 8) X. G. Li, S. Takahashi, K. Watanabe, Y. Kikuchi, M. Koishi: *Nano Lett.*, **1** (2001) 475-480.
- 9) X. Sun, A. Gutierrez, M. J. Yacaman, X. Dong, S. Jin: *Mater. Sci. Eng. A*, **286** (2000) 157-160.
- 10) E. P. Murray, T. Tsai, S. A. Barnett: *Nature*, **400** (1999) 649-651.
- 11) A. Corma, P. Atienzar, H. Garcia, J. Y. C. Ching: *Nat. Mater.*, **3** (2004) 394-397.
- 12) H. J. Beie, A. Gnorich: *Sens. Actuators B*, **4** (1991) 393-399.
- 13) Q. Fu, H. Saltsburg, M. Flytzani-Stephanopoulos: *Science*, **301** (2003) 935-938.
- 14) J. Xu, J. Harmer, G. Li, T. Chapman, P. Collier, S. Longworth, S. C. Tsang: *Chem. Commun.*, **46** (2010) 1887-1889.
- 15) H. C. Yao, Y. F. Yu Yao: *J. Catal.*, **86** (1984) 254-265.
- 16) R. K. Herz, J. A. Sell: *J. Catal.*, **94** (1985) 166-174.
- 17) E. C. Su, W. G. Rothschild: *J. Catal.*, **99** (1986) 506-510.
- 18) M. Ozawa, M. Kimura, A. Isogai: *J. Alloys Compd.*, **193** (1993) 73-75.
- 19) M. Sugiura, M. Ozawa, A. Suda, T. Suzuki, T. Kanazawa: *Bull. Chem. Soc. Jpn.*, **78** (2005) 752-767.
- 20) S. Matsumoto, H. Shinjoh: *Adv. Chem. Eng.*, **33** (2008) 1-47.
- 21) K. Sohlberg, S. T. Pantelides, S. J. Pennycook: *J. Am. Chem. Soc.*, **123** (2001) 6609-6611.
- 22) T. X. T. Sayle, S. C. Parker, D. C. Sayle: *Phys. Chem. Chem. Phys.*, **7** (2005) 2936-2941.
- 23) J. Zhang, H. Kumagai, K. Yamamura, S. Ohara, S. Takami, A. Morikawa, H. Shinjoh, K. Kaneko, T. Adschiri, A. Suda: *Nano Lett.*, **11** (2011) 361-364.
- 24) T. Hattori, K. Kobayashi, M. Ozawa: *Jpn. J. Appl. Phys.*, **56** (2017) 01AE02.
- 25) J. T. Kummer: *Prog. Energy Combust. Sci.*, **2** (1980) 177-199.
- 26) M. Bonne, M. Haneda, D. Duprez, M. Ozawa: *Catal. Commun.*, **19** (2012) 74-79.
- 27) H. He, H. X. Dai, K. W. Wong, C. T. Au: *Appl. Catal. A*, **251** (2003) 61-74.
- 28) T. Taniguchi, K. Katsumata, S. Omata, K. Okada, N. Matsushita: *Cryst. Growth Des.*, **11** (2011) 3754-3760.
- 29) K. Kobayashi, M. Haneda, M. Ozawa: *ECS Trans.*, **50** (2013) 39-49.
- 30) P. Scherrer: *Math.-Phys. Klasse*, **2** (1918) 98-100.
- 31) T. Desauvay, G. Bonura, V. Chiodo, S. Freni, J.-P. Couzinie, J. Bourgon, A. Ringuede, F. Labat, C. Adamo, M. Cassir: *J. Catal.*, **297** (2013) 193-201.
- 32) A. Laachir, V. Perrichon, A. Badri, J. Lamotte, E. Catherine, J. C. Lavalley, J. El Fallah, L. Hilaire, F. Le Normand, E. Quemere, N. S. Sauvion, O. Touret: *J. Chem. Soc., Faraday Trans.*, **87** (1991) 1601-1609.