

Decomposition of N_2O on Rh/CeO₂/ZrO₂ composite catalyst

Seiichiro Imamura ^{a,*}, Rei Hamada ^a, Yoshio Saito ^a, Keiji Hashimoto ^b,
Hitoshi Jindai ^c

^a Faculty of Engineering and Design, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606, Japan

^b Osaka Municipal Technical Research Institute, Morinomiya, Jyoto-ku, Osaka 530, Japan

^c Nippon Fine Gas Co., Takasago 1-4, Takaishi, Osaka 592, Japan

Received 18 December 1997; accepted 30 April 1998

Abstract

Nitrous oxide (N_2O) was decomposed over Rh supported on ceria/zirconia (Ce/Zr) composite oxide, and the effects of the composition of the oxide and of its calcination temperature on the catalytic performance of Rh were investigated. Ceria was fragile against high temperature calcination, while addition of Zr remarkably increased its thermal stability to retain high surface area even at the calcination temperature of 900°C. Rh was supported on these oxides and was calcined at 550°C. The Rh supported on the composite oxide with a Ce/Zr molar ratio of 7/3 which had been calcined at 900°C exhibited the highest activity. TEM and ESCA analyses revealed that the Rh strongly interacted with the oxide, and there was a possibility that a part of Rh even dissolved into its bulk. The Rh exposed to the surface of the composite oxide in a highly dispersed state exhibited the high catalytic activity. However, when the calcination temperature of the composite oxide (Ce/Zr molar ratio of 7/3) was increased to 1200°C, its surface area decreased remarkably and the supported Rh was present in an aggregated state. The Rh in this state had only low catalytic activity despite its high surface concentration. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Rh; CeO₂; ZrO₂; Composite oxide; Decomposition of N_2O ; State of Rh

1. Introduction

Nitrous oxide (N_2O) is manufactured commercially by the decomposition of ammonium nitrate or by the catalytic oxidation of ammonia and is employed mainly as an anesthetic in medical treatment [1]. It has been used as a monitoring agent or oxidizing agent in the field of catalysis. For example, the decomposition of

N_2O has been regarded as an appropriate test reaction to clarify the function of various catalysts where oxygen species play important roles [2–6]. The active oxygen from N_2O is utilized in the synthetic reactions such as oxidative coupling or partial oxidation of methane [7,8], direct phenol synthesis from benzene [9,10], epoxidation of ethylene [11], partial oxidation of ethane [12], and so on. N_2O is also attracting attention these days from the standpoint concerning the environmental problems because of its detrimental green house effect as well as its

* Corresponding author. Tel.: +81-75-724-7534; Fax: +81-75-724-7580; E-mail: imamura@ipc.kit.ac.jp

ozone-depleting action [13]. N_2O is emitted from various sources such as combustion systems in the factories, automobile catalytic converters, and adipic acid manufacturing process using cyclohexanol and nitric acid as the starting materials. Thus, the development of active catalysts to detoxify N_2O is becoming an important issue. However, not so many works have been reported on the active catalysts to detoxify N_2O [14–18]. Previously, we found that Rh supported on ceria exhibited a high activity in the decomposition of N_2O [19]. Its high activity is ascribed to the inherent function of Rh coupled with the oxygen deficient sites in ceria which also decompose N_2O . The state of Rh on the ceria, however, could not be clarified. Subsequent investigation using colloidal Rh showed that Rh interacts very strongly with ceria which make the detection of its state by TEM analysis difficult [20]. However, ceria itself has poor thermal stability, and, when calcined at high temperatures, it loses its ability to disperse Rh; Rh aggregates on the surface of Ce. The present work aims at maintaining the high durability of ceria against temperature by combining with zirconia. Rh was supported on the ceria/zirconia composite oxide and its performance in the decomposition of N_2O was investigated in relation to its state on the surface of the composite oxide.

2. Experimental

2.1. Catalyst preparation

The composite oxide of ceria and zirconia (designated by Ce/Zr) was prepared by a coprecipitation method. Ammonia (3N) was added to an aqueous solution containing known amounts of cerium(III), nitrate and zirconium (IV) oxynitrate until the pH of the solution was 10. The resultant precipitate was washed three times with enough amount of water and was dried at 80°C overnight, followed by calcination at prescribed temperatures in air for 3 h. Ceria

(CeO_2) and zirconia (ZrO_2) were prepared according to the same method.

$Rh(NO_3)_3$ was dissolved in deionized water dispersed with Ce/Zr, CeO_2 or ZrO_2 . After the solution was stirred for 1 h at a room temperature, it was evaporated to dryness using an evaporator. The catalysts thus obtained were dried at 80°C overnight, followed by calcination at 550°C for 3 h in air. The amount of Rh loaded was 1 wt.%. The catalysts were pressed into a disc and were cut into 8–14 mesh size before use.

2.2. Apparatus and procedure

The decomposition of N_2O was carried out with an ordinary flow reactor under an atmospheric pressure. One milliliter of the catalyst was charged in a tubular quartz reactor (inner diameter of 6 mm), and 1% of N_2O in He was passed into the reactor at a space velocity of 6000 h^{-1} . Space velocity was defined as the ratio of the volumetric feed rate of the reaction gas (at a room temperature and under an atmospheric pressure) to the catalyst bed volume. The temperature of the catalyst bed was increased at a rate of 5°C/min with an electric furnace, and the remaining N_2O at the exit of the reactor was determined with a gas chromatograph. It was confirmed that the diffusion of the reactant (N_2O) inside the catalyst granule was not rate-limiting; the reaction rate was independent of the size of the catalyst particle.

2.3. Analyses

N_2O was determined with a Shimadzu GC-8A gas chromatograph equipped with a thermal conductivity detector on an activated charcoal column (1 m) at 90°C. Stoichiometric amounts of N_2 and O_2 were produced from N_2O as determined on a molecular sieve column (3 m) at 100°C. ESCA and TEM analyses were carried out by the use of a Shimadzu ESCA 750 spectrophotometer and a Hitachi H-800 transmission electron microscope, respectively. In

order to get the clear TEM image of Rh, the catalysts were reduced under a hydrogen atmosphere at 400°C for 1 h. XRD patterns of the catalysts were obtained with a Rigaku Denki Geigerflex 2012 X-ray analyzer.

3. Results and discussion

After the Ce/Zr composite oxides (including CeO₂ and ZrO₂) were calcined at various temperatures, Rh (1 wt.%) was supported on these oxides with the treatment at 550°C. Fig. 1 shows the effect of the Zr content on the surface area of the Rh supported Ce/Zr. CeO₂ is fragile against high temperatures, and its surface area drastically decreases with an increase in the calcination temperature. On the other hand, Zr helps retain high surface area despite the fact that ZrO₂ itself does not show high durability against temperature. For example, the sample with 30 mol% of Zr retains the surface area of 21.2 m²/g even after the calcination at 900°C, while the surface area of CeO₂ treated at the same temperature is only 1.2 m²/g. Interestingly, there are two maxima in the surface area at every calcination temperature: one at low Zr content and the other in the higher Zr content region. Ce and Zr form composite oxides with

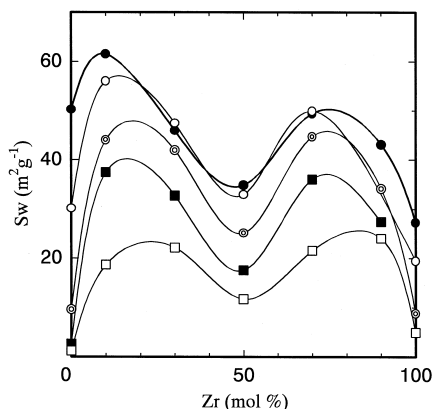


Fig. 1. Effect of the composition and calcination temperature on the surface area of Rh–Ce/Zr. Calcination temperature (°C): (●) 550, (○) 600, (⊙) 700, (■) 800, (□) 900. Rh was supported on the oxides and was calcined at 550°C in air for 3 h.

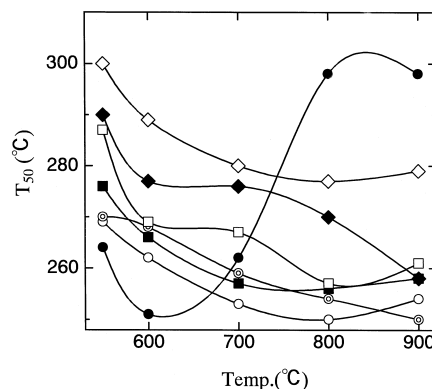


Fig. 2. Effect of the composition and calcination temperature on the catalytic activity of Rh–Ce/Zr in the decomposition of N₂O. Ce/Zr atomic ratio: (●) 100/0, (○) 90/10, (⊙) 70/30, (■) 50/50, (□) 30/70, (◆) 10/90, (◇) 0/100. Rh loaded: 1 wt.%, N₂O: 1.0% in He, catalyst: 1 ml, space velocity: 6000 h⁻¹. The temperature of the catalyst bed was increased at a rate of 5°C/min, and the activity of the catalyst is expressed by the temperature at which 50% of N₂O was decomposed (T₅₀).

the composition of Ce_{0.75}Zr_{0.25}O₂ and Ce₂Zr₂O₇ [21]. Although the appearance of the two peaks may be due to the formation of these composite oxides, the XRD analysis shown below did not indicate their presence. Thus, the cause for the two peaks is not known.

The result of the decomposition of N₂O on these catalysts is shown in Fig. 2. The activity of the catalysts [expressed by the temperature of 50% conversion of N₂O (T₅₀)] was plotted against the calcination temperature. When the calcination temperature of CeO₂ was increased from 550 to 600°C, the catalytic activity increased. However, the further increase in the temperature resulted in a remarkable deactivation of this catalyst. When Zr was incorporated, the higher activity was generally attained at higher calcination temperature: the activity of the catalysts with Ce/Zr calcined at high temperatures (800 and 900°C) is much higher than that of the catalysts in which Rh was supported on the CeO₂ calcined at the same temperatures. Especially the catalyst prepared with the composite oxide containing 30 mol% of Zr and calcined at 900°C [denoted as Rh–Ce/Zr(7/3)-900] has almost the same activity as the Rh

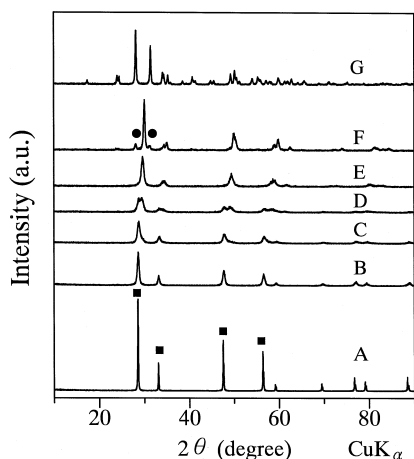


Fig. 3. XRD analysis of Rh–Ce/Zr. The calcination temperature of the oxides was 900°C. Ce (mol%): (A) 100, (B) 90, (C) 70, (D) 50, (E) 30, (F) 10, (G) 0. (●) ZrO₂ The lattice constant of CeO₂ was calculated on the basis of the four peaks assigned by the mark (■).

loaded CeO₂ calcined at 600°C [Rh–CeO₂-600] which has the highest activity among the Rh/CeO₂ series. In a separate experiment, the activity of Rh–Ce/Zr(7/3)-900 and Rh–Ce/Zr-600 was compared with that of silica gel which was assumed to be an inert substance for N₂O decomposition. The comparison was made by the temperature at which the rate of N₂O decomposition reached a constant value; the rate, mol N₂O decomposed/unit surface area of the catalyst in a unit time, was employed for accurate activity comparison. The rate reached 0.005 mol/m² h (obtained under a condition of a differential reactor) at 212, 223, and 773°C for Rh–Ce/Zr(7/3)-900, Rh–CeO₂-600, and silica gel, respectively. Thus, Rh-loaded catalysts accelerate the reaction remarkably compared with the thermal reaction (on silica gel). Fig. 3 shows XRD patterns of Rh–Zr/Ce, Rh–CeO₂, and Rh–ZrO₂ calcined at 900°C. The Rh–Ce/Zr with 30 mol% of Zr and below shows only the patterns due to cubic CeO₂ phase. However, the peaks deviate to higher angle position with an increase in Zr content; the lattice constant a_0 was 5.411, 5.400, and 5.373 Å for 0 mol%, 10 and 30 mol% of Zr, respectively. This means that Zr dissolved into CeO₂ to form a solid

solution. For Zr contents of 50 and 70 mol%, the peaks due to unknown phase emerged. The peaks for monoclinic ZrO₂ appeared only after an addition of as much as 90 mol% of Zr. Fornasiero et al. [22] obtained the same result for Ce–Zr mixed oxides. No Rh peak was observed in all diffraction patterns. The generally observed weak peaks for the Rh–Ce/Zr catalysts compared with those of Rh–CeO₂ and Rh–ZrO₂ indicate the poor degree of crystallization of the mixed oxide and reflect the higher surface area of Rh–Ce/Zr than those of Rh–CeO₂ or Rh–ZrO₂ as is shown in Fig. 1.

The temperature dependence of the activity and surface area of Rh–CeO₂ and Rh–Ce/Zr(7/3) is again depicted in Fig. 4 based upon the data shown in Figs. 1 and 2; the data for Rh–Ce/Zr(7/3) calcined above 900°C are added. The surface area decrease of CeO₂ is remarkable with an increase in the calcination temperature. However, the activity of Rh–CeO₂ first increased at a calcination temperature of 600°C and, then, decreased. The decrease in the surface area of Rh–Ce/Zr(7/3) against temperature is mild; higher than 20 m²/g of the surface area was maintained at 900°C. It is interesting to note that the activity of Rh–Ce/Zr(7/3) increased with the calcination temperature up to 900°C despite its monotonous

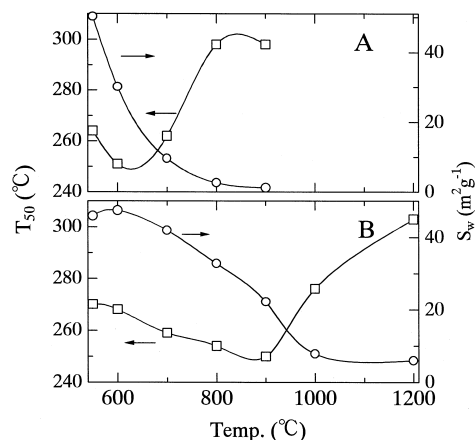


Fig. 4. Effect of the calcination temperature on the activity and surface area of (A) Rh–CeO₂ and (B) Rh–Ce/Zr(7/3). (○) Surface area, (□) T_{50} . The reaction condition is shown in Fig. 2.

surface area decrease. Thus, the surface area of the catalysts does not necessarily induce the high catalytic activity. However, further temperature increase (1200°C) led to the remarkable activity loss. The maximum activity of Rh–CeO₂ was attained with the surface area of 30.1 m²/g (calcination temperature of 600°C) and that of Rh–Ce/Zr(7/3) with the surface area of 22.1 m²/g (calcination temperature of 900°C); both values are the same order of magnitude. Although the oxygen deficient sites of CeO₂ induced by the action of Rh work as active sites [19], the main catalyst component is Rh. Thus, the results shown in Fig. 4 reasonably indicate the importance of the state of Rh on CeO₂ and Ce/Zr(7/3) whose surface natures are controlled by the calcination temperature.

In the previous work, we investigated the behavior of colloidal Rh on the surface of CeO₂ [20]. As the CeO₂ calcined at low temperature (550°C) had high surface area and, therefore, high surface energy, it interacted strongly with Rh; some part of Rh even seemed to penetrate inside the bulk of the CeO₂. This state of Rh on the surface was very active in the decomposition of methanol to CO and H₂. However, when Rh was supported on CeO₂ calcined at higher temperature (950°C), it aggregated on the surface and no more exhibited high performance for methanol decomposition. In order to see the state of Rh in the present case, ESCA and TEM analyses were carried out. Fig. 5 exhibits the change in the surface Rh concentration on CeO₂ and Ce/Zr(7/3) against calcination temperatures as observed by an ESCA technique. As the escape depth of 3d electron of Rh (mean kinetic energy: 309.8 eV) was calculated to 10 plus Å, the surface Rh concentration defined here is that detected in the layer to about 10 Å depth from the surface [23]. The amount of Rh loaded was 1 wt.% and this amount corresponds to 1.66 and 1.53 mol% for CeO₂ and Ce/Zr(7/3), respectively. The surface Rh concentrations are the same order of magnitude as the bulk Rh concentrations (calculated on the assumption that Rh is homogeneously distributed in the bulk oxide) up

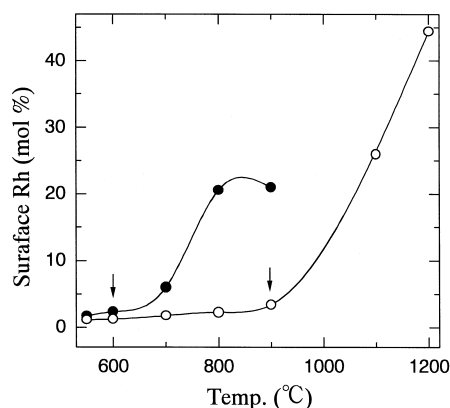


Fig. 5. Surface Rh concentration vs. calcination temperature. (●) Rh–CeO₂, (○) Rh–Ce/Zr(7/3). Rh loading was 1 wt.%, which corresponds to 1.66 and 1.53 mol% loading for CeO₂ and Ce/Zr(7/3), respectively. The arrows show the points of the highest activity.

to the calcination temperature of 600°C for Rh–CeO₂ and 900°C for Rh–Ce/Zr(7/3). If the charged Rh presides only on the surface, its surface concentration as estimated by an ESCA analysis should be higher than that when Rh is loaded homogeneously in the bulk oxide. Thus, there is the possibility that the Rh penetrates inside the CeO₂ or Ce/Zr(7/3) [20]. When the calcination temperature was further increased, the surface Rh increased remarkably, indicating the decrease in the ability of CeO₂ and Ce/Zr(7/3) to incorporate Rh. This corresponds to the noted decrease in the surface areas shown in Fig. 4: above 600°C for Rh–CeO₂ and above 900°C for Rh–Ce/Zr(7/3). Figs. 6 and 7 show the TEM photographs and diffraction patterns of Rh–CeO₂-900 (calcination temperature: 900°C) and Rh–Ce/Zr(7/3)-1200 (calcination temperature: 1200°C). Diffraction ring due to Rh is observed for both catalysts, and aggregated Rh particles are seen in the TEM photographs. Therefore, the high concentration of Rh in these catalysts as observed by the ESCA analysis is due to the aggregated surface Rh particles. However, these catalysts are not active in decomposing N₂O as is shown in Fig. 4. On the other hand, Rh–Ce/Zr(7/3)-900 showed no diffraction ring due to Rh and the Rh image

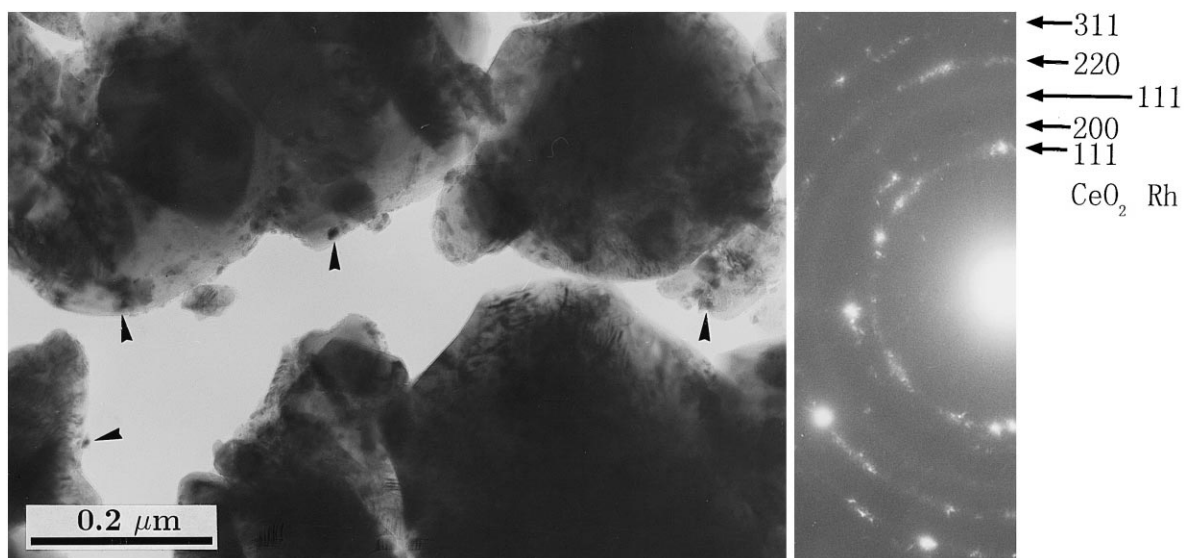


Fig. 6. TEM analysis of Rh–CeO₂-900 (calcination temperature of 900°C).

could not be obtained. (Fig. 8) TEM analysis of Rh–CeO₂-600 neither presented the information on the state of Rh although the result is not shown in the figure; the same result was obtained in the previous work for the colloidal Rh–CeO₂-550. Thus, Rh must be in a highly dispersed state in these catalysts, and a part of

Rh probably dissolves into the bulk of CeO₂. As shown in Fig. 4, the highest activity was attained at the calcination temperatures of 600°C for Rh–CeO₂ and 900°C for Rh–Ce/Zr(7/3) although their surface areas are lower than the corresponding catalysts calcined at lower temperatures. However, the surface Rh contents are

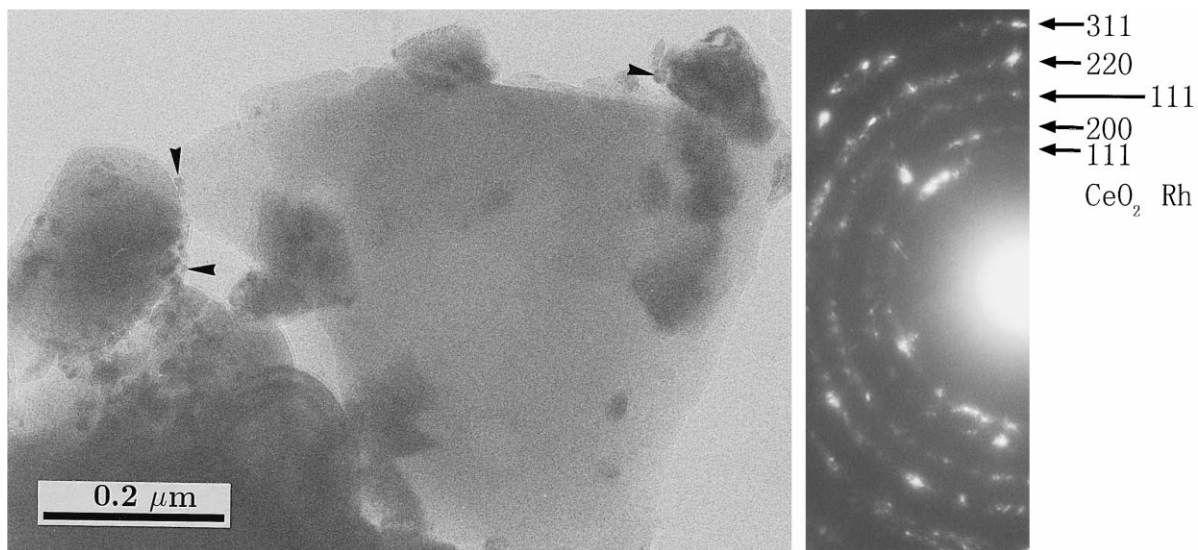


Fig. 7. TEM analysis of Rh–Ce/Zr(7/3)-1200 (calcination temperature of 1200°C).

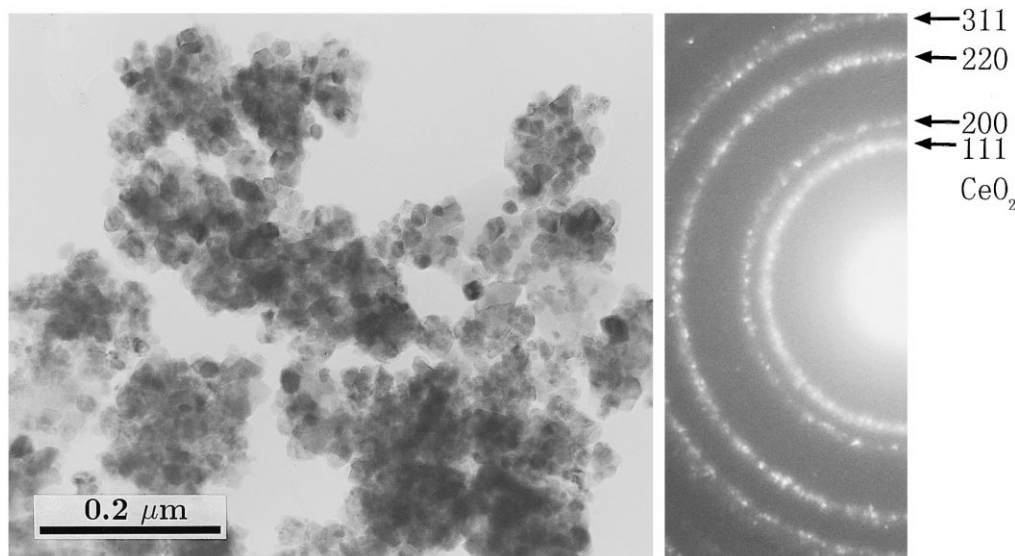


Fig. 8. TEM analysis of Rh–Ce/Zr(7/3)-900 (calcination temperature of 900°C).

higher for the formers than the latter group as shown in Fig. 5; the smaller surface area results in the larger surface Rh content because more Rh is expelled onto the surface from the bulk CeO_2 . Therefore, the highest activity is obtained when the maximum surface concentration of Rh is attained under the condition that this Rh is in a highly dispersed state. In other word, high catalytic activity will not be obtained with aggregated Rh even if its surface concentration is high. Therefore, the activity is controlled on the balance between the amount of surface Rh and its degree of dispersion. This balance is, in turn, controlled by the surface nature (surface area) of CeO_2 and, hence, by its calcination temperature. Incorporation of Zr into CeO_2 expands the range which attains this optimum condition to the higher temperature region.

4. Conclusion

N_2O was decomposed over Rh (1 wt.%) supported on CeO_2 and Ce/Zr composite oxides which were calcined at various temperatures. The oxides with high surface area seemed to dissolve a part of Rh. The increase in the calci-

nation temperature decreased the surface area of the oxides, and the Rh was present in an aggregated state on the oxides with small surface areas. However, the aggregated Rh had only low activity to decompose N_2O despite its high surface concentration. CeO_2 calcined at 600°C and Ce/Zr(7/3) calcined at 900°C exhibited the highest performance. The surface concentration of Rh supported on these oxides was relatively high and this Rh was in a highly dispersed state; thus, the Rh exhibited the highest activity in decomposing N_2O .

Acknowledgements

The authors thank Mr. K. Utani of Kyoto Institute of Technology for his kind cooperation.

References

- [1] T. Asahara (Ed.), in: *Kagaku Benran, Applied Chemistry I*, Maruzen, Tokyo, 1986, p. 302.
- [2] D.E. Petrakis, P.J. Pomonis, A.T. Sdoukos, *J. Chem. Soc., Faraday Trans. 1* 85 (1989) 3173.

- [3] A.K. Ladavos, P.J. Pomonis, *J. Chem. Soc., Faraday Trans.* 87 (1991) 3291.
- [4] J. Christopher, C.S. Swamy, *React. Kinet. Catal. Lett.* 39 (1989) 129.
- [5] J. Christopher, C.S. Swamy, *J. Mol. Catal.* 68 (1991) 199.
- [6] J. Christopher, C.S. Swamy, *J. Mater. Sci.* 27 (1992) 1353.
- [7] G.J. Hutchings, M.S. Scubel, J.R. Woodhouse, *Chem. Soc. Rev.* 18 (1989) 251.
- [8] H.F.S. Liu, R.S. Liu, L.Y. Liew, R.E. Johnson, J.H. Lunsford, *J. Am. Chem. Soc.* 106 (1984) 4117.
- [9] M. Iwamoto, J. Hirata, K. Matsukami, K. Kagawa, *J. Phys. Chem.* 87 (1983) 903.
- [10] E. Suzuki, K. Nakashiro, Y. Ono, *Chem. Lett.* (1988) 953.
- [11] S.A. Tan, R.B. Grant, R.M. Lambert, *J. Catal.* 104 (1987) 156.
- [12] K. Aika, M. Isobe, K. Kido, T. Moriyama, Y. Onishi, *J. Chem. Soc., Faraday Trans.* 1 83 (1987) 3139.
- [13] M. Tamaki, T. Hiraki, T. Mizoguchi, *J. Environ. Pollut. Control* 25 (1989) 775.
- [14] Y.-F. Chang, J.G. McCarty, E.D. Wachsman, V.L. Wong, *Appl. Catal. B4* (1994) 283.
- [15] Y.-F. Chang, J.G. McCarty, *Catal. Lett.* 34 (1995) 163.
- [16] M. Tabata, H. Hamada, Y. Kintaichi, M. Sasaki, T. Ito, *Chem. Express* 7 (1992) 77.
- [17] Y. Li, N. Armor, *Appl. Catal. B1* (1992) L21.
- [18] J. Oi, A. Obuchi, A. Ogata, H. Yagita, G.R. Bamwenda, K. Mizuno, *Chem. Lett.* (1995) 453.
- [19] S. Imamura, N. Okamoto, Y. Saito, T. Ito, H. Jindai, *Sekiyu Gakkaishi* 39 (1996) 350.
- [20] S. Imamura, T. Yamashita, R. Hamada, Y. Saito, Y. Nakao, N. Tsuda, K. Kaito, *J. Mol. Catal.*, in press.
- [21] W.F. McClune (Ed.), *Powder Diffraction File—Inorganic Phases*, JCPDS International Centre for Diffraction Data, Swarthmore, 1982, p. 174.
- [22] P. Fornasiero, R.D. Monte, G.R. Rao, J. Kašpar, S. Meriani, A. Trovarelli, M. Graziani, *J. Catal.* 151 (1995) 168.
- [23] T.A. Carlson (Ed.), *Photoelectron and Auger Spectroscopy*, Plenum, New York, 1978, p. 264.