OPEN ACCESS

Effect of heat treatment on oxygen storage capacity and oxygen release kinetics of alumina-supported ceria

To cite this article: Masakuni Ozawa et al 2011 IOP Conf. Ser.: Mater. Sci. Eng. 18 182010

View the article online for updates and enhancements.

You may also like

- <u>Degradation Mitigation in Polymer</u> <u>Electrolyte Membranes using Free Radical</u> <u>Scavengers</u> Panagiotis Trogadas, Javier Parrondo and V. Ramani
- Mechanical properties of M-Zr (M=Cr. Al. Mn) co-doped ceria: A first-principles study Wei Xiao, Jingmin Shi, Lu Sun et al.
- <u>Laminated CeO2/HfO2 High-K Gate</u> <u>Dielectrics Grown by Pulsed Laser</u> <u>Deposition in Reducing Ambient</u> Koray Karakaya, Beatriz Barcones, Andrei Zinine et al.





DISCOVER how sustainability intersects with electrochemistry & solid state science research



This content was downloaded from IP address 3.135.207.129 on 05/05/2024 at 17:48

Effect of heat treatment on oxygen storage capacity and oxygen release kinetics of alumina-supported ceria

Masakuni Ozawa, Masaaki Haneda, Masatomo Hattori

Nagoya Institute of Technology, Tajimi, Gifu, 5070071 Japan

E-mail: ozawa@nitech.ac.jp

Abstract. The microstructural feature, oxygen storage capacity and hydrogen reduction reaction of alumina-supported ceria were examined to determine the activation energy of hydrogen consumption. The scanning and transmission electron microscopy under high magnification indicate the small agglomeration and the surface coverage of CeO₂ on alumina. The activation energy E was 80-140 kJ/mol for reduction peaks at around 420 °C and 550 °C in the first reduction run. However, in the second run, E for the second peak changed depending on the CeO2 content. The results suggest the surface modification of CeO2 surface with alumina via heat treatment in both reducing and oxidizing atmosphere.

Introduction

The removal of CO, hydrocarbons and nitrogen oxides from gasoline automotive exhaust gas is based on the so-called three-way catalyst (TWC), containing alumina, ceria and precious metals. The main idea of the TWC is that the complete conversion of the reducing pollutants can be achieved if the concentrations of these species are exactly controlled in the best air-fuel ratio. Technologically, this condition is met by using an electronic engine control device, which employs a signal from an exhaust oxygen sensor. However, exact control for the best air-fuel mixture in a narrow range around stoichiometry is limited by sensor response, so that is difficult just in time for catalytic reactions with such sensors. The important catalytic component of ceria is required for controlling oxygen content by oxygen storage capacity (OSC) [1-5]. The oxygen storage capacity has been known as that dynamic condition can be relaxed by the redox and nonstoichiometry of ceria-related compounds, and especially, ceria-zirconia has shown the excellent OSC in the practical catalyst so far [2,6-7]. Also, the alumina-supported ceria is a traditional composition, and even now it is useful as inexpensive automotive and de-pollution catalysts for air environmental technology. The hydrogen temperature programmed reduction (H₂-TPR) of alumina-supported ceria as a function of temperature has been measured, and the kinetic reactions can be examined using temperature-programmed reaction as well as assessment of oxygen storage capacity [8-11]. The kinetic data are often not clear because of the effect of microstructure and powder mixture of supported catalyst and dispersed ceria [12]. In this work, we provide the microstructure of ceria catalyst subjected to kinetic examination in the maximum rate temperature.

2. Experimental

Alumina-supported ceria catalyst (to a final Ce loading of 5, 10, 30 and 50 mol% per Al_2O_3) was prepared by impregnation of alumina powder (Sumitomo chemical, surface area 105 m²/g) with an

ICC3: Symposium 12: Porous Ceramics for Environmental Protection and Advanced Industries IOP Publishing IOP Conf. Series: Materials Science and Engineering **18** (2011) 182010 doi:10.1088/1757-899X/18/18/182010

aqueous solution of $Ce(NO_3)_3 6H_2O$ (Wako, 99.9% purity). The mixture thus obtained was dried overnight at 110 °C and heated at 500 °C for 3 h in air. The starting sample was heated at 600 or 800 °C for 3 h in air.

The phase in powders was identified by an X-ray powder diffractometer (XRD, Rigaku rint2000) with CuK α X-ray source (40 kV – 40 mA). A scanning electron microscope (SEM, Jeol-JSM7000F) and transmission electronic microscope (TEM, Jeol-JEM2000EX) were used for analysis of the morphology in the composite samples. The XPS analysis of the catalyst sample was performed using Jeol-Jump10 spectrometer. Specific surface area was measured by nitrogen adsorption at 77 K on heated powder at 200 °C using Shibata SA1100 system.

Temperature-programmed reduction (TPR) was performed by using a lab-made apparatus, which is equipped with a micro-reactor of quartz and a thermal conductivity detector (TCD), to monitor the composition change of gas. 5% H₂/Ar flowing gas was passed over 0.1 g catalyst powder pressed at temperatures of 50-600°C with a heating rate of 10°C /min. The TPR profiles are presented as TCD signals (H₂ consumption (arbitrary units)) versus temperature. The heating rate was changed for experiments from 5 K/min to 20 K/min. The activation energy, E, is measured by assumption of the first order reaction between H₂ and CeO₂.

 $CeO_2 + xH_2 = CeO_{2-x} + xH_2O$ (1)

Actually, the surface of CeO_2 is partially reduced by this reaction in H_2/Ar atmosphere, so that the reaction should be limited by the active site on CeO_2 particle. Since H_2 gas content is excess for the reaction without gaseous oxygen, the concentration of active site to produce oxygen for H_2 consumption should determine to kinetics with the first order. At the maximum rate temperature T, the rate constant k is obtained by the first order kinetics using routine operation. The plot of ln (k) versus 1/T provides a straight line so that E is simply obtained by the measurements with several different heating rates in TPR.

The measurement of oxygen storage capacity (OSC) was done as following. After heat treatment of catalyst samples 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% H₂/Ar, oxygen gas pulse was injected to the sample, then total amount of oxygen absorbed was identified as the OSC at 600 °C. In addition, the second TPR and OSC run was performed in the same apparatus without changing the sample, temperature-gas schedule and apparatus just after cooled down in the first run.

3. Result and discussion

The XRD indicated the mixture of CeO₂ and γ -Al₂O₃ for all the prepared powders after heat treatment. The XPS suggests that the dispersion of Ce on alumina support is not complete so that surface composition is 0.32 (atomic ratio Ce/Al) for 5 mol% Ce-Al₂O₃ (total Ce/Al=0.05). Homogeneous dispersion of Ce on alumina surface was not achieved because of the agglomeration of CeO₂. The crystallite size of ceria was measured as 8 – 12 nm from XRD peak broadness (Sherrer's equation). The SEM demonstrates this morphology as in Fig.1. Figure 1(a) shows the ordinary secondary electron micrograph with high resolution, where the agglomeration of powders is observed. The image in (b) of Fig.1 shows the reflection electron intensity distribution, which was taken with < 3 nm beam. The bright image corresponds to the heavy metal composition containing Ce, thus the agglomeration of CeO₂ exits in alumina matrix. The TEM, under high magnification, indicates the existence of small agglomeration and partial surface coverage of CeO₂ on alumina.

The H₂-TPR profiles in the temperature range of 40 - 600 °C for three samples are compared in Fig.2. Alumina-supported CeO₂ shows three peaks; the first peak is desorption of water from a powder, the second peak (peak A) is the initial hydrogen consumption, and the third peak (peak B) is the main peak for reaction between H₂ and surface oxygen in CeO₂. The peaks distributed at around 120 - 150 °C, 420 - 450 °C and 550 - 580 °C, respectively. The peak of water desorption appeared in alumina support (in Fig.2(a)), however peaks A and B are due to the reduction of ceria on alumina.

The first peak disappeared by pre-heat-treatment of ceria catalyst in oxidizing atmosphere (Fig.2(c)). The peak A was also weakened by the reoxidation treatment at 600 °C after the first TPR

ICC3: Symposium 12: Porous Ceramics for Environmental Protection and Advanced Industries IOP Publishing IOP Conf. Series: Materials Science and Engineering **18** (2011) 182010 doi:10.1088/1757-899X/18/18/182010

experiments (Fig.2(c)). However the board trace around this temperature remained even in the second TPR profile. The result suggests that the surface structure corresponding to the peak A has degenerated as an active site of hydrogen consumption. Thus, the surface rearrangement for active oxygen production is induced by the TPR run. This peak also disappeared after annealing at 800 °C in air. Since the elimination of oxygen on CeO₂ surface induces the rearrangement of surface with the formation of defect site, the modified and stable structure on surface should be formed after heat treatment at above 600 °C under reducing and oxidizing condition. On the other hand, the peak B showed high H₂-consumption amount in the repeated TPR experiments. Since we measured the OSC just above the temperature at peak B, the amount of adsorbed oxygen should indicate the active oxygen capacity from peak B. Yao et al. [7] have first indicated the three TPR peaks at 500, 750 and 850 °C for CeO₂-Al₂O₃ catalyst after pretreatment, and suggested that the lowest-temperature peak corresponded to the surface capping oxygen of CeO₂.



Figure 1 Electron micrograph of (a)secondary elentron image and (b) reflection electron image.

The OSC per Ce was ranged between 0.043 and 0.051 for ceria on alumina as heated at 600 °C. After heat treatment at 800°C, the OSC decreased to 0.028. The OSC per Ce corresponds to the degree of dispersion of Ce on alumina, if the native surface structure is the same as for each ceria particle. This is probably because the active oxygen is produced only on surface layer of CeO₂ crystal. Therefore, the results of OSC values suggest that as the content of Ce increases, the agglomeration of CeO₂ particles results in the surface area decrease.

In order to get information on the kinetics for the reduction behaviour of CeO₂ supported on alumina the activation energy for hydrogen consumption at each peak in TPR profile was evaluated. The activation energy E of alumina-supported ceria with 10mol% and 50 mol% Ce-Al₂O₃ were measured to be 80 kJ/mol for peak A, and 140 kJ/mol for peak B in the first TPR run. In the second run, E for peak B of 10 and 50 mol% Ce-Al₂O₃ was 173 and 145 kJ/mol, respectively. The reducingoxidizing (TPR-OSC) cycle induces the different activation energy depending on CeO₂ content. The less activated oxygen is caused by the surface rearrangement of CeO₂ during redox cycle or heat treatment. In the reducing atmosphere, alumina-supported ceria causes the solid state reaction between ceria and alumina on their interface which induce the production of CeAlO₃ [13-15] Therefore, the increase of activation energy observed for 10 mol% Ce-Al₂O₃ indicates the surface modification of CeO_2 with heat treatment in TPR. On the other hand, no significant change in activation energy for peak B in the second TPR profile was observed for 50 mol% Ce-Al₂O₃. Its activation energy was slightly increased from 141 to 145 kJ/mol. This suggests that the CeO₂ surface in this catalyst sample is partially rearranged during redox cycle or heat treatment. This is probably because there are many surface of agglomerated CeO₂ itself, which cannot react with alumina surface. Since the active OSCrelated oxygen site of CeO₂ is limited around surface, the structural change at surface is the most important factor in alumina-supported ceria for application as OSC or combustion catalyst.

ICC3: Symposium 12: Porous Ceramics for Environmental Protection and Advanced Industries IOP Publishing IOP Conf. Series: Materials Science and Engineering **18** (2011) 182010 doi:10.1088/1757-899X/18/18/182010



Figure 2 TPR curves of (a) alumina, (b) 10%ceria-alumina at the 1st run, (c) 10%ceriaalumina at the 2nd run.

4. Conclusion

We examined the microstructural feature, OSC, TPR, and determined the activation energy for hydrogen consumption on alumina-supported ceria. The SEM and TEM under high magnification indicate the small agglomeration, and the surface coverage

of CeO₂ on alumina. TPR indicated three peaks below the temperature of 600°C. The activation energy, E, was 80kJ/mol for the peak A at around 420 °C, and 140 kJ/mol for the peak B at around 550°C in the first TPR run. In the second run, E for the peak B of 10mol% Ce-Al₂O₃ changed to 173 kJ/mol. The reducing-oxidizing cycle induces the different activation energy depending on CeO₂ content. The results suggest the possible surface rearrangement of CeO₂ surface with heat treatment with reducing and oxidizing atmosphere in alumina-supported ceria

Work supported by Grant-in-Aids No.22655069 by Ministry of Education, Culture, Sports, Science and Technology, of Japanese Government.

References

[1]H.Muraki, G.Zhang, Catalysis Today, 63(2-4)(2000)337-345

[2]M. Sugiura, M. Ozawa, A. Suda, T. Suzuki, T.Kanazawa, Bull.Chem.Soc.Jpn. 78(2005)752

[3]M.Ozawa, J.Alloys Compds., 408-412(2006)1090-1095

[4]H.C.Yao, Y.F.Yu-Yao, J. Catal., 86(1984)254

[5]C.Descorme, R.Taha, N.Mouaddib-Moral, D.Duprez, Appl.Catal.A, 223(1-2)(2002)287-299

[6]M. Ozawa, M, Kimura, A. Isogai, J.Alloys Compds. 193(1993)73

[7]M.Boaro, F.Giordano, S.Recchia, V.D.Santo, M.Giona, A.Trovarelli, Appl.Catal.B 52 (2004)225-237

[8]H. A. Al-Madfaa, M. M. Khader, Mater. Chem. Phys., 86(1) (2004)180-188

[9]V. P. Zhdanov, B. Kasemo Appl.Surf.Sci.,135(1-4)(1998)297-306

[10]F.C. Gennari, C. Neyertz, G. Meyer, P. Fornasiero, M. Graziani , J.Alloys Compds.,404-406(2005)317-322

[11]F.Giordano, A.Trovarelli, C.Leitenburg, M.Giona, J.Catal., 193(2) (2000)273-282

[12]M.Ozawa, M.Hattori, T.Yamaguchi, J.Alloys Compds., 451(1-2) (2008)621-623

[13]M.Haneda, T.Mizushima, N.Kakuta, A.Ueno, Y.Sato, S.Matsuura, K.Kasahara and M.Sato,

Bull.Chem.Soc,Jpn, 66(1993)1279-1288

[14]K.Kakuta, Hyomen, 37(7) (1999)413-428

[15]M.Haneda, T.Mizushima, N.Kakuta , J.Chem.Soc.Jpn, (3) (1997)169-178