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# Rh/Ce<sub>0.25</sub>Zr<sub>0.75</sub>O<sub>2</sub> Catalyst for Steam Reforming of Propane at Low Temperature

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**Abstract:** Solid oxide fuel cells (SOFCs) show high energyconversion efficiency and thus emit less CO<sub>2</sub> than conventional combustion engines. Although SOFCs can directly convert hydrocarbons such as liquefied petroleum gas, these fuels readily induce coking on the electrodes of fuel cell stacks. To avoid coking, hydrocarbons can be subjected to a preliminary endothermic steamreforming step at a relatively low temperature using waste heat from the stack. Herein, we report that a Rh/Ce<sub>0.25</sub>Zr<sub>0.75</sub>O<sub>2</sub> catalyst exhibited higher propane-steam-reforming activity than other Rh/Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub> catalysts and Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Catalyst characterization revealed that Rh/Ce<sub>0.25</sub>Zr<sub>0.75</sub>O<sub>2</sub> had excellent redox property and high H<sub>2</sub>Oadsorption activity, which contributed to the activation of steam and thus enhanced the propane-steam-reforming activity of this catalyst.

#### Introduction

Energy-saving technological innovations such as fuel cells are in high demand around the world. Fuel cells can directly convert chemical energy into electrical energy more efficiently than internal-combustion engines and have therefore attracted considerable attention as environmentally friendly powergeneration devices.<sup>[1–9]</sup> Among the various types of fuel cells, solid oxide fuel cells (SOFCs) show the highest energy-conversion efficiency and therefore emit less CO<sub>2</sub> than conventional combustion engines.<sup>[10–16]</sup> However, the operation temperature of the currently available SOFC systems is so high (700–1000 °C) that starting and shutting them down is time-consuming, and the component parts deteriorate readily. Therefore, a considerable amount of research on lowering the operation temperature of SOFCs has been conducted.<sup>[12,17–23]</sup>

One potential fuel for SOFCs is liquefied petroleum gas (LPG), which consists mainly of propane ( $C_3H_8$ ). LPG has a higher energy density than natural gas, is easy to store, and has a well-established distribution infrastructure.<sup>[8,10,24–27]</sup> However, although SOFCs can convert LPG directly, heavier hydrocarbons can induce coking on the electrodes of fuel cell stacks and in the system pipes.<sup>[27–31]</sup> Therefore, a catalytic low-temperature (300–400 °C) pre-reforming step that eliminates heavier hydrocarbons by converting them to CH<sub>4</sub>, H<sub>2</sub>, and CO<sub>x</sub> using waste heat from the stack is important. This pre-reforming step requires a noblemetal catalyst that shows high activity at low temperature.

Although Ni catalysts are widely used for steam reforming of hydrocarbons in industry owing to their high activity and low  $\cos t$ ,<sup>[30-33]</sup> these catalysts tend to induce coke formation.

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Elements Strategy Initiative for Catalysis and Batteries (ESICB), Kyoto University, Kyoto 615-8245 (Japan) Consequently, catalysts based on noble metals, especially Rh, are attracting increasing attention because of their high activity for hydrocarbon reforming at low temperature.<sup>[7,34–36]</sup> Moreover, Alphonse *et al.* have found that  $Ce_{0.5}Zr_{0.5}O_2$  and TiO<sub>2</sub>, which interact strongly with Rh, are effective catalyst supports for low-temperature steam reforming of propane.<sup>[37]</sup> However, as far as we know, these investigators did not optimize the Ce/Zr ratio or elucidate the function of the  $Ce_{0.5}Zr_{0.5}O_2$  support.

In this study, we prepared Rh catalysts on various Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub> supports, and we investigated their activity for steam reforming of propane at 200–400 °C. We used a conventional Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst for comparison. Rh/Ce<sub>0.25</sub>Zr<sub>0.75</sub>O<sub>2</sub> showed the highest activity among the catalysts studied. To investigate the role of the supports, we used characterization techniques such as temperature-programmed reduction (TPR), H<sub>2</sub>O–temperature-programmed desorption (TPD), and a transient response test using H<sub>2</sub><sup>18</sup>O.

#### **Results and Discussion**

The temperature dependences of the catalytic activities of Rh/Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub> and Rh/y-Al<sub>2</sub>O<sub>3</sub> are shown in Figure 1a. At 200 °C, no propane consumption was observed over Rh/y-Al<sub>2</sub>O<sub>3</sub>, and conversion was low over all the Rh/Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub> catalysts. At 250 °C, some of the propane was consumed, and the propane-conversion activities of the catalysts decreased in the order Rh/Ce<sub>0.25</sub>Zr<sub>0.75</sub>O<sub>2</sub> > Rh/Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> > Rh/Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> > Rh/CeO<sub>2</sub> > Rh/ZrO<sub>2</sub> > Rh/y-Al<sub>2</sub>O<sub>3</sub>. At the target temperature for this study (300 °C), Rh/Ce<sub>0.25</sub>Zr<sub>0.75</sub>O<sub>2</sub> showed the best activity: the propane conversion reached 55%, which was 6 times that over Rh/y-Al<sub>2</sub>O<sub>3</sub>. At 300 °C, the catalyst activities for propane conversion decreased in the order  $Rh/Ce_{0.25}Zr_{0.75}O_2 > Rh/Ce_{0.5}Zr_{0.5}O_2 >$ Rh/ZrO<sub>2</sub> > Rh/Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> > Rh/CeO<sub>2</sub> (Figure 1b). At 350 °C, propane conversion over Rh/Ce0.25Zr0.75O2 and Rh/ZrO2 reached 100%, and the activities of the other catalysts decreased in the order Rh/Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> > Rh/Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> > Rh/CeO<sub>2</sub>. At 400 °C, conversion reached 100% over all the catalysts except Rh/CeO2 and Rh/Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub>. Notably, Rh/γ-Al<sub>2</sub>O<sub>3</sub> exhibited much lower activity than the other catalysts at 200-350 °C. To determine why Rh/Ce<sub>0.25</sub>Zr<sub>0.75</sub>O<sub>2</sub> showed the highest activity over the entire temperature range, we used various techniques to characterize the catalysts.

Figure 2 shows the X-ray diffraction patterns of the Rh/Ce<sub>1</sub>.  $_xZr_xO_2$  and Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts. In the pattern for Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, the major peaks assigned to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were observed. The pattern for Rh/CeO<sub>2</sub> showed peaks that were assigned to a typical cubic fluorite structure. With the addition of ZrO<sub>2</sub> to CeO<sub>2</sub>, the diffraction peaks assignable to the cubic fluorite structure shifted to higher theta values. These results indicate that Zr<sup>4+</sup>, which has a smaller cation radius than Ce<sup>4+</sup> (0.84 vs. 0.97 Å, respectively), was incorporated into the CeO<sub>2</sub> lattice by cation exchange and that a solid solution of CeO<sub>2</sub> and ZrO<sub>2</sub> was formed. Note also that in the patterns for the Zr<sup>4+</sup>-doped catalysts we observed no extra peaks assigned to monoclinic zirconia were identified. Phases related to the presence of Rh species could not be identified in any of the

## **FULL PAPER**





	A	
Table 1. Physical properties of the supported Rh catalysts.		
Catalyst	Specific surface area (m <sup>2</sup> g <sup>-1</sup> )	Dispersion of Rh <sup>[a]</sup> (%)
Rh/CeO <sub>2</sub>	22	41
Rh/Ce <sub>0.75</sub> Zr <sub>0.25</sub> O <sub>2</sub>	27	50
Rh/Ce <sub>0.5</sub> Zr <sub>0.5</sub> O <sub>2</sub>	33	50
Rh/Ce <sub>0.25</sub> Zr <sub>0.75</sub> O <sub>2</sub>	17	51
Rh/ZrO <sub>2</sub>	10	45
Rh/γ-Al₂O₃	165	85
[a] Determined from hy	drogen-adsorption capacit	y by assuming $H/Rh = 1$ .



Figure 2. X-ray diffraction patterns of the supported Rh catalysts.

catalysts, owing to the low Rh loading.

The physical properties of the catalysts are shown in Table 1. The Brunauer–Emmett–Teller surface areas of the Rh/Ce<sub>1</sub>.<sub>x</sub>Zr<sub>x</sub>O<sub>2</sub> catalysts were in the 10–33 m<sup>2</sup> g<sup>-1</sup> range, and the value for Rh/γ-Al<sub>2</sub>O<sub>3</sub> was 147 m<sup>2</sup> g<sup>-1</sup>. It seems likely that the higher specific surface area of the γ-Al<sub>2</sub>O<sub>3</sub> support contributed to an increase in Rh dispersion: the dispersion over this support was 85%, compared with 41–50% for the Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub> supports. However, at  $\leq$ 350 °C, Rh/γ-Al<sub>2</sub>O<sub>3</sub> showed much lower propane conversion than Rh/Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub> could not be explained in terms of an increase in the number of Rh active sites. These results indicate that the properties of the support, rather than those of the Rh, were crucial determinants of catalyst activity.



Figure 3. H<sub>2</sub>-TPR profiles of the supported Rh catalysts.

To investigate the redox properties of the supported Rh catalysts, we performed H<sub>2</sub>-TPR analysis (Figure 3). Owing to the nonreducibility of Al<sup>3+</sup>, we attributed the reduction peaks observed for Rh/γ-Al<sub>2</sub>O<sub>3</sub> at temperatures lower than 300 °C to the reduction of Rh<sub>2</sub>O<sub>3</sub>. In contrast, the H<sub>2</sub>-TPR profile of Rh/CeO<sub>2</sub> showed peaks in two regions: lower than 300 °C and higher than 600 °C. At temperatures lower than 300 °C, the amount of hydrogen consumed over Rh/CeO<sub>2</sub> was larger than the amount consumed over Rh/γ-Al<sub>2</sub>O<sub>3</sub>. This result indicates that not only Rh<sub>2</sub>O<sub>3</sub> but also surface CeO<sub>2</sub> was reduced at low temperature. The reduction peak at higher temperature corresponds to the reduction of bulk CeO<sub>2</sub>.<sup>[38-40]</sup> As the Zr content was increased, the high-temperature reduction peak shifted to lower temperature and simultaneously decreased in intensity, owing to the decrease in lattice tension resulting from incorporation of Zr<sup>4+</sup> into the CeO<sub>2</sub>

## **FULL PAPER**

structure and the corresponding decrease in the amount of reducible Ce<sup>4+</sup>.<sup>[41–43]</sup> When CeO<sub>2</sub> is reduced, Ce<sup>4+</sup> is converted to Ce<sup>3+</sup>, which has a larger cation radius. So introduction of the smaller Zr<sup>4+</sup> cation into the CeO<sub>2</sub> lattice decreased the lattice tension during the reduction and promoted reduction of the support. As a result, reduction of the support at and below 300 °C was promoted by the increase in the amount of Zr<sup>4+</sup>. For Rh/ZrO<sub>2</sub>, the reduction peaks at temperatures lower than 300 °C were attributed to the reduction of Rh<sub>2</sub>O<sub>3</sub>, owing to the irreducibility of Zr<sup>4+</sup>. These results reveal that addition of Zr<sup>4+</sup> to the CeO<sub>2</sub> support markedly enhanced the redox properties of the support.



**Figure. 4.** H<sub>2</sub>O-TPD profiles of the supported Rh catalysts, with monitoring by mass spectrometry at (a) m/z 18 (H<sub>2</sub>O) and (b) m/z 2 (H<sub>2</sub>).

We carried out H<sub>2</sub>O-TPD analysis of the catalysts to evaluate their ability to adsorb and activate H<sub>2</sub>O, which is one of the reactants (Figure 4; see Table S1 in the supporting information for the amounts of H<sub>2</sub>O desorbed). H<sub>2</sub>O desorption on Rh/CeO<sub>2</sub> (3.0 µmol m<sup>-2</sup>) was observed at 130–450 °C. However, upon addition of Zr<sup>4+</sup> to the support, H<sub>2</sub>O desorption was observed at 200–400 °C and the amount of H<sub>2</sub>O desorbed was increased compared with that desorbed on Rh/CeO<sub>2</sub>; the amount of H<sub>2</sub>O desorbed was the highest for Rh/ZrO<sub>2</sub> (9.8 µmol m<sup>-2</sup>). These results indicate that H<sub>2</sub>O-adsorption ability was enhanced by increasing the amount of Zr<sup>4+</sup> in the support. The amount of H<sub>2</sub>O desorbed on Rh/γ-Al<sub>2</sub>O<sub>3</sub> was 3.5 µmol m<sup>-2</sup>.

These experiments also revealed that  $H_2$  formed on  $Rh/CeO_2$  at the same time as  $H_2O$  desorption (Figure 4b), by means of the following reaction:

$$CeO_{2-y} + yH_2O \rightarrow CeO_2 + yH_2$$
(1)

The H<sub>2</sub>-formation temperature decreased with increasing  $ZrO_2$  content. However, H<sub>2</sub> did not form on Rh/ZrO<sub>2</sub> or Rh/y-Al<sub>2</sub>O<sub>3</sub>,

neither of which contains a redox-active element. The H<sub>2</sub>O-TPD results indicate that adding Zr<sup>4+</sup> to CeO<sub>2</sub> improved the H<sub>2</sub>O-activation ability of the reduced support and that the improvement was greatest over Rh/Ce<sub>0.25</sub>Zr<sub>0.75</sub>O<sub>2</sub>. This result was due to enhancement of the redox properties of the support, as evidenced by the H<sub>2</sub>-TPR analysis.

At 300 °C, the Rh/ZrO<sub>2</sub> catalysts exhibited higher propaneconversion activity than the Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, which indicates that the ability of ZrO<sub>2</sub> to adsorb steam was important for catalyzing steam reforming of the propane. Furthermore, the fact that Rh/Ce<sub>0.25</sub>Zr<sub>0.75</sub>O<sub>2</sub> exhibited the highest propane-conversion activity among the Rh/Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub> catalysts at 300 °C indicates that the excellent H<sub>2</sub>O-activation and H<sub>2</sub>O-adsorption activities of this catalyst efficiently promoted propane steam reforming at low temperature.



Figure 5. Amounts of  $^{18}\text{O-containing}$  products formed per specific surface area over (a) Rh/γ-Al\_2O\_3 and (b) Rh/Ce\_{0.25}Zr\_{0.75}O\_2 at 300 °C.

As mentioned above, excellent redox property was the most important determinant of the high catalytic activity of the Rh/Ce<sub>0.25</sub>Zr<sub>0.75</sub>O<sub>2</sub> catalyst. To elucidate how the redox properties of this catalyst contributed to activation of H<sub>2</sub>O and propane during the propane steam reforming, we performed transient response experiments using H<sub>2</sub><sup>18</sup>O. For comparison, we used Rh/γ-Al<sub>2</sub>O<sub>3</sub>, which does not contain a redox-active element. After H<sub>2</sub> pretreatment, C<sub>3</sub>H<sub>8</sub> and H<sub>2</sub><sup>18</sup>O + H<sub>2</sub>O were supplied to the

catalyst for 30 min at 300 °C. Subsequently, the reaction vessel was purged with Ar, C<sub>3</sub>H<sub>8</sub> and H<sub>2</sub>O were fed to the catalyst, and the products were analyzed by mass spectrometry (MS). Only small amounts of <sup>18</sup>O-containing species formed over Rh/y-Al<sub>2</sub>O<sub>3</sub> (Figure 5a), whereas large amounts of <sup>18</sup>O-containing species formed over Rh/Ce<sub>0.25</sub>Zr<sub>0.75</sub>O<sub>2</sub> (Figure 5b). On the basis of these results, along with the H2-TPR and H2O-TPD results, we attributed the formation of products containing <sup>18</sup>O (CO<sup>18</sup>O and C<sup>18</sup>O<sub>2</sub>) to the participation of H218O-derived lattice oxygen atoms in the Ce<sub>0.25</sub>Zr<sub>0.75</sub>O<sub>2</sub> support. Note that distinguishing the mass spectra of  $C^{18}O$  and  $C_2H_6$  was difficult because the  $C^{18}O$  fragment and the molecular ion of  $C_2H_6$  have the same m/z value (30). Because CO was not detected over Rh/Ce<sub>0.25</sub>Zr<sub>0.75</sub>O<sub>2</sub> (see Figure 6b for product distribution) during the catalytic activity test, the mass spectra was not ascribed to the mass spectra of C<sup>18</sup>O. On the other hand, formation of a large amount of C18O2 indicates that C18O produced by the reaction between propane and lattice oxygen atoms was further reacted with lattice oxygen atoms [Eq. (2)]. Therefore, these results demonstrate that the redox property of  $Ce_{0.25}Zr_{0.75}O_2$ strongly activated both steam and propane.

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{2}$$

Next, to clarify the reaction mechanism over Rh/Ce<sub>0.25</sub>Zr<sub>0.75</sub>O<sub>2</sub>, we investigated the product distribution and the propane and H<sub>2</sub>O conversions (Figure 6; see Figure S1 in the supporting information for the equilibrium yields). Over Rh/y-Al<sub>2</sub>O<sub>3</sub> (Figure 6a), a high concentration of CO2 and low concentrations of CH4, CO, and C<sub>2</sub>H<sub>6</sub> were observed at 250 °C. When the reaction temperature was increased, the CO selectivity initially increased slightly (at 300 °C) and then decreased. In contrast, the CO<sub>2</sub> and C<sub>2</sub>H<sub>6</sub> selectivities decreased with increasing temperature, whereas the CH<sub>4</sub> selectivity increased. These results indicate that the watergas shift reaction [Eq. (2)] predominated at 250 °C and that CO methanation [Eq. (3)] became faster than the shift reaction as the temperature was increased. Note that the decrease in  $C_2H_6$ concentration with increasing temperature indicates that steam cracking of propane [Eq. (4)] was retarded and steam reforming was enhanced.

$$CO + 3H_2 \rightarrow CH_4 + H_2O \tag{3}$$

$$C_3H_8 + H_2O \rightarrow C_2H_6 + 2H_2 + CO$$
 (4)

The results obtained over Rh/Ce<sub>0.25</sub>Zr<sub>0.75</sub>O<sub>2</sub> are presented in Figure 6b. At 200 °C, high concentrations of CO<sub>2</sub> and C<sub>2</sub>H<sub>6</sub> were produced, whereas the CH<sub>4</sub> concentration was low and CO generation was not observed. When the reaction temperature was increased, the  $CH_4$  selectivity increased and the  $C_2H_6$ selectivity decreased, owing to the predominance of propane steam reforming over cracking at the higher temperatures. The CO<sub>2</sub> selectivity also decreased slowly with increasing temperature over the entire range. CO methanation was accelerated at higher temperature until 300 °C, as in the reaction over  $Rh/\gamma$ -Al<sub>2</sub>O<sub>3.</sub> Notably, CO was not detected over Rh/Ce<sub>0.25</sub>Zr<sub>0.75</sub>O<sub>2</sub> at any temperature, which contrasts with the results obtained over Rh/y-Al<sub>2</sub>O<sub>3</sub>. This difference indicates that the rates of CO-consuming reactions such as the water-gas shift reaction and CO methanation were much faster over Rh/Ce<sub>0.25</sub>Zr<sub>0.75</sub>O<sub>2</sub> than over Rh/y-Al<sub>2</sub>O<sub>3</sub>. Regarding this, we observed that at 200–350 °C, H<sub>2</sub>O conversion over Rh/Ce0.25Zr0.75O2 was higher than that over Rh/γ-Al<sub>2</sub>O<sub>3</sub>, a result that is due to the high H<sub>2</sub>O-activation activity of Rh/Ce<sub>0.25</sub>Zr<sub>0.75</sub>O<sub>2</sub>. In addition, at low temperatures (200–300 °C), higher H<sub>2</sub> concentrations were observed over Rh/Ce<sub>0.25</sub>Zr<sub>0.75</sub>O<sub>2</sub> than over Rh/y-Al<sub>2</sub>O<sub>3</sub>, whereas at high temperatures (350-400 °C), H<sub>2</sub> concentrations were comparable for both catalysts

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Figure 6. Effect of reaction temperature on product distributions of propane steam reforming over (a)  $Rh/\gamma-Al_2O_3$  and (b)  $Rh/Ce_{0.25}Zr_{0.75}O_2$ .

 $C_3H_8 + 3H_2O \rightarrow 3CO + 7H_2$ 

Next, we compared the rates of the CO-consuming reactions that occurred after propane steam reforming over Rh/y-Al2O3 and Rh/Ce<sub>0.25</sub>Zr<sub>0.75</sub>O<sub>2</sub>. For these experiments, a reactant mixture consisting of CO/H<sub>2</sub>/H<sub>2</sub>O in a ratio of 3/7/3 was fed to the catalyst on the assumption that the propane was completely consumed by steam reforming to produce CO and H<sub>2</sub> [Eq. (5)]. When the reaction was carried out over Rh/y-Al<sub>2</sub>O<sub>3</sub> (Figure 7a), reaction of CO started at 250 °C, and conversion reached 9% at 300 °C, 58% at 350 °C, and 100% at 400 °C. CH<sub>4</sub> was the only product at 250 °C. As the reaction temperature was increased, the  $\text{CH}_4$ selectivity decreased and the CO<sub>2</sub> selectivity gradually increased. However, even at 400 °C, CO methanation predominated. Furthermore, small amounts of C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub> were generated at 300-350 °C, indicating that some C-C bond formation occurred at that temperature range in this condition. In contrast, when the reaction was carried out over Rh/Ce<sub>0.25</sub>Zr<sub>0.75</sub>O<sub>2</sub> (Figure 7b), reaction of CO started at 250 °C, as was the case over Rh/y-Al<sub>2</sub>O<sub>3</sub>,

## **FULL PAPER**



Figure 7. Effect of temperature on reactions of CO/H<sub>2</sub>/H<sub>2</sub>O over (a) Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and (b) Rh/Ce<sub>0.25</sub>Zr<sub>0.75</sub>O<sub>2</sub>.

but CO conversion increased drastically with temperature, reaching 100% at 350 °C, which was lower by 50 °C than the corresponding temperature over Rh/y-Al<sub>2</sub>O<sub>3</sub>. These results reveal the much higher activity of Rh/Ce0.25Zr0.75O2 for catalyzing CO consumption. Furthermore, at and below 300 °C, the product distribution over Rh/Ce<sub>0.25</sub>Zr<sub>0.75</sub>O<sub>2</sub> was completely different from that over  $Rh/\gamma$ -Al<sub>2</sub>O<sub>3</sub>; specifically, the CO<sub>2</sub> concentration over Rh/Ce<sub>0.25</sub>Zr<sub>0.75</sub>O<sub>2</sub> was higher than the CH<sub>4</sub> concentration. These results indicate that the water-gas shift reaction was much faster over Rh/Ce<sub>0.25</sub>Zr<sub>0.75</sub>O<sub>2</sub> than over Rh/γ-Al<sub>2</sub>O<sub>3</sub> and that CO was effectively consumed owing to the excellent H<sub>2</sub>O-activation activity of Rh/Ce<sub>0.25</sub>Zr<sub>0.75</sub>O<sub>2</sub>, which was due to its excellent redox properties. When the reaction temperature was increased to 350 °C, the CO<sub>2</sub> selectivity decreased further. At temperatures of 350°C and higher, the CH<sub>4</sub> concentration was higher than the CO<sub>2</sub> concentration, indicating that CO methanation was faster than the water-gas shift reaction.

It has been reported that during steam reforming reactions, the support is the principal site for water activation and that metal sites are responsible for hydrocarbon activation.<sup>[44–46]</sup> In the cases of Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Rh/ZrO<sub>2</sub>, propane was adsorbed on active Rh surface sites, and steam was adsorbed on support surface sites. The higher H<sub>2</sub>O-adsorption activity of Rh/ZrO<sub>2</sub> resulted in its higher activity for propane steam reforming. In the case of

Rh/Ce<sub>0.25</sub>Zr<sub>0.75</sub>O<sub>2</sub>, the conventional reaction pathway was accompanied by a reaction between propane and lattice oxygen atoms derived from H<sub>2</sub>O. Although we suspected that differences in the electronic state of Rh might be responsible for the different catalytic activities of the catalysts, Rh K-edge XANES spectra for Rh/Ce<sub>0.25</sub>Zr<sub>0.75</sub>O<sub>2</sub>, Rh/γ-Al<sub>2</sub>O<sub>3</sub>, and Rh/ZrO<sub>2</sub> after H<sub>2</sub> treatment were comparable with the spectrum of Rh foil (Figure S3 in the supporting information), indicating that Rh was present in the catalysts in the metallic state.



Figure 8. Mechanism of propane steam reforming over  $Rh/Ce_{0.25}Zr_{0.75}O_2$  at low temperature.



**Figure 9.**  $C_3H_8$  conversion as a function of reaction time during propane steam reforming over Rh/Ce<sub>0.25</sub>Zr<sub>0.75</sub>O<sub>2</sub>. Conditions: ( $\textcircled{\bullet}$ ) 350 °C, space volume = 3.9 L h<sup>-1</sup> g<sup>-1</sup> and ( $\textcircled{\bullet}$ ) 380 °C, space volume = 77.1 L h<sup>-1</sup> g<sup>-1</sup>.

On the basis of the characterization results, we propose the reaction mechanism outlined in Figure 8 for steam reforming of propane over the Rh/Ce<sub>0.25</sub>Zr<sub>0.75</sub>O<sub>2</sub> catalyst at low temperature. The H<sub>2</sub>-TPR profile revealed that the redox property of the support is high and that reduction of the support occurs readily at low temperature owing to the presence of the smaller Zr<sup>4+</sup> cation in the CeO<sub>2</sub> lattice. During H<sub>2</sub> reduction, Ce<sub>0.25</sub>Zr<sub>0.75</sub>O<sub>2</sub> is reduced, and an oxygen defect is thus generated. Activation of steam by

## **FULL PAPER**

the oxygen defect is accompanied by H<sub>2</sub> formation, and propane reacts with the activated-oxygen species to form CO. In addition, the water–gas shift reaction [Eq. (2)] is promoted by the Rh/Ce<sub>0.25</sub>Zr<sub>0.75</sub>O<sub>2</sub> catalyst, owing to the presence of the abovementioned activated-oxygen species, and this reaction efficiently oxidizes CO to CO<sub>2</sub>. Therefore, CO generation is not observed.

We also evaluated the long-term stability of the Rh/Ce<sub>0.25</sub>Zr<sub>0.75</sub>O<sub>2</sub> catalyst (Figure 9). When steam reforming was carried out for 50 h, propane conversion decreased from 24% to 20% at 380 °C and from 99% to 98% at 350 °C. In addition, the product selectivities remained largely unchanged with time (Figures S4 and S5 in the supporting information). After the reaction, carbon deposition on the used catalyst was quantified by means of temperature-programmed oxidation, which revealed that a trace amount of carbon had been deposited on the catalysts (0.11 and 0.10 wt% at 350 and 380 °C, respectively), revealing the high stability of the catalyst.

### Conclusions

We found that at 300 °C, a temperature suitable for SOFC systems, Rh/Ce<sub>0.25</sub>Zr<sub>0.75</sub>O<sub>2</sub> exhibited higher propane-steamreforming activity than Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and other Rh/Ce<sub>u.</sub>Zr<sub>1-x</sub>O<sub>2</sub> catalysts. In addition to the conventional mechanism involving water adsorption and subsequent activation on the oxide support, H<sub>2</sub>O was also activated by oxygen defect sites that formed on the Rh/Ce<sub>0.25</sub>Zr<sub>0.75</sub>O<sub>2</sub> catalyst, owing to the excellent redox property of the support. This activation mechanism promoted propane steam reforming and subsequent water–gas shift reaction. Stability tests revealed that Rh/Ce<sub>0.25</sub>Zr<sub>0.75</sub>O<sub>2</sub> resisted coking and showed stable activity for at least 50 h, making the catalyst a promising candidate for pre-reforming of hydrocarbons for SOFC applications.

### **Experimental Section**

#### Catalyst preparation

For preparation of the Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub> supports, an aqueous solution containing ZrO(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O (Wako Pure Chemical Industries) and Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (Wako) was added to a 25% aqueous NH<sub>3</sub> solution. Co-precipitation occurred, and the co-precipitates were kept in suspension by stirring at room temperature overnight and were then filtered, washed with distilled water, dried overnight at 70 °C, and precalcined at 700 °C to afford Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub>, where x =0, 0.25, 0.5, 0.75, and 1.0. A  $\gamma\text{-Al}_2\text{O}_3$  sample (JRC-ALO-8) was obtained from the Catalysis Society of Japan, precalcined at 700 °C, and used for wet impregnation with aqueous  $Rh(NO_3)_3 \cdot nH_2O$ (Mitsuwa Pure Chemicals). The final concentration of Rh was 0.5 wt%. All the samples were dried at room temperature, and subsequently at 70 °C overnight, and the dried samples were calcined at 450 °C in flowing air. The powdery catalysts were pressed into pellets, crushed, and sieved to obtain grains with diameters between 250 and 500  $\mu$ m.

#### Catalytic activity tests

Tests of catalyst activity for steam reforming of propane were conducted in a fixed-bed flow reactor system at atmospheric pressure. The  $C_3H_8/H_2O/N_2$  ratio in the feed gas was 1/6/7 vol% (total flow rate, 32.1 mL min<sup>-1</sup>; space velocity, 3.9 L h<sup>-1</sup> g<sup>-1</sup>; or total flow rate, 128.5 mL min<sup>-1</sup>; space velocity, 77.1 L h<sup>-1</sup> g<sup>-1</sup>), as

determined by assuming total conversion of CO to  $CO_2$  in the entire reaction [Eq. (6)]. The steam-to-carbon ratio was kept at 2/1. Each catalyst (500 or 100 mg) was reduced in pure H<sub>2</sub> (total flow rate, 20 mL min<sup>-1</sup>) at 600 °C for 1 h. The reaction was carried out either at 200–400 °C or at 380 °C. The rates of product formation were determined by means of gas chromatography (GC) with thermal conductivity detection. The amount of C<sub>3</sub>H<sub>8</sub> converted and selectivity for carbon-containing products were calculated from the carbon balance, because the amount of coke deposited was very small to negligible. The equations used are shown in the supporting information.

 $C_3H_8 + 6H_2O \rightarrow 3CO_2 + 10H_2$ 

(6)

For measurement of the activity of the catalysts for COconsuming reactions, the ratio in the feed gas was 3/7/3/7 vol % CO/H<sub>2</sub>/H<sub>2</sub>O/N<sub>2</sub> (total flow rate, 45.8 mL min<sup>-1</sup>; space velocity, 5.5 L h<sup>-1</sup> g<sup>-1</sup>). Each catalyst (500 mg) was reduced in pure H<sub>2</sub> at a total flow rate of 20 mL min<sup>-1</sup> at 600 °C for 1 h. The reaction temperatures were in the 200–400 °C range. The rates of product formation were analyzed by means of GC with thermal conductivity detection. The amount of CO converted and selectivity for carbon-containing products were calculated from the carbon balance. The equations used are shown in the supporting information.

Transient response tests using labeled  $H_2^{18}O$  were conducted to ascertain the contribution of lattice oxygen in the support. Each catalyst (500 mg) was reduced in flowing  $H_2$  at 600 °C, cooled to 300 °C in Ar, and then analyzed as follows:

(1) Reactant gas containing  $C_3H_8/H_2^{16}O$  (17.5%  $H_2^{18}O$ )/Ar at a ratio of 1/6/7 vol% and a total flow rate of 32.1 mL min<sup>-1</sup> was supplied to the catalyst for 30 min.

(2) The reaction vessel was purged with Ar for 3 h.

(3) Reaction gas containing  $C_3H_8/H_2^{16}O/Ar$  at a ratio of 1/6/7 and a total flow rate of 32.1 mL min<sup>-1</sup> was supplied to the catalyst, and simultaneously the exit gas was analyzed by means of quadrupole MS. Ar was added as an internal standard. The following <sup>18</sup>O species were analyzed: *m/z* 20 (H<sub>2</sub><sup>18</sup>O), *m/z* 30 (C<sup>18</sup>O), *m/z* 46 (CO<sup>18</sup>O), and *m/z* 48 (C<sup>18</sup>O<sub>2</sub>).

#### Characterization

X-ray diffraction patterns were recorded on a SmartLab X-ray diffractometer with a Cu K $\alpha$  radiation (Rigaku, Japan) source operating at 40 kV and 30 mA.

The specific surface areas of the catalysts were estimated by the Brunauer–Emmett–Teller method with a BELSORP-mini instrument (BEL Japan Inc., Japan) at –196 °C with N<sub>2</sub> as the analysis gas. Before each measurement, the sample was outgassed at 300 °C for 2 h.

H<sub>2</sub>-TPR measurements were performed by heating the catalysts (50 mg) from room temperature to 1000 °C at a rate of 10 °C min<sup>-1</sup> in flowing H<sub>2</sub>/Ar gas (5 vol%; flow rate, 30 mL min<sup>-1</sup>). H<sub>2</sub> consumption was monitored by means of GC with thermal conductivity detection.

The dispersion of Rh metal was determined by a H<sub>2</sub> pulse chemisorption method. Each catalyst (200 mg) was reduced in flowing H<sub>2</sub> at 600 °C for 1 h (heating rate, 5 °C min<sup>-1</sup>). After reduction, the catalyst was heated at 600 °C for 30 min under flowing Ar to desorb any H<sub>2</sub> that spilled over the support and was then cooled to room temperature under flowing Ar. The H<sub>2</sub> uptake measurements were performed at -76 °C.

 $H_2O.TPD$  measurements were performed with a BELCAT II- VP-C chemisorption analyzer (Microtrac-BEL). Catalyst (200 mg) was loaded into a quartz reactor and reduced in a stream of  $H_2$  at

600 °C for 1 h; the reactor was then purged with a stream of He for 1 h and cooled to 100 °C. After 5% H<sub>2</sub>O in He gas (flow rate, 30 mL min<sup>-1</sup>) was fed to the catalyst for 30 min at 100 °C, the oven temperature was increased at 10 °C min<sup>-1</sup> to 800 °C. The H<sub>2</sub>O and H<sub>2</sub> desorption profiles were monitored by quadrupole MS at m/z 18 and m/z 2, respectively.

The formation of the carbonaceous deposits was quantified by temperature-programmed oxidation of the used catalyst. Used catalyst (50 mg) was placed in a quartz reactor, and the reactor was heated from room temperature to 1000 °C at a rate of 10 °C min<sup>-1</sup> under a flow of  $O_2$ /Ar gas (5 vol%; flow rate, 28.5 mL min<sup>-1</sup>). The effluents were analyzed by GC with flame ionization detection.

X-ray absorption fine structure measurements for the Rh Kedges were performed on the BL01B1 beamline at SPring-8. A Si used for two-crystal monochromator was (311) the measurements of absorption edges. After being reduced under a flow of pure H<sub>2</sub> at 600 °C for 1 h, the samples were cooled in Ar, recovered from the tubular reactor, and encapsulated in plastic bags filled with Ar. All the procedures for recovery and transfer of the samples to the plastic bags were carried out under Ar to avoid altering the samples through air exposure. The plastic bags were transferred to the beamline and spectra of the catalyst disks were measured. Measurements of the Rh K-edge were carried out in transmittance mode with two ion chambers. The X-ray energy was calibrated against the spectra of standard Rh foils. Data analysis was performed with the Athena and Artemis programs (ver. 0.9.25) included in the Demeter package. [47]

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