FULL PAPER

Influence of crystal structure of Y-doped ZrO_2 as support oxide on the three-way catalytic performance of supported Rh catalyst

Yasutaka TOMIDA¹ and Masaaki HANEDA^{1,2,†}

¹Advanced Ceramics Research Center, Nagoya Institute of Technology, 10-6-29 Asahigaoka, Tajimi, Gifu 507-0071, Japan

²Frontier Research Institute for Materials Science, Nagoya Institute of Technology, Gokiso-cho, Showaku, Nagoya 465-8555, Japan

The effect of crystal structure of Y-doped ZrO_2 as support on the three-way catalytic performance of Rh catalyst was investigated. Rh catalyst supported on 3Y- ZrO_2 with tetragonal phase showed higher activity than that on 3Y/ ZrO_2 with monoclinic phase. The difference in the Rh-support oxide interaction was suspected from the measurements of temperature-programmed reduction by CO (CO-TPR). The use of Y-doped ZrO_2 as support was found to contribute to the formation of easily reducible Rh species, resulting in high catalytic activity. Rh species can more strongly interact with 3Y/ ZrO_2 than with 3Y- ZrO_2 , resulting in the formation of catalytically active reducible Rh species in Rh/3Y- ZrO_2 , which showed the highest activity. From Fourier transform infrared (FT-IR) spectroscopy following CO adsorption, no qualitative difference in the surface valence state of Rh particles irrespective of crystallite structure of Y-doped ZrO_2 was observed. On the other hand, a large fraction of the surface of Rh particles in Rh/3Y- ZrO_2 was found to be Rh^0 sites rather than Rh^+ sites. This is related to the interaction of Rh particles with Y species in tetragonal 3Y- ZrO_2 . We concluded that the tetragonal structure of 3Y- ZrO_2 with which Rh can interact via Y species is a key-factor to obtain highly active Rh catalysts.

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1. Introduction

In recent years, one of the major environmental concerns that were paid a lot of attention is the air pollution caused by the exhausts of vehicles. Three-way catalysts (TWCs) represent the most innovative technologies for automotive emission control. TWCs can work simultaneously and efficiently to reduce NO and to oxidize CO and hydrocarbons (HCs) in a narrow window of air-to-fuel ratio, close to the stoichiometric point. Although more than 99 % of emissions are purified by using TWCs, further improvement of the performance of TWCs is highly required to achieve strict emission regulations, which are constantly becoming more stringent worldwide.^{1),2)} Especially, the efficient removal of pollutants emitted during cold-start operation before warming up the catalytic converter must be an important issue.³⁾

Among the catalytic components employed for TWCs, platinum group metals (PGMs) such as Pt, Pd and Rh are regarded as promising active component. Therefore, an increase in the loading of PGMs would be one of the strategies to improve the performance of TWCs.⁴⁾ However, PGMs have been determined as critical raw mate-

rials,⁵⁾ which were defined to the materials combining a high economic importance with a high risk associated with their supply. The development of highly active TWCs with less PGMs loading has to be achieved for “Sustainable Development Goals”.

Producing the optimum interaction between PGM and support oxide may be another strategy for the achievement of high catalytic performance.^{6)–13)} Nagai et al.^{8),9)} reported that the use of CeO_2 and CeO_2 - ZrO_2 , which possess surface basicity, can improve the dispersion state of Pt and Rh. This was explained by the formation of PGM-O-Ce bonds, which act as anchor for PGM particles on CeO_2 -based oxides. The interaction of Rh with basic oxide was also pointed out to cause the formation of irreducible RhO_x species,¹⁰⁾ resulting in low catalytic performance. On the other hand, Kawabata et al.^{11)–13)} investigated the TWC performance of Rh catalyst supported on La-containing ZrO_2 (Rh/Zr-La-O), and found that Rh/Zr-La-O was highly active for the removal of NO_x and HCs from a synthetic auto exhaust. They explained its high performance of Rh/Zr-La-O by the stabilized Rh species in low oxidation state.

The catalytic performance of noble metals is known to be affected by the crystal structure of support oxide.^{14)–17)} For example, Li et al.¹⁵⁾ reported that Au catalyst supported on ZrO_2 with monoclinic phase showed higher activity

[†] Corresponding author: M. Haneda; E-mail: haneda.masaaki@nitech.ac.jp

for water-gas shift reaction than that on ZrO_2 with tetragonal phase. The hydroxyl groups on the surface of ZrO_2 with monoclinic phase seem to play an important role in the water-gas shift reaction. Murata et al.¹⁶⁾ investigated the catalytic activity of Pd supported on Al_2O_3 with different crystal phase for CH_4 oxidation, and reported that Pd/ θ - Al_2O_3 and Pd/ α - Al_2O_3 showed a volcano-shaped dependence of the catalytic activity on the size of Pd particles, while the catalytic activity of Pd/ γ - Al_2O_3 increased with the particle size. The Pd- Al_2O_3 interaction is strongly dependent on the crystal phase of Al_2O_3 , resulting in the different distribution of catalytically active sites on Pd particle surface.

We have recently investigated the additive effect of various rare earths on the TWC performance of Rh/ ZrO_2 to gain the knowledge on Rh-support interaction, and found that Rh-support interaction can control the dispersion state and the surface oxidation state of Rh.^{18),19)} Y_2O_3 was the best additive for Rh/ ZrO_2 . We have also reported the advantages to use Y-stabilized ZrO_2 as support oxide for Pt and Rh in HCs oxidation and TWC reactions.^{20)–22)} The use of Y-stabilized ZrO_2 caused an enhancement of the reducibility of Rh species, resulting in the stabilization of Rh in active metallic state during the reaction. On the other hand, the crystal structure of Y-stabilized ZrO_2 is known to be systematically controlled by changing the thermal treatment conditions and the Y_2O_3 content.^{23),24)} This suggests that Rh catalysts possessing different interaction with support can be obtained by using Y-stabilized ZrO_2 with different crystal structure, leading us to consider the effect of crystal structure on the TWC performance. In the present study, we have employed Y-doped ZrO_2 with monoclinic and tetragonal phases as support oxide for Rh catalyst, and then evaluated the catalytic performance for TWC reactions. The effect of crystal structure of Y-doped ZrO_2 on the TWC performance of Rh catalyst was investigated.

2. Experimental procedure

Two kinds of Y-doped ZrO_2 were employed. One is a commercial sample purchased from Tosoh denoted as 3Y- ZrO_2 (TZ-3Y; $16\text{ m}^2\text{ g}^{-1}$), where the loading of Y_2O_3 was 3 mol %. Another Y-doped ZrO_2 with 3 mol % Y_2O_3 loading, denoted as 3Y/ ZrO_2 , was prepared by impregnation of ZrO_2 (Tosoh, TZ-0; $14\text{ m}^2\text{ g}^{-1}$) with an aqueous solution of yttrium(III) nitrate (Fujifilm Wako Pure Chemical Corporation), followed by drying and calcination at 600°C for 5 h in air. Rh was deposited on ZrO_2 , 3Y- ZrO_2 and 3Y/ ZrO_2 by immersing a solution of $\text{Rh}(\text{NO}_3)_3$ (Tanaka Kikinzoku Kogyo), followed by drying and calcination at 900°C for 5 h in air.

The catalytic activity test was carried out using a flow reactor system by passing a stoichiometric reaction gas mixture containing NO (0.1 %), CO (0.3 %), C_3H_6 (0.04 %), O_2 (0.28 %) and H_2O (2 %) diluted in N_2 at a rate of $500\text{ cm}^3\text{ min}^{-1}$ over 0.1 g of catalyst ($\text{SV} = \text{ca. } 450,000\text{ h}^{-1}$), which had been pretreated in situ in a flow of the reaction gas at 800°C for 1 h. The activity was measured while raising the temperature from 40 to 800°C at a rate of

$10^\circ\text{C min}^{-1}$. The concentrations of NO_x , O_2 , CO and CO_2 and the total HCs in the effluent gas were continuously monitored using an on-line gas analyzer, Horiba, PG-240 and Shimadzu, VMS-1000F, respectively.

X-ray diffraction (XRD) patterns were recorded using a Rigaku MiniFlex diffractometer with $\text{Cu K}\alpha$ radiation at 30 kV and 15 mA. Raman spectra were measured with a Micor-RAM300/NK (Lambda Vision) equipped with a TE-cooled charge coupled device detector and a green laser ($\lambda = 532\text{ nm}$) under the ambient atmosphere. Electron probe microanalysis (JEOL, JXA-8230) was used to evaluate the distribution of Y species in the Y-doped ZrO_2 samples.

The dispersion of Rh was calculated from CO chemisorption measured by the pulse method at room temperature. The sample was first reduced with H_2 at 400°C for 1 h and then cooled to room temperature in flowing He. Several pulses of CO were introduced into the sample until no more adsorption was observed. As for the stoichiometric ratio of CO/Rh_s, Belton and Schmiege determined the stoichiometric ratio of 1.0 from the comparison of the particle size of Rh and the amount of CO desorption for Rh/ Al_2O_3 model catalyst.²⁵⁾ The use of 1.0 CO/Rh adsorption stoichiometry was also reported to reasonable for the evaluation of Rh dispersion.^{26),27)} Therefore, the Rh dispersion was calculated from the amount of CO chemisorption by assuming a stoichiometric ratio of 1.0 CO/Rh_s.

Temperature-programmed reduction by CO (CO-TPR) was performed to investigate the reducibility of the catalysts. Prior to each experiment, the sample (0.1 g) was pretreated in situ in a flow of 5 % O_2/He at 500°C for 1 h and then cooled to room temperature. After purging with He, the TPR profiles were obtained from room temperature to 600°C in a $20\text{ cm}^3\text{ min}^{-1}$ flow of 0.5 % CO/He at a heating rate of $10^\circ\text{C min}^{-1}$. The effluent gas was analyzed with an on-line quadrupole mass spectrometer (PFEFFER OminiStar).

Fourier transform infrared (FT-IR) spectra of adsorbed CO as a probe molecule were taken with a Nicolet 6700 FT-IR spectrometer (Thermo Scientific) at a resolution of 4 cm^{-1} . Prior to each experiment, a self-supporting sample disk of about 20 mg cm^{-2} placed in an IR cell with CaF_2 windows was first pretreated at 400°C in a flow of the reaction gas containing NO (0.1 %), CO (0.3 %), C_3H_6 (0.04 %) and O_2 (0.25 %) diluted in He at a stoichiometry and then cooled to 50°C in flowing He. Observation of adsorbed CO species was carried out in a flow of 0.35 % CO/He at 50°C for 10 min, followed by purging with He for 10 min.

3. Results and discussion

Figure 1(A) shows the XRD patterns of ZrO_2 , 3Y- ZrO_2 and 3Y/ ZrO_2 as support. Distinct XRD peaks indexed to a monoclinic phase were detected for ZrO_2 . The same XRD pattern was observed for 3Y/ ZrO_2 , indicating that Y^{3+} ions impregnated onto ZrO_2 did not change the crystal structure of ZrO_2 . On the other hand, 3Y- ZrO_2 was found to possess a mixture of monoclinic and tetragonal phases, suggesting the coexistence of thermodynamically metastable

Fig. 1. (A) XRD patterns and (B) Raman spectra of ZrO_2 , 3Y-ZrO_2 and 3Y/ZrO_2 .

Fig. 2. Scanning electron microscope (SEM) image and elemental distribution of Zr and Y for (A) 3Y-ZrO_2 and (B) 3Y/ZrO_2 .

and stable phases. To confirm the crystal structure of ZrO_2 -based materials, Raman spectra were measured, because Raman spectroscopy is sensitive technique to the crystal symmetry.²⁸⁾ As seen in Fig. 1(B), ZrO_2 and 3Y/ZrO_2 showed the same Raman spectrum. All the peaks detected at 176, 188, 219, 305, 330, 345, 379, 472, 499, 534, 554, 611 and 632 cm^{-1} are well consistent with those observed for ZrO_2 with monoclinic phase (m- ZrO_2).^{29,30)} In case of 3Y-ZrO_2 , the intensity of the peaks due to m- ZrO_2 was clearly decreased compared with that for ZrO_2 . Besides, an appearance of characteristic peaks at 144 and 260 cm^{-1} , which can be ascribed to tetragonal phase of ZrO_2 (t- ZrO_2),^{29,30)} was observed. These results indicate the coexistence of t- ZrO_2 and m- ZrO_2 in 3Y-ZrO_2 . The results obtained from Raman spectroscopy are well consistent with those from XRD measurements.

Considering the preparation method of 3Y/ZrO_2 , Y species are suspected to be deposited on the surface of ZrO_2 . In fact, as show the elemental distribution of Y in Fig. 2(B), an aggregation of Y species was observed for 3Y/ZrO_2 . Aggregated Y species do not affect the crystal structure of ZrO_2 . On the other hand, the presence of relatively well dispersed Y species was observed for 3Y-ZrO_2

[Fig. 2(A)]. In accordance with the results of XRD and Raman, Y species are incorporated in the lattice of ZrO_2 , resulting in the formation of tetragonal phase.

In order to confirm the influence of Rh deposition on the crystal structure, XRD patterns and Raman spectra of Rh/ ZrO_2 , Rh/ 3Y-ZrO_2 and Rh/ 3Y/ZrO_2 were measured. Figures 3(A) and 3(B) show the XRD patterns and the Raman spectra, respectively. From the comparison of Fig. 3(A) with Fig. 1(A), no difference in the XRD patterns were observed for Rh/ ZrO_2 and Rh/ 3Y/ZrO_2 . However, as seen in Fig. 3(B), the Raman peaks were broadened by the presence of Rh. In Figs. S1(A) and S1(B) (see in "Supplementary File") are compared the Raman spectra of ZrO_2 and 3Y/ZrO_2 before and after calcination at 900°C for 5 h in air. It appears that no significant difference in the position and intensity of Raman peaks was observed, suggesting that heat-treatment at 900°C does not cause structural change of ZrO_2 . Therefore, the broadened Raman peaks of Rh/ ZrO_2 and Rh/ 3Y/ZrO_2 would be due to the formation of structural disordered ZrO_2 with monoclinic phase caused by the interaction with Rh.³¹⁾

On the other hand, in case of Rh/ 3Y-ZrO_2 , XRD peaks due to monoclinic phase of ZrO_2 were significantly

Fig. 3. (A) XRD patterns and (B) Raman spectra of Rh/ZrO₂, Rh/3Y-ZrO₂ and Rh/3Y/ZrO₂.

Table 1. Physico-chemical properties of supported Rh catalyst

	BET surface area/m ² g ⁻¹	Rh dispersion (CO/Rh)
Rh/ZrO ₂	10.0	0.12
Rh/3Y-ZrO ₂	10.0	0.15
Rh/3Y/ZrO ₂	12.8	0.53

weakened [Fig. 3(A)]. In addition, no Raman peaks due to m-ZrO₂ were observed in the Raman spectrum [Fig. 3(B)]. Therefore, Rh/3Y-ZrO₂ seems to mainly consist of tetragonal phase of ZrO₂. The XRD patterns of 3Y-ZrO₂ before and after calcination at 900 °C for 5 h in air were compared in Fig. S2 (see in “Supplementary File”). Although a slight decrease in the intensity of the peaks due to monoclinic phase was observed, no significant change in the crystal structure of 3Y-ZrO₂ was observed. The same result was obtained in Raman spectra given in Fig. S1(B). Therefore, the disappearance of monoclinic phase in Rh/3Y-ZrO₂ would be ascribed to the interaction with 3Y-ZrO₂. Machida et al.³²⁾ reported that Rh₂O₃ with hexagonal phase can strongly interact with AlPO₄ with monoclinic phase leading to the formation of Rh–O–P bonding. Tanabe et al.^{9),33)} also reported the strong interaction of Rh species with Nd₂O₃ surface-enriched tetragonal ZrO₂, resulting in the formation of Rh–O–Nd bonding. In the present study, Rh/3Y-ZrO₂ was calcined at 900 °C in air, so that thermodynamically stable Rh oxide (Rh₂O₃) would be formed. Considering the report of Machida et al.³²⁾ and Tanabe et al.,^{33),34)} Rh₂O₃ is suspected to strongly interact with not only monoclinic phase but also tetragonal phase of 3Y-ZrO₂, resulting in the distortion of monoclinic and tetragonal ZrO₂ phase, which causes the disappearance of XRD peaks due to monoclinic phase and the broadened Raman peaks.

No peaks ascribed to Rh were detected in XRD patterns and Raman spectra for all the samples, suggesting high dispersion state of Rh species. In fact, as summarized in Table 1, Rh dispersion as high as 10 % was achieved for Rh/ZrO₂ and Rh/3Y-ZrO₂. It is also noteworthy that the highest Rh dispersion was obtained for Rh/3Y/ZrO₂.

Figure 4 shows the temperature dependence of conversion efficiencies of NO, CO and C₃H₆ over Rh/ZrO₂, Rh/3Y-ZrO₂ and Rh/3Y/ZrO₂. It appears that the use of Y-doped ZrO₂ as support caused an increase in the catalytic activity of Rh/ZrO₂. Namely, the light-off curves of

Fig. 4. Conversion efficiencies of (A) NO, (B) CO and (C) C₃H₆ as a function of temperature for three-way catalytic reactions over Rh/ZrO₂, Rh/3Y-ZrO₂ and Rh/3Y/ZrO₂.

Rh/3Y-ZrO₂ and Rh/3Y/ZrO₂ were shifted to low temperature region compared with that of Rh/ZrO₂. From the comparison of the activity of Rh/3Y-ZrO₂ and Rh/3Y/ZrO₂, the former catalyst showed higher activity for NO reduction and CO/C₃H₆ oxidation than the latter one in the temperature range of 200–250 °C. Since Y-doped ZrO₂ without Rh does not effectively catalyze the TWC reactions,³⁴⁾ Rh must be the catalytically active component. Therefore, the dispersion state of Rh species is considered to be an important factor affecting the catalytic activity, because catalytic reactions take place on catalyst surfaces. As given in Table 1, the highest Rh dispersion was obtained for Rh/3Y/ZrO₂, which showed lower activity.

Fig. 5. Temperature dependence of CO_2 formation in CO-TPR for Rh/ZrO₂, Rh/3Y-ZrO₂ and Rh/3Y/ZrO₂.

Therefore, the high catalytic activity of Rh/3Y-ZrO₂ can not be explained by the dispersion state of Rh. From the results of XRD and Raman measurements (Fig. 3), the use of Y-doped ZrO_2 with tetragonal phase seems to be effective to obtain highly active Rh catalyst.

In order to understand the intrinsic role of crystal structure of Y-doped ZrO_2 , various characterizations were carried out. CO-TPR measurements were first performed to gain insights on the Rh–support interaction. In CO-TPR measurements, CO_2 is formed via the reaction of CO with oxygen species present either on the surface or in the bulk of a sample. Therefore, CO_2 formation temperature is dependent on, for example, dispersion state of supported metals,³⁵⁾ metal–support interaction¹⁷⁾ and so on. **Figure 5** shows the temperature dependence of CO_2 formation as CO-TPR profile of supported Rh catalysts. Distinct CO_2 formation was observed in the temperature range of 100–500 °C. Since ZrO_2 and Y-doped ZrO_2 do not possess oxygen species which can react with CO, the CO_2 formation is related to the reaction of CO with oxygen attributed to Rh and/or Rh–support oxide interface. Therefore, the finding that different CO-TPR profile was observed for each Rh catalyst suggests that the reducibility of Rh species is different depending on the support oxide. As seen in Fig. 5, Rh/ZrO₂ gave the CO_2 formation peaks at 188 and 240 °C along with broad peaks in 300–450 °C range. Tanabe et al.^{9),33)} observed three reduction peaks at around 90, 130 and 180 °C in the H_2 -TPR profile of Rh/Nd₂O₃–ZrO₂ and then ascribed the peaks to the reduction of three-dimensional, two-dimensional Rh₂O₃ and Rh species interacting strongly with Nd₂O₃, respectively. Burch and Loader³⁶⁾ also reported that Rh species, which had little interaction with support, are easily reduced at lower temperature, while those with strong support interaction are reduced at higher temperature. Taking into account the lower reduction ability of CO compared with H_2 , the CO_2 formation peaks detected in the CO-TPR profile of Rh/ZrO₂ are ascribed to the reduction of Rh₂O₃ surface, Rh–ZrO₂ interface, and Rh species interacting strongly with ZrO_2 , respectively, from low temperature.

As seen in Fig. 5, CO-TPR profile of Rh catalysts supported on Y-doped ZrO_2 is also basically composed of three peaks at 188, ca. 220 and ca. 300 °C. It appears that the CO_2 formation peak at 240 °C observed for Rh/ZrO₂ was clearly shifted to lower temperature, when Y-doped ZrO_2 was employed as support. The use of Y-doped ZrO_2 seems to weaken the interaction of Rh with ZrO_2 . In other words, the reducibility of Rh species supported on Y-doped ZrO_2 was improved. Metallic state of Rh is known to act as catalytically active sites for TWC reactions.³⁷⁾ In fact, Rh/3Y-ZrO₂ and Rh/3Y/ZrO₂ showed higher catalytic activity than Rh/ZrO₂ (Fig. 4). Therefore, one of the roles of Y-doped ZrO_2 would be to form easily reducible Rh species.

On the other hand, the interaction of Rh species with Y-doped ZrO_2 seems to be different depending on the dispersion state of Y species. As seen in Fig. 5, Rh/3Y-ZrO₂ showed a peak at 218 °C, which can be ascribed to the reduction of the interface between Rh and Y species in t-ZrO₂, while Rh/3Y/ZrO₂ gave the peak at higher temperature (224 °C). This suggests that Rh supported on the surface of 3Y/ZrO₂ possesses stronger interaction than Rh on 3Y-ZrO₂, in which Y dissolved in ZrO_2 lattice. Since the strong interaction of Rh with support oxide leads to the difficulty of the formation of catalytically active reducible Rh species, Rh/3Y-ZrO₂ showed higher catalytic activity than Rh/3Y/ZrO₂ (Fig. 4).

As seen in Fig. 5, an additional peak was observed at 260 °C in the CO-TPR profile of Rh/3Y-ZrO₂. Considering that the CO_2 formation peak at 240 °C in the CO-TPR profile of Rh/ZrO₂ is ascribed to the reduction of Rh–m-ZrO₂ interface, the peak at 260 °C would be due to the reduction of Rh–t-ZrO₂ interface. Rh species seems to more strongly interact with t-ZrO₂ than with m-ZrO₂. Our results are well consistent with the report of Heo et al.¹⁴⁾ They investigated the interaction of Rh and ZrO_2 with different crystallite phases, and then reported that Rh had a stronger interaction with tetragonal ZrO_2 than with the monoclinic form. The interaction of Rh with Y species in tetragonal 3Y-ZrO₂ is also suspected by the disappearance of XRD peaks due to monoclinic phase and the broadened Raman peaks as described before (Fig. 3).

Since catalytic reactions take place on catalyst surfaces, the Rh–support interaction is suspected to control the surface valence state of Rh species. In order to gain information on the surface valence state of Rh species, FT-IR spectra of CO species adsorbed on Rh catalysts pretreated with the TWC reaction gas were measured. **Figure 6** shows a typical result obtained for Rh/3Y-ZrO₂, where IR spectra were continuously measured during CO/He flowing and subsequent He purge with an interval of 1 min. As seen in Fig. 6, three IR bands at 2089, 2056 and 2015 cm^{-1} were observed immediately after the introduction of 0.35 % CO/He flow. These bands were increased with time on stream, and then slightly decreased by purging with He. After purging with He in 10 min, distinct three IR bands, which are due to CO species adsorbed on Rh sites, were still detected. The IR spectra obtained after purging

Fig. 6. Change of FT-IR spectra of adsorbed CO species formed on Rh/3Y-ZrO₂ during CO/He flowing and subsequent He purge with an interval of 1 min.

Fig. 7. FT-IR spectra of CO species adsorbed on Rh/ZrO₂, Rh/3Y-ZrO₂ and Rh/3Y/ZrO₂. IR spectra were recorded after purging with He in 10 min.

with He in 10 min were compared for supported Rh catalysts.

Figure 7 shows the FT-IR spectra of CO species adsorbed on Rh/ZrO₂, Rh/3Y-ZrO₂ and Rh/3Y/ZrO₂. It appears that Rh/ZrO₂ gave different IR spectra from the case of Rh/3Y-ZrO₂ and Rh/3Y/ZrO₂. Two IR bands at 2083 and 2010 cm⁻¹ were observed in the IR spectrum for Rh/ZrO₂. These two bands can be assigned to the stretching vibration of a gem-dicarbonyl species on Rh⁺ [Rh⁺(CO)₂].^{38)–40)} The bands located at higher and lower wavenumber are due to the symmetric and asymmetric stretching vibrations, respectively. On the other hand, in case of Rh/3Y-ZrO₂ and Rh/3Y/ZrO₂, in addition of the IR bands due to a gem-dicarbonyl species, the IR band at 2056 cm⁻¹ ascribed to a linearly bonded CO species on Rh⁰ (Rh⁰CO)^{40)–42)} was observed. Raskó et al.⁴³⁾ and Cavanagh et al.⁴⁴⁾ reported that the appearance of the IR band due to linearly bonded CO species is favorable in case of Rh/Al₂O₃ with higher Rh content. In other words, the appear-

ance of linearly bonded CO species is related to the presence of two/three-dimensional Rh_x crystallites in which there are Rh⁰ atoms surrounded only by Rh⁰ atoms. This is probably due to the interaction of Rh species with Y species in 3Y/ZrO₂ and 3Y-ZrO₂. Here, the area ratio, denoted as A₂₀₅₆/A₂₀₈₉, of IR bands at 2056 and 2089 cm⁻¹ was evaluated for Rh/3Y-ZrO₂ and Rh/3Y/ZrO₂, to compare the surface valence state of Rh. As a result of peak deconvolution, the ratio of A₂₀₅₆/A₂₀₈₉ was found to be 1.04 and 0.53 for Rh/3Y-ZrO₂ and Rh/3Y/ZrO₂, respectively. Note that no difference in the area ratio (A_{sym}/A_{asym}) of IR bands due to symmetric and asymmetric stretching vibrations of a gem-dicarbonyl species was observed for Rh/3Y-ZrO₂ and Rh/3Y/ZrO₂ (A_{sym}/A_{asym} = 1.02 and 1.04, respectively). The high value of A₂₀₅₆/A₂₀₈₉ suggests that two/three-dimensional Rh_x crystallites are preferentially present on the surface of Rh in Rh/3Y-ZrO₂. Yoshida et al.⁴⁵⁾ investigated the structure sensitivity for CO-NO reaction between overlayer (thin-film) and nanoparticle Rh catalysts, and then reported that two-dimensional Rh overlayer is highly active catalytic structure.

In the present study, the use of Y-doped ZrO₂ as support contributes to form easily reducible Rh species, resulting in high catalytic activity. In addition, a large fraction of Rh particles in Rh/3Y-ZrO₂, which showed the highest TWC activity (Fig. 4), consists of two-dimensional Rh₂O₃ interacting with Y species in 3Y-ZrO₂. The presence of a large fraction of two-dimensional Rh₂O₃, which would be reduced to Rh⁰ state by the pretreatment with the reaction gas, is responsible for high TWC activity of Rh/3Y-ZrO₂. The tetragonal structure of 3Y-ZrO₂ with which Rh can strongly interact via Y species is a key-factor to obtain highly active Rh catalysts.

4. Conclusion

The activity of Rh catalysts supported on Y-doped ZrO₂ for three-way catalytic reactions is strongly dependent on the crystal structure of Y-doped ZrO₂. Rh/3Y-ZrO₂ with tetragonal phase showed higher activity than Rh/3Y/ZrO₂ with monoclinic phase. Since higher dispersion state of Rh was obtained for the latter catalyst, the high catalytic activity of the former catalyst can not be explained by the dispersion state of Rh. CO-TPR measurements revealed the difference in the reducibility of Rh species dispersed on ZrO₂ and Y-doped ZrO₂ with either monoclinic or tetragonal phase. The reducibility of Rh species was improved when Y-doped ZrO₂ was employed, resulting in higher catalytic activity. Rh species can more strongly interact with 3Y/ZrO₂ than with 3Y-ZrO₂, resulting in the formation of catalytically active reducible Rh species in Rh/3Y-ZrO₂. In the IR spectra of CO species adsorbed on Rh, two kinds of IR bands due to a gem-dicarbonyl species on Rh⁺ and a linear CO species on Rh⁰ were observed for both Rh/3Y-ZrO₂ and Rh/3Y/ZrO₂, suggesting no qualitative difference in the surface valence state of Rh particles. However, a large fraction of the surface of Rh particles in Rh/3Y-ZrO₂ was found to be Rh⁰ sites rather than Rh⁺ sites. This was ascribed to the presence of two-

dimensional Rh₂O₃ interacting with Y species in tetragonal 3Y-ZrO₂. We concluded that the tetragonal structure of 3Y-ZrO₂ with which Rh can interact via Y species is a key-factor to obtain highly active Rh catalysts.

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