Paper

Oxygen Release Property of Ceria/Alumina Composite Powder in Reducing Atmosphere at Low Temperatures

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ABSTRACT

Oxygen release property of ceria (CeO_2) in ceria/alumina composite powder by hydrogen was examined by the temperature-programmed reduction technique below the temperature of 600°C . The results suggested the strong interaction and the structural relaxation at the interface of CeO_2 and Al_2O_3 after the redox treatment at low temperatures. The activation energy of oxygen release by hydrogen was determined as 85 ± 15 kJ/mol for the interface of $\text{CeO}_2/\text{Al}_2\text{O}_3$. Furthermore it increased to 194 ± 25 kJ/mol after the redox treatment, because oxygen was stabilized at the interface between alumina and ceria. This means that the interface is stabilized to produce the relaxed structure of interface in which oxygen is also stabilized.

KEY WORDS

ceria, alumina, interface, oxygen release, oxygen storage capacity

1 Introduction

Cerium oxide (CeO_x) is useful as a textural and structural promoter of ceramics as well as an additive for stabilization of alumina catalytic support¹⁻⁴⁾. The crystalline oxides of cerium have two polymorphs, CeO_2 and Ce_2O_3 , and also a series of CeO_{2-x} with oxygen defects are available as catalyst and oxygen getter in redox process^{5,6)}. The composite material between CeO_2 and Al_2O_3 is a typical raw composition and one of important catalytic materials for the removal of CO, hydrocarbons and nitrogen oxides from gasoline engine exhaust gas. The ceria also is required for controlling oxygen content by oxygen storage capacity (OSC) for achieving the precise oxygen pressure in reaction conditions^{1,3,4,7,8)}. The OSC has been known to be related to the redox and nonstoichiometry of CeO_2 -related compounds, and modified by the addition of ZrO_2 . In the system of CeO_2 - Al_2O_3 , CeO_2 stabilize the metastable phase of alumina and inhibit the sintering at elevated temperature⁹⁻¹¹⁾. Also, the solid state reaction between CeO_2 and Al_2O_3 forms crystalline CeAlO_3 at as higher temperature as 900°C if it is treated under reducing condition including hydrogen-containing gas^{11,12)}. While recently, it was reported that in the low temperature region ceria has been stabilized as nanoparticles on alumina, and induced better oxygen evolution properties¹³⁾. CeO_2 nanoparticle is potentially useful as active catalyst and

additive agents for sintering at low temperatures, so the interaction between nanoparticles and its substrate or support at the interface will become important factor. In this work, by using the hydrogen temperature-programmed reduction technique, we have indicated the existence of strong interaction at the interface between CeO_2 and Al_2O_3 particles under reducing atmosphere below 600°C . We have found unordinary phenomena of ceria particles mixed with alumina, in which the redox of $\text{CeO}_2/\text{Al}_2\text{O}_3$ is possible in as low temperature region as 600°C . This is new findings about ceria additive in alumina which will potentially be useful in the case of use of ceria as agent in redox heat condition as well as heterogeneous catalytic reaction.

2 Experimental

The composite powder between CeO_2 and Al_2O_3 ($\text{CeO}_2 : \text{Al}_2\text{O}_3 = 3 : 10$ in molar ratio) was prepared by the impregnation-mixing process of alumina powder (Sumitomo chemical, AKPG015, surface area $135 \text{ m}^2/\text{g}$, Japan) into an aqueous solution of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Wako, 99.9 % purity, Japan). The mixed slurry was dried overnight at 110°C , and heated at 500°C for 3 h in air, and then was heated at 600°C for 3 h in air. The crystalline phase in powders was identified by an X-ray powder diffractometer (XRD, Rigaku Rint-2000) with $\text{CuK}\alpha$ X-ray source (40 kV–40 mA) and laser Raman spectroscopy

(JASCO NRS-3100). A field emission scanning electron microscope (FESEM, JEOL-JSM7000F) and transmission electronic microscope (TEM, JEOL-JEM2000EX) were used for analyses of the morphology in the samples. Specific surface area was measured by nitrogen adsorption at 77 K on heated powder at 200 °C using Shibata SA1100 system.

Oxygen evolution from powders was examined by temperature-programmed reduction in H_2 (H_2 -TPR)^{16–18}. It was performed by using a lab-designed BP-1S (Okura-Riken Co.), which is equipped with a microreactor of quartz and a thermal conductivity detector (TCD) to monitor the composition change of gas. 5 % H_2 /Ar flowing gas was passed over 0.1 g powder at temperatures of 50–600 °C with a constant heating rate. The change of gas composition was presented as TCD signals (the consumption of H_2 due to $H_2 + O(\text{surface}) \rightarrow H_2O$) versus temperature. The heating rate was changed in a series of experiments from 5 °C/min to 20 °C/min. The activation energy E and rate constant k for the reaction: $CeO_2 + xH_2 = CeO_{2-x} + xH_2O$ was measured by assumption of the first order reaction between H_2 and CeO_2 . Here, CeO_2 release oxygen on its surface and immediately the oxygen react with H_2 . The plot of $\ln(k)$ versus $1/T$ provides a straight line, where k is rate constant at the rate-maximum (peak in TPR curve) temperature, so that E is simply obtained by the measurements with several different heating rates in reducing heat treatment of TPR experiments.

The oxygen absorption amount was measured after the reducing heat treatment of the powder at temperatures of 50–600 °C with a heating rate of 10 °C/min and kept at 600 °C for 20 min in flowing 5 % H_2 /Ar. The oxygen gas pulse was injected to the sample at 600 °C in flowing He,

and then total amount of oxygen absorbed was identified as the oxygen absorption amount. This is equal to total amount of oxygen storage capacity (OSC) of a powder in practice. In addition, the second TPR and O_2 pulses run was performed in the same apparatus without changing the sample set, temperature-gas schedule and apparatus just after cooled down in the first run.

3 Result and discussion

3.1 Crystalline phase and microstructure

The XRD indicated the mixture of two phases: CeO_2 and $\gamma\text{-Al}_2O_3$ in a prepared powder after heat treatment at 600 °C, as shown in Fig. 1. The crystallite size of CeO_2 was measured, using Hall's equation from XRD peak broadness versus diffraction angle, and was determined as 20 nm in diameter. Figure 2 shows the Raman spectra of commercial CeO_2 powder and present CeO_2/Al_2O_3 composite. Although the crystalline CeO_2 itself shows only a single peak around 450 cm^{-1} (Fig. 2 (a)), additional scattering peaks at around 250 and 600 cm^{-1} was observed in present composite powder (Fig. 2 (b)). These signals suggested the existence of the defects introduced in the CeO_2 crystal lattice, which were characteristics for the dispersed CeO_2 on Al_2O_3 . The impregnation process followed by heat treatment might induce the diffusion of Al and Ce at interface as well as surface of powders, so that surface and interface defect of CeO_2 is introduced by small amount of Al cation (trivalent) into CeO_2 . Other factor, which affects Raman spectra, is the large distortion of CeO_2 lattice which is forced by surface of Al_2O_3 . However, the new signal representing different symmetry (250 and 600 cm^{-1}) is more likely to defects by contacting or doping of Al_2O_3 .

Fig. 1 XRD of a prepared powder after heat treatment at 600 °C. ■: CeO_2 , ○: $\gamma\text{-Al}_2O_3$.

Fig. 2 Raman spectra of commercial CeO_2 powder (a) and present CeO_2/Al_2O_3 composite (b).

Figure 3 shows the FESEM images, demonstrating the morphology and dispersion of CeO_2 on Al_2O_3 . The image (b) of Fig. 4 (REM image) shows the reflection electron intensity distribution, and the bright part indicates the area with the heavy metal composition of CeO_2 in alumina matrix. The agglomeration sphere containing much of CeO_2 is estimated as 100–500 nm in diameter. These CeO_2 colonies are formed in the micropores of alumina where the crystalline CeO_2 and Al_2O_3 particles become tight contact one another. The sphere-like colony will be induced by partially evaporated water in the mixture of aqueous Ce nitrate and Al_2O_3 powders during the drying process at 110 °C. This texture of present $\text{CeO}_2/\text{Al}_2\text{O}_3$ is one of the characteristics by micrometer-scale observation of present composites.

Figure 4 shows the TEM observation of $\text{CeO}_2/\text{Al}_2\text{O}_3$ composite powder. The image demonstrates that CeO_2 is well contact with Al_2O_3 particles, and indicates the existence of partial coverage of nanometer-sized CeO_2 along Al_2O_3 nanoparticles and CeO_2 crystallites make larger interface area in $\text{CeO}_2/\text{Al}_2\text{O}_3$ composite powder. The shape of CeO_2 is likely thin layer along the surface of alumina particles. The crystallite size is in consistence with the size measured from XRD. This is also consistent to Raman spectrum, which indicates that CeO_2 particles have defects and been distorted structure in the surface (Al-doping) and interface ($\text{CeO}_2/\text{Al}_2\text{O}_3$). Then the strong atomistic contact

Fig. 3 FESEM image (a) and corresponding REM image (b).

Fig. 4 TEM image of $\text{CeO}_2/\text{Al}_2\text{O}_3$ composite powder.

is expected for the composite of two kinds of nanoparticles with large interface area between CeO_2 and Al_2O_3 . The microstructural feature and surface coverage geometry of CeO_2 with Al_2O_3 will be related to the activation of oxygen by the reaction with hydrogen. Also, the possible interface rearrangement of CeO_2 with Al_2O_3 will be expected after heat treatment in reducing and oxidizing atmosphere. In next section, we determine the activation energy for hydrogen consumption by oxygen on $\text{CeO}_2/\text{Al}_2\text{O}_3$.

3.2 Temperature programmed reduction and activation energy

Figure 5 shows the H_2 -TPR profiles of $\text{CeO}_2/\text{Al}_2\text{O}_3$ at 40–600 °C at the 1st and 2nd runs in the repeated experiments. They show three peaks; the 1st peak is desorption of water from powder surface, the 2nd peak (peak A) is the hydrogen consumption at lower temperature, and the 3rd peak (peak B) is the main peak for reaction between H_2 and surface oxygen of CeO_2 . The peaks distributed at around 120–150 °C, 420–450 °C and 550–580 °C, respectively. The peak of water desorption appeared in only the starting sample, but this peak does not appear at the 2nd run. Yao et al.¹⁾ have indicated the three TPR peaks at 500, 750 and 850 °C for $\text{CeO}_2/\text{Al}_2\text{O}_3$ catalyst after pretreatment in Ar, and suggested that the lowest-temperature peak corresponded to the surface-capping, the 2nd for surface oxygen and the 3rd is bulk oxygen of CeO_2 . Duprez¹⁴⁾ has determined that the major oxygen which reacts with hydrogen is surface oxygen at the top layer of CeO_2 using oxygen isotope method. Also, this result should be compared with $\text{CeO}_2/\text{Al}_2\text{O}_3$ catalyst which was examined with TPR and XPS analysis by Shyu et al.¹⁹⁾. They assumed the formation of CeAlO_3 on Al_2O_3 over a temperature of 800 K (527 °C) in reduction condition,

Fig. 5 H_2 -TPR profiles of $\text{CeO}_2/\text{Al}_2\text{O}_3$ at 40–600 °C at the 1st (black line) and 2nd runs (grey line).

and discussed that a TPR peak in the temperature region around 400 °C was attributed to surface oxygen on CeAlO₃ although no repeated TPR data were indicated. In our data, the peak A was weakened by the reoxidizing treatment of powder at 600 °C as shown a curve in the 2nd TPR experiment. However, the broad trace around 400–450 °C remained even in the 2nd TPR profile, thus the oxygen adsorption function seems to remain as active sites of surface in low temperature region. The change of the 1st and 2nd TPR suggests that the surface structural rearrangement occurs during the cyclic redox heat treatment.

Table 1 summarizes the oxygen absorption and reaction parameters measured in this work. The activation energy *E* of CeO₂/Al₂O₃ were determined to be 85 ± 15 kJ/mol for peak A, and 135 ± 20 kJ/mol for peak B at the 1st TPR run. Since the peak A corresponds to capping oxygen after the elimination of water on surface, this oxygen should be more active than oxygen of B and easily reacted with hydrogen at lower temperatures. Regarding the peak B, the oxygen species should be supplied by the surface layer in the crystal lattice of CeO₂. This corresponds to that the *E* is required to be as large as 135 ± 20 kJ/mol, which is associated with the diffusion or displacement of oxygen on surface of CeO₂ in addition of decomposition of the Ce–O bond and reaction to hydrogen. At the 2nd run of CeO₂/Al₂O₃, the *E* for peak B was determined to be 194 ± 25 kJ/mol. Thus, the reducing-oxidizing cyclic treatment induced larger activation energy in the reaction. It means the formation of the less active oxygen site, which is caused by the interface rearrangement during redox cycle and heat treatment in CeO₂/Al₂O₃. Here, we should note that the change occurs at 600 °C with no obvious change of bulk solid state which could be observed by XRD and Raman spectra. Since the same Al₂O₃/CeO₂ shows the solid state reaction between CeO₂ and Al₂O₃ by heat treatment in the reducing atmosphere (5 % H₂/Ar) at 900 °C, there is large possibility of structural change due to lattice relaxation by the formation of trivalent Ce at their interface in lower temperature region than 900 °C. So in this work we can suggest the atomistic interaction of Al–O–Ce at the interface in CeO₂/Al₂O₃ composite at lower temperature region.

3.3 Oxygen absorption property

The oxygen absorption at 600 °C was measured as 2.03 ± 0.06 ml/g after the 1st reducing heat treatment at 600 °C in flowing 5 % H₂/Ar gas. It increased to 2.17 ± 0.06 ml/g after the 2nd run, and after 3rd run this value was the same. It is newly found the slight improvement in oxygen absorption, which means oxygen storage capacity in catalyst, after the reduction-oxidation treatment at 600 °C. This is probably due to the additional active oxygen site which is produced in the interface layer of CeO₂ with Al₂O₃.

The oxygen evolution of pure CeO₂ is related to oxygen only in a surface layer but not to the lattice oxygen inside crystal lattice³⁾. Therefore, the structural change at the interface between CeO₂ and Al₂O₃ is strongly suggested, regarding the increase of oxygen absorption. Since there was no obvious microstructural change in the bulk state elucidated by XRD and Raman analyses, the interaction is limited in atomistic bond relaxation in the interface of two crystalline oxides. The activation energy of oxygen evolution after redox treatment was increased by redox treatment of CeO₂/Al₂O₃ composite powder, although the amount of released oxygen increased. This also means that the structural modification and stabilized oxygen site should be induced by relaxing bond strength (and length) between oxygen and cations (Ce and Al) at the interface. Thus, the oxygen is locally stabilized to make relaxed structure in interface region, and then the high activation energy of oxygen evolution is due to the modification of structure after redox treatment. Also, the relaxed structure slightly increases to form more sites of oxygen releasing and absorbing properties. It is expected that the addition of Al₂O₃ on CeO₂ catalyst is effective if the interface oxygen is evolved with the reaction such as oxygen storage capacity. New oxygen releasing and absorbing property at interface of CeO₂/Al₂O₃ after redox treatment is suggested by the TPR experiments and speculated by the initial microstructure in CeO₂/Al₂O₃ with nanometer-scale. This work has found a novel mechanism of OSC at interface of CeO₂/Al₂O₃ at low temperature region below 600 °C.

4 Conclusion

Oxygen release property of ceria (CeO₂) at interface

Table 1 Surface area, crystallite size, OSC, and TPR characters for 30 mol% CeO₂/Al₂O₃.

Surface area (m ² /g)	Size D (nm)	1st TPR OSC (ml/g)	1st TPR Activation Energy E _A (kJ/mol) E _B (kJ/mol)		2nd TPR OSC (ml/g)	2st TPR Activation Energy E _B (kJ/mol)
71.7	29	2.03±0.06	85±15	135±20	2.17±0.06	194±25

between alumina and ceria by hydrogen was examined by the temperature-programmed reduction technique below the temperature of 600 °C. We found a slight improvement of oxygen absorption amount in the reduction and oxidation condition at 600 °C. The activation energy E was 135 ± 20 kJ/mol and 194 ± 25 kJ/mol before and after redox treatment, respectively, for a major oxygen release peak of $\text{CeO}_2/\text{Al}_2\text{O}_3$. The strong interaction at the interface between CeO_2 and Al_2O_3 was observed under redox condition even at as low temperatures as 600 °C. The oxygen is locally stabilized in the relaxed structure of interface region in which oxygen is also stabilized. The high activation energy of oxygen evolution is due to the modification of structure after redox treatment.

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References

- 1) H.C. Yao, Y.F. Yu-Yao: "Ceria in Automotive Exhaust Catalysts", *Journal of Catalysis*, **86**(1984)254-265.
- 2) Y. Zhou, M.N. Rahaman: "Effect of redox reaction on the sintering behavior of cerium oxide", *Acta Materialia*, **45**(1997)3635-3639.
- 3) A. Trovarelli: "Catalytic Properties of Ceria and CeO_2 -Containing Materials", *Catalysis Review*, **38**(1996) 439-520.
- 4) M. Sugiura, M. Ozawa, A. Suda, T. Suzuki, T. Kanazawa: "Development of Innovative Three-Way Catalysts Containing Ceria-Zirconia Solid Solutions with High Oxygen Storage/Release Capacity", *Bulletin of Chemical Society of Japan*, **78**(2005)752-759
- 5) G. Adachi: "Science of rare earth", *Kgaku-Doujin*, (1999)848-849.
- 6) M. Ozawa, C.-K. Loong: "In situ X-ray and neutron powder diffraction studies of redox behavior in CeO_2 -containing oxide catalysts", *Catalysis Today*, **50**(1999) 329-342.
- 7) M. Ozawa, M. Kimura, A. Isogai: "Application of Ce-Zr oxide solid solution to automotive three way catalyst", *Journal of Alloys and Compounds*, **193**(1993)72-75.
- 8) M. Ozawa: "Role of cerium-zirconium mixed oxides as catalysts for car pollution: A short review", *Journal of Alloys and Compounds*, **275-277**(1998)886-890.
- 9) M. Ozawa, M. Kimura: "Thermal Stability of Ce Added $\gamma\text{-Al}_2\text{O}_3$ ", *J. Jpn. Soc. Powder Powder Metallurgy*, **37**(1990)466-473.
- 10) M. Ozawa, M. Kimura, A. Isogai: "Thermal stability and characterization of gamma alumina modified with rare earths", *Journal of Less-common Metals*, **162**(1990)297-308.
- 11) A. Piras, A. Trovarelli, G. Dolcetti: "Remarkable stabilization of transition alumina operated by ceria under reducing and redox conditions", *Applied Catalysis, B Environmental*, **28**(2000)L77-L81.
- 12) M. Haneda, T. Mizushima, N. Kakuta, A. Ueno, Y. Sato, S. Matsuura, K. Kasahara, M. Sato: "Structural Characterization and Catalytic Behavior of Al_2O_3 -Supported Cerium Oxides", *Bulletin of Chemical Society of Japan*, **66**(1993)1279-1288.
- 13) H. Imagawa, A. Suda, K. Yamamura, S. Sun: "Monodisperse CeO_2 Nanoparticles and Their Oxygen Storage and Release Properties", *Journal of Physical Chemistry C*, **115**(2011)1740-1745.
- 14) D. Duprez: "Study of surface reaction mechanisms by $^{16}\text{O}/^{18}\text{O}$ and H/D isotopic exchange", *Catalysis Today*, **112**(2006)17-22.
- 15) M. Ozawa, M. Hattori, T. Yamaguchi: "Thermal stability of ceria catalyst on alumina and its surface oxygen storage capacity", *Journal of Alloys and Compounds*, **451**(2008)621-623.
- 16) V.P. Zhdanov, B. Kasemo: "Kinetic models of oxygen supply from CeO_x to active nanometer particles", *Applied Surface Science*, **135**(1998)297-3066.
- 17) F. Giordano, A. Trovarelli, C. Leitenburg, M. Giona: "A Model for the Temperature-Programmed Reduction of Low and High Surface Area Ceria", *Journal of Catalyst*, **193**(2000)273-282.
- 18) H.A. Al-Madfaa, M.M. Khader: "Reduction kinetics of ceria surface by hydrogen", *Materials Chemistry and Physics*, **86**(2004)180-188.
- 19) J.Z. Shyu, W.H. Weber, H.S. Gandhi: "Surface characterization of alumina-supported ceria", *J. Phys. Chem.*, **92**(1988)4964-4970.