1. Introduction

Demand for petroleum oil and natural gas continues to be high, leading to fears that the recoverable reserves of the fossil resources will become depleted. Therefore, it is important to develop innovative technologies for reducing oil and gas consumption. Fuel cells (FCs) can convert chemical energy directly into electrical energy at high efficiencies without the limitations of the Carnot cycle. Therefore, fuel cells may offer the solution to problems arising from the limited supply of fossil fuels. In particular, polymer electrolyte fuel cells (PEFCs) have high potential as stationary power generators for domestic use and other applications, due to its low working temperature of around 373 K. However, innovations in both fuel cell materials and fuel cell engineering, including the hydrocarbon reforming process, are essential to permit fuel cells to compete with conventional internal combustion engines.

In general, the hydrogen fuel for FCs is produced by steam reforming (SR) of hydrocarbons. However, SR is an endothermic reaction with high operation temperatures of 973-1073 K, which require long startup times of the reformer and continued external heating of the catalyst bed during the reaction. In contrast, oxidative reforming (OR) of hydrocarbons combines exothermic combustion and endothermic reforming, so the heat produced by the combustion can be used for the reforming. In OR, after hydrocarbon combustion is initiated at the catalytic auto-ignition temperature of about 523 K in the presence of noble metals, heat generated by the reaction is directly supplied to the catalyst bed. Consequently, the catalyst bed temperature rapidly reaches the operation temperature and immediately produces hydrogen and other gases, and subsequently the reaction proceeds spontaneously. Furthermore, OR can produce hydrogen with high rate and high energy efficiency due to the combinations of these exothermic and endothermic processes. Therefore, OR is expected to be more suitable than conventional SR for the local production of hydrogen at hydrogen filling stations and for on-site reformers of domestic FCs, which will involve frequently repeated start-up and shut-down processes. However, OR will still require external heating to heat the catalyst bed from ambient temperature to the catalytic auto-ignition temperature, as well as adequate time for heating, and this
time lapse will delay the onset of hydrogen formation. Various strategies have been explored to reach the temperature instantaneously, including electrical heating of the catalysts, and homogeneous combustion. However, the problems regarding energy consumption and time delay during start-up are yet to be solved.

2. Design of OR Process Triggered at Ambient Temperature

Previously, we demonstrated a new cold start process for OR of hydrocarbons from ambient temperature without the need for external heat input or other complicated procedures. In this process, the catalysts are heated rapidly from ambient temperature to the catalytic auto-ignition temperature by the heat generated by self-heating of the catalyst (Fig. 1). These catalysts consist of metal nanoparticles supported on reducible oxides. OR used n-butane, one of the main components of liquefied petroleum gas (LPG), as the hydrocarbon in the following reaction (Eq. (1)).

$$\text{C}_4\text{H}_{10} + 2\text{O}_2 \rightarrow 5\text{H}_2 + 4\text{CO}$$

$$\Delta H (298 \text{ K}) = -316 \text{ kJ}$$

The schematic of our catalytic OR reforming process is shown in Fig. 2. At first, the catalyst is treated in H2 at high temperature to reduce the catalyst support to AO2–x. Then, the feed gas containing n-C4H10 and O2 is supplied to the catalyst at ambient temperature or 273 K, resulting in oxidation of the support to AO2 and strong evolution of heat. This evolved heat rapidly increases the temperature of the catalyst to 523 K and OR then starts. The temperature of part of the catalyst is higher than 873 K, and H2 and CO are produced during the OR reaction. Consequently, in-situ reduction of AO2 by the produced H2 is possible. This reduced state of the support is maintained as the catalyst is cooled down to ambient temperature in inert gases, so that the OR can be triggered in subsequent cycles without H2 reduction.

Here we explain the OR process triggered at ambient temperature with the use of the Rh/CeO2 and clarify the mechanism of the start-up process. The suitability of other reducible rare earth oxides, such as Pr6O11, Tb4O7, and Ce0.5Zr0.5O2, and the crucial characteristics of the support for the proposed OR process are evaluated.

3. OR Process Triggered over Rh/CeO2

Catalytic activity was measured with a conventional flow system. The catalysts were reduced in pure hydrogen at 873 K for 1 h and then cooled to ambient temperature in Ar. The furnace was opened, and the quartz reactor was wrapped with ceramic insulation material for subsequent reaction under quasi-adiabatic conditions. α-Al2O3 balls were packed into the remaining space inside the reactor. After supplying a feed gas consisting of n-C4H10/O2/Ar/N2 (molar ratio = 1 : 2 : 7 : 1) at ambient temperature to Rh/ CeO2 reduced at 873 K, the concentration of the dry gas product was measured as shown in Fig. 3. Note that we determined the feed gas composition assuming the reaction of Eq. (1). Only CO and CO2 were produced at the beginning (4 s). However, H2 was rapidly produced after that time and the formation rate of H2 was much higher than those of CO and CO2 at the end. Such increase in H2 formation rate occurred simultaneously with the increase in catalyst bed temperature. These results indicate that initiation of combustion (Eq. (2)) and subsequently reforming
(Eqs. (3) and (4)) reactions of \( n \)-butane occurred.
\[
\text{n-C}_4\text{H}_{10} + 6.5\text{O}_2 \rightarrow 5\text{H}_2\text{O} + 4\text{CO}_2 \\
\Delta H (298 \text{ K}) = -2657 \text{ kJ}
\]  

\[
\text{n-C}_4\text{H}_{10} + 4\text{H}_2\text{O} \rightarrow 9\text{H}_2 + 4\text{CO} \\
\Delta H (298 \text{ K}) = -651 \text{ kJ}
\]  

\[
\text{n-C}_4\text{H}_{10} + 4\text{CO}_2 \rightarrow 5\text{H}_2\text{O} + 8\text{CO} \\
\Delta H (298 \text{ K}) = -816 \text{ kJ}
\]  

Formation of low concentration of \( \text{CH}_4 \) indicates the occurrence of the methanation reaction of \( \text{CO} \) (Eq. (5)) and \( \text{CO}_2 \) (Eq. (6)) through the following reactions.
\[
\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O} \\
\Delta H (298 \text{ K}) = -206 \text{ kJ}
\]  

\[
\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \\
\Delta H (298 \text{ K}) = -165 \text{ kJ}
\]  

After 14 s, the \( \text{H}_2 \) concentration increased to 15 %, which was about 80 % of the stable value. At the same time, the catalyst bed temperature reached 1133 K. These results revealed that OR was triggered rapidly over reduced \( \text{Rh/CeO}_2 \) without external heat input. Note that complete consumption of \( \text{O}_2 \) and 90 % conversion of \( n\text{-C}_4\text{H}_{10} \) were obtained after 30 min without external heat input to the catalyst. At that time, the heats of the exothermic and endothermic reactions and the external heat losses were fully balanced.

Here we investigate the mechanism of the OR triggered at such low temperature, \textit{i.e.} ambient temperature. Thermodynamic calculations indicate that \( \text{O}_2 \) consumption and corresponding \( n\text{-C}_4\text{H}_{10} \) combustion (Eq. (2)) will progress at any temperature. However, any combustion reaction requires a minimum temperature, \textit{i.e.} the auto-ignition temperature, to proceed at a rate that releases more heat than is removed from the system by convection from the flowing gas. Once the reaction is initiated, an exothermic reaction quickly reaches the operation point, which is controlled by the sum of the heat fluxes produced by the exothermic and endothermic reactions and the removal of heat through convection and transmission through the wall of the reactor.

The OR was not triggered at ambient temperature over \( \text{Rh/CeO}_2 \) reduced at \( \leq 673 \text{ K} \) and over \( \text{Rh/Al}_2\text{O}_3 \) reduced at any temperature. The catalyst bed temperature rose only slightly on exposure to the feed gas, indicating that only minor oxidation of the catalyst occurred. Neither oxidation nor reforming of \( n\text{-C}_4\text{H}_{10} \) occurred over these catalysts. \( \text{Al}_2\text{O}_3 \) is irreducible under the reduction conditions employed, indicating that the heat produced by oxidation of \( \text{Rh} \) is insufficient to trigger the OR at ambient temperature. Therefore, we concluded that heat produced by re-oxidation of \( \text{CeO}_2\text{,} \) to \( \text{CeO}_2 \) supplied additional heat to the \( \text{Rh/CeO}_2 \) reduced at \( \approx 873 \text{ K} \) resulting in the catalyst reaching the catalytic auto-ignition temperature.

To prove our hypothesis, the catalytic auto-ignition temperature was measured by the temperature-
programmed reduction (TPR) method. Here, the reactant mixture \((n\text{-C}_4\text{H}_{10}/\text{O}_2/\text{Ar})\) was supplied to the catalyst at ambient temperature and the catalyst was heated using the furnace heater with a ramping rate of 10 K min\(^{-1}\). Catalyst bed temperature with time on stream is shown in Fig. 5\(^{22}\). At the beginning, the catalyst bed temperature of Rh/CeO\(_2\) increased linearly with time on stream. However, the catalyst bed temperature rapidly increased after 23 min. At that time, rapid increases in H\(_2\), CO, and CO\(_2\) were observed with the on line quadrupole mass spectrometer. These results indicate that exothermic OR was initiated over Rh/CeO\(_2\) at that temperature indicating that the catalytic auto-ignition temperature was 498 K. Next, heat generation by self-heating of the Rh/CeO\(_2\) catalyst was examined. For that purpose, O\(_2\)/Ar mixture was fed to Rh/CeO\(_2\) reduced at 873 K and the catalyst bed temperature was monitored using a thermocouple (Fig. 6\(^{16}\)).

On exposure to the gas mixture, catalyst bed temperature rapidly increased from ambient temperature to 513 K within 4 s, and subsequently decreased slowly to ambient temperature. Note that such increase in catalyst bed temperature was not observed over Rh/CeO\(_2\) reduced at 673 K or Rh/Al\(_2\)O\(_3\) reduced at 673-1073 K. These results confirmed that Rh/CeO\(_2\) reduced at \(\geq 873\) K is heated above the catalytic auto-ignition temperature (498 K) by oxidation of the catalyst from CeO\(_{2-x}\) to CeO\(_2\).

To investigate the oxidation process, O\(_2\) sorption on the reduced catalysts was measured by pulsing O\(_2\) at 323 K (Table 1\(^{20}\)). After reduction at 673 K and 773 K, O\(_2\) sorption was slightly higher than theoretical amount (73 \(\mu\text{mol g}^{-1}\)) used for oxidizing Rh\(_0\) to Rh\(_2\)O\(_3\) included in Rh/CeO\(_2\), indicating that only Rh in the catalyst was reduced by the hydrogen treatment. On the other hand, O\(_2\) sorption increased sharply after H\(_2\) reduction at \(\geq 873\) K, which indicates part of the CeO\(_2\) as well as Rh\(_2\)O\(_3\) was reduced, and such reduction of CeO\(_2\) contributes to the dramatic increase in O\(_2\) sorption at 323 K. O\(_2\) sorption used for oxidation of Rh (73 \(\mu\text{mol g}^{-1}\)) was subtracted from the O\(_2\) sorption value to calculate the reduction extent of Ce\(_{4+}\) to Ce\(_{3+}\). Reduction of Ce\(_{4+}\) started slowly after reduction at 673 K, and was sharply increased after reduction at \(\geq 873\) K. Reduction extent of Ce\(_{4+}\) over Rh/CeO\(_2\) was 18.1 % and 48.6 % after reduction at 873 K and 1073 K, respectively. After O\(_2\) sorption was measured for Rh/CeO\(_2\) reduced at 873 K, the catalyst was heated in Ar to 723 K and O\(_2\) was pulsed again to the catalysts. Only trace amount of O\(_2\) was consumed at this second exposure to O\(_2\). This result indicated that CeO\(_{2-x}\) and Rh\(_0\) were almost completely oxidized at ambient temperature and the resultant material was thermally stable. Therefore, heat generation over Rh/CeO\(_2\) reduced at \(\geq 873\) K is mainly due to oxidation of CeO\(_{2-x}\) and the critical composition for triggering OR under the current conditions was estimated to be about CeO\(_{1.91}\).

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**Table 1** O\(_2\) Absorption Capacity at 323 K over Rh/CeO\(_2\) Reduced at Different Temperatures\(^{20}\)

| Reduction [K] | O\(_2\) Absorption [\(\mu\text{mol g}^{-1}\)] | Reduction extent of Ce\(_{4+}\) [%] |
|---------------|-----------------------------------|---------------------------------|
| 673           | 101                               | 2.0                             |
| 773           | 124                               | 3.6                             |
| 873           | 333                               | 18.1                            |
| 1073          | 771                               | 48.6                            |

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Reaction condition: SV (122 L h\(^{-1}\) g\(^{-1}\)), quasi-adiabatic conditions.

Fig. 5 Profile of the Catalyst Bed Temperature during the TPR-reaction\(^{22}\).

Fig. 6 Time on Stream of Catalyst Bed Temperature over Rh/CeO\(_2\) Reduced at 873 K after Addition of O\(_2\)/Ar at Ambient Temperature\(^{16}\).

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To investigate the involvement of Rh and CeO₂, activity was measured over bare CeO₂ reduced at 873 K. Although complete consumption and 89 % \( n \)-C₄H₁₀ conversion were obtained, yields of CO, CO₂, CH₄ and C₂-C₃ hydrocarbons were 50, 15, 11 and 20 %, respectively. These results indicate that only combustion and cracking of \( n \)-C₄H₁₀ proceeds over bare CeO₂. Heat generation by oxidation of CeO₂–\( x \) to CeO₂ was also confirmed to be crucial for heating the catalyst to the catalytic auto-ignition temperature of OR and that Rh is essential to catalyse \( n \)-butane reforming.

Furthermore, we investigated the crucial involvement of Rh/CeO₂ for triggering the OR at ambient temperature by using CeO₂ with different characters. CeO₂ with high surface area was favoured as the carrier of Rh particles for the following reasons: (1) large exothermic heat is obtained after reduction at low temperature because easily reducible surface CeO₂ sites are abundant on the high surface area CeO₂, and (2) catalytic auto-ignition temperature is low because a large number of exposed Rh sites which catalyse the reaction between \( n \)-butane and O₂ are present on the fine Rh particles formed on high surface area CeO₂.

Next, the catalytic cycle described in Fig. 2 was examined with the use of Rh/CeO₂ (Fig. 7). For the first cycle, the feed gas of the OR was supplied to the catalyst reduced at 873 K and the OR was triggered immediately. After the exit gas was analyzed by GC after reaction for 30 min, the \( n \)-C₄H₁₀/O₂/Ar reactant was replaced with Ar after 35 min for terminating the reaction, and the catalyst was cooled to ambient temperature. The reactant was then again supplied to the catalyst. This purge-feed sequence was repeated for another two times. For all cycles, H₂ was produced immediately after supplying the feed gas and the H₂ level reached stable values after several minutes.
Complete consumption of O\textsubscript{2} and 90 % conversion of \textit{n}-C\textsubscript{4}H\textsubscript{10} were achieved for all cycles. CO, CO\textsubscript{2}, CH\textsubscript{4} and H\textsubscript{2}O were also produced. These results indicate that CeO\textsubscript{2} was reduced \textit{in-situ} during the OR. Although O\textsubscript{2} was included in the reactant gas, O\textsubscript{2} was consumed at the inlet part of the catalyst bed, so most of the catalyst was not exposed to O\textsubscript{2} and was reduced by H\textsubscript{2} and CO produced by the OR. 

The catalyst bed temperature was higher than 1073 K, which was high enough to reduce CeO\textsubscript{2} to CeO\textsubscript{2–x}. Rh/CeO\textsubscript{2} exhibited high and stable activity for 150 h, with only minor amounts of coke formed (1.9 wt%)\textsuperscript{16).}

4. Use of Other Rare Earth Oxides as the Carrier of Rh

In the proposed OR process described in Fig. 2, CeO\textsubscript{2} provides oxygen storage capacity (OSC), \textit{i.e.} absorbs and releases oxygen repeatedly. Generally, OSC is used in several other catalytic processes, such as oxidation\textsuperscript{23)–29)} and automotive three-way reactions\textsuperscript{30)–34). On the other hand, our catalytic OR process provides a new application for oxygen storage materials. In this section, we investigated the suitability of other rare earth oxides as oxygen storage materials in the process. Ce, Pr, and Tb have trivalent and quadravalent oxidation states, and the oxides of these elements have the cubic fluorite-type structure (CeO\textsubscript{2}, Pr\textsubscript{2}O\textsubscript{3}, and Tb\textsubscript{2}O\textsubscript{3}) and hexagonal A- or cubic bixbyite C-type rare earth sesquioxide structures (Ce\textsubscript{2}O\textsubscript{3}, Pr\textsubscript{2}O\textsubscript{3}, and Tb\textsubscript{2}O\textsubscript{3})\textsuperscript{35). Therefore, the single component of these oxides and their solid solutions show OSC\textsuperscript{23,26,28,33,36–38). We evaluated Pr\textsubscript{2}O\textsubscript{3} and Tb\textsubscript{2}O\textsubscript{3} as well as CeO\textsubscript{2} as supports for the proposed OR process, and investigated the physicochemical and redox properties necessary for a catalyst carrier in the proposed OR process. We measured the catalytic activity of Rh/CeO\textsubscript{2}, Rh/Pr\textsubscript{2}O\textsubscript{3}, and Rh/Tb\textsubscript{2}O\textsubscript{3} after reduction at different temperatures (Table 2)\textsuperscript{21). As already mentioned, OR was triggered at ambient temperature over Rh/CeO\textsubscript{2} after reduction at \geq 873 K, and high \textit{n}-C\textsubscript{4}H\textsubscript{10} and O\textsubscript{2} conversions were obtained after reaction for 30 min. In contrast, OR was not triggered at ambient temperature over Rh/Pr\textsubscript{2}O\textsubscript{3} and Rh/Tb\textsubscript{2}O\textsubscript{3} after reduction at any temperature. The catalyst bed temperature rose only slightly on exposure to the reactant, which indicates minor oxidation of the catalysts. Neither oxidation nor reforming of \textit{n}-C\textsubscript{4}H\textsubscript{10} proceeded over the catalysts.

To explain why OR was not triggered over Rh/Pr\textsubscript{2}O\textsubscript{3} and Rh/Tb\textsubscript{2}O\textsubscript{3}, we decided to characterize the catalysts by several methods.

Physicochemical properties of the supported Rh catalysts are presented in Table 3\textsuperscript{21). The specific surface area was 47 m\textsuperscript{2} g\textsuperscript{–1} for Rh/CeO\textsubscript{2} but was less than 10 m\textsuperscript{2} g\textsuperscript{–1} for the other catalysts. Rh dispersion estimated by CO chemisorption measurements was much higher for Rh/CeO\textsubscript{2} than for Rh/Pr\textsubscript{2}O\textsubscript{3} and Rh/Tb\textsubscript{2}O\textsubscript{3}. We thought that the difference in catalytic activity could

### Table 2: Catalytic Activity of Supported Rh Catalysts Reduced at Different Temperatures for OR Measured after 30 min\textsuperscript{21)

| Catalyst | Reduction temperature [K] | Conversion [%] | Yield of products [%] | H\textsubscript{2} formation rate [L h\textsuperscript{–1} g\textsuperscript{–1}] |
|----------|--------------------------|----------------|----------------------|-----------------------------|
|          |                          | \textit{n}-C\textsubscript{4}H\textsubscript{10} | O\textsubscript{2} | H\textsubscript{2} | CO\textsubscript{2} | CO | CH\textsubscript{4} |
| Rh/CeO\textsubscript{2} | 473 | 0 | 0 | 0 | 0 | 0 | 0 |
|          | 673 | 0 | 0 | 0 | 0 | 0 | 0 |
|          | 873 | 97 | 100 | 79 | 6 | 84 | 8 | 44 |
|          | 1073 | 91 | 100 | 83 | 5 | 85 | 1 | 46 |
| Rh/Pr\textsubscript{2}O\textsubscript{3} | 473 | 0 | 0 | 0 | 0 | 0 | 0 |
|          | 673 | 0 | 0 | 0 | 0 | 0 | 0 |
|          | 873 | 0 | 0 | 0 | 0 | 0 | 0 |
| Rh/Tb\textsubscript{2}O\textsubscript{3} | 473 | 0 | 0 | 0 | 0 | 0 | 0 |
|          | 673 | 0 | 0 | 0 | 0 | 0 | 0 |
|          | 873 | 0 | 0 | 0 | 0 | 0 | 0 |

Reaction conditions: SV (122 L h\textsuperscript{–1} g\textsuperscript{–1}), initial temperature (ambient temperature), quasi-adiabatic conditions.

### Table 3: Physicochemical Properties of Supported Rh Catalysts\textsuperscript{21)

| Catalyst | Specific surface area\textsuperscript{a) [m\textsuperscript{2} g\textsuperscript{–1}] | CO adsorption\textsuperscript{b) [mol g\textsuperscript{–1}] | Dispersion of Rh\textsuperscript{c) [%] |
|----------|-------------------------|------------------|------------------------|
| Rh/CeO\textsubscript{2} | 47 | 32 | 33 |
| Rh/Pr\textsubscript{2}O\textsubscript{3} | 8 | 13 | 13 |
| Rh/Tb\textsubscript{2}O\textsubscript{3} | 2 | 5 | 6 |

\textsuperscript{a) After calcination.}  
\textsuperscript{b) After reduction at 873 K.}  
\textsuperscript{c) Calculated by assuming CO/Rh mol ratio of 1.}
be ascribed to the difference in specific surface area, but OR was triggered from ambient temperature over Rh/CeO$_2$ after reduction at 873 K, in which Rh was supported on CeO$_2$ with low surface area of 3 m$^2$ g$^{-1}$ and Rh dispersion was estimated to 27%. These results indicate that the critical characteristics for triggering OR can be attributed to type and characteristics of the rare earth elements. In the proposed OR process, the heat produced by oxidation of the reduced catalyst will raise the temperature of the catalyst to the catalytic auto-ignition temperature of the OR and reaction starts afterwards. Reduction and re-oxidation of the catalyst are thus critical steps for triggering OR at ambient temperature.

At first, TPR was performed over the supported Rh catalyst to compare the reducibility of the catalysts (Fig. 8) [21]. Higher H$_2$ consumption compared with reduction of Rh$_2$O$_3$ was observed for all the catalysts, which indicates that the rare earth oxides were reduced. In the case of Rh/CeO$_2$, reduction of the CeO$_2$ started above 773 K. On the other hand, reduction of Pr$_6$O$_{11}$ in Rh/Pr$_6$O$_{11}$ and Tb$_4$O$_7$ in Rh/Tb$_4$O$_7$ started from much lower temperatures below 473 K, which indicates that reduction of Rh/Pr$_6$O$_{11}$ and Rh/Tb$_4$O$_7$ occurred at much lower temperatures than for Rh/CeO$_2$. Therefore, the cause of the inactivity of Rh/Pr$_6$O$_{11}$ and Rh/Tb$_4$O$_7$ for triggering OR was not ascribed to insufficient reduction of the carrier.

Next, to compare the maximum temperature achieved by self-heating, O$_2$/Ar mixture was fed to the supported Rh catalysts after reduction at 873 K. In contrast to Rh/CeO$_2$ in which a sharp rise in catalyst bed temperature up to 513 K was observed (see Fig. 6), the catalyst bed temperatures of Rh/Pr$_6$O$_{11}$ and Rh/Tb$_4$O$_7$ did not increased at all. These results indicated that Pr$_6$O$_{11-\gamma}$ and Tb$_4$O$_{7-\gamma}$ formed by reduction at 873 K were stable and not re-oxidized on exposure to O$_2$ at ambient temperature. To examine this characteristic of absence of re-oxidation, we performed TG measurements of the catalysts under air flow (Fig. 9) [21]. After reduction at 873 K, the catalysts were transferred to the TG apparatus at ambient temperature and heated up to 1073 K under air flow. Rh/CeO$_2$ did not increase in weight during the measurements, indicating that CeO$_{2-z}$ was completely oxidized to CeO$_2$ at ambient temperature on exposure to air. In contrast, Ru/Pr$_6$O$_{11}$ and Ru/Tb$_4$O$_7$ showed increases in weight at around 373 K and 573 K, respectively. These results clarified that heat treatment is essential to oxidize Pr$_6$O$_{11-\gamma}$ and Tb$_4$O$_{7-\gamma}$ and self-heating of the catalysts by oxidation of the carriers from ambient temperature is not possible.

To elucidate the structural change of Rh/Pr$_6$O$_{11}$ and Rh/Tb$_4$O$_7$ induced by reduction, X-ray diffraction (XRD) patterns of the catalysts were measured before and after reduction. For Rh/Pr$_6$O$_{11}$, the fluorite structure corresponding to Pr$_6$O$_{11}$ and PrO$_2$ was observed for fresh catalyst but not after reduction at 473 K and 873 K (Fig. 10) [21]. The diffraction peaks of the fluorite were shifted to smaller angles which indicated lattice expansion. In addition, new peaks were formed due to the formation of Pr$_2$O$_3$ with a C-type rare earth sesquioxide structure after reduction at 473 K. After reduction at 873 K, the peak intensities increased due to sintering of the material. The results indicate that Pr$_6$O$_{11}$ and PrO$_2$ were already reduced at 473 K, Pr$_2$O$_3$ was formed at that temperature, and Pr$_6$O$_{11}$ was not re-oxidized on exposure to atmospheric air at ambient temperature. Similarly to Rh/Pr$_6$O$_{11}$, reduction of the support, i.e. Tb$_4$O$_7$ to Tb$_2$O$_3$ with a C-type rare earth sesquioxide structure, occurred for Rh/Tb$_4$O$_7$ after reduction at 473 K and sintering of the Tb$_2$O$_3$ phase was observed after reduction at 873 K [21]. On the other hand, in the case of Rh/CeO$_2$, all samples, fresh and re-

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**Fig. 8** Temperature-programmed Reduction Profiles for (a) Rh/CeO$_2$, (b) Rh/Pr$_6$O$_{11}$, and (c) Rh/Tb$_4$O$_7$ [21].

**Fig. 9** TG Profiles in an Air Flow for Supported Rh Catalysts Reduced at 873 K and Exposed to Air at Ambient Temperature [21].
duced at 473 K and 873 K, showed the same diffraction pattern for the fluorite structure\(^{21}\)). No peak shift ascribed to change of the lattice parameters was not observed. This result is in agreement with the observation of thermogravimetry (TG) that indicates complete re-oxidation of CeO\(_2\) to CeO\(_2\) at ambient temperature in atmospheric air. Therefore, the characteristic of the oxide support to undergo not only reduction by heat treatment under H\(_2\) but also re-oxidation at ambient temperature is crucial for triggering OR at ambient temperature.

5. OR Process Triggered over Rh/Ce\(_{0.5}\)Zr\(_{0.5}\)O\(_2\)

The present catalytic OR process can be repeatedly triggered at ambient temperature. However, the use of the Rh/CeO\(_2\) requires high temperature to reduce CeO\(_2\) sufficiently prior to the first cycle. In addition, the feed-purge cycle must be carried out in a quasi-adiabatic reactor, where external heat losses are strictly inhibited. Limitations to the type of the reactor may hinder effective heat integration of the total system of the fuel cell. If this new catalytic OR system is to be useful, the temperature for reducing the catalyst must be lowered to below the catalytic auto-ignition temperature. One way to lower the reduction temperature is to modify CeO\(_2\) by the addition of other elements. Such a catalyst may permit operation under non-adiabatic conditions, in which external heat losses are strictly inhibited. In this context, addition of Zr\(^{4+}\) to CeO\(_2\) and resultant Ce\(_{1-x}\)Zr\(_{x}\)O\(_2\) solid solution is well known to enhance the redox property of Ce\(_{4\text{+}}\)\(^{39}\). Therefore, we applied Rh/Ce\(_{0.5}\)Zr\(_{0.5}\)O\(_2\) to the proposed OR process and compared its behaviour with Rh/CeO\(_2\). Carriers of Rh, CeO\(_2\), and Ce\(_{0.5}\)Zr\(_{0.5}\)O\(_2\), were prepared by the precipitation method\(^{17}\). Formation of Ce\(_{0.5}\)Zr\(_{0.5}\)O\(_2\) solid solution was confirmed by XRD measurements. For activity tests, a total space velocity of 244 L h\(^{-1}\) g\(^{-1}\) were used.

Fig. 10 XRD Patterns of Rh/Pr\(_6\)O\(_{11}\) Catalysts Reduced at Different Temperatures: (a) fresh, (b) 473 K, and (c) 873 K\(^{21}\)

Fig. 11 Catalytic Activities of Rh/CeO\(_2\) (open circles) and Rh/Ce\(_{0.5}\)Zr\(_{0.5}\)O\(_2\) (solid squares) Reduced at Various Temperatures during OR\(^{17}\)

244 L h\(^{-1}\) g\(^{-1}\) were used.

At first, the effect of reduction temperature of the catalysts on triggering OR at ambient temperature was investigated (Fig. 11\(^{17}\)). Here, the tests were carried out under quasi-adiabatic conditions. As shown above, the H\(_2\) concentration sharply increased over Rh/CeO\(_2\) after reduction at 873 K, which indicates that OR was triggered at ambient temperature. However, neither oxidation nor reforming of n-C\(_4\)H\(_{10}\) was triggered at ambient temperature over Rh/CeO\(_2\) reduced at ≤ 673 K. In contrast, OR was triggered at ambient temperature over Rh/Ce\(_{0.5}\)Zr\(_{0.5}\)O\(_2\) even after reduction at 373 K, indicating that the lowest reduction temperature for triggering OR was reduced by 500 K with the use of Rh/Ce\(_{0.5}\)Zr\(_{0.5}\)O\(_2\). Note that OR was not triggered over Rh/ZrO\(_2\) reduced at any temperature. These results indicate that use of the Ce\(_{0.5}\)Zr\(_{0.5}\)O\(_2\) solid solution induced a sharp decrease in the reduction temperature for triggering OR at ambient temperature.

To understand the character of the catalysts leading to the different triggering behaviours of Rh/Ce\(_{0.5}\)Zr\(_{0.5}\)O\(_2\) and Rh/CeO\(_2\), we measured the temperature-programmed reaction profile of Rh/Ce\(_{0.5}\)Zr\(_{0.5}\)O\(_2\). A rapid increase in H\(_2\) concentration and catalyst bed temperature, which indicate the catalytic auto-ignition temperature of the OR, occurred at 513 K. This catalytic auto-ignition temperature was identical to that of Rh/CeO\(_2\), at 515 K, under same SV of 244 L h\(^{-1}\) g\(^{-1}\), although the Rh dispersion of Rh/Ce\(_{0.5}\)Zr\(_{0.5}\)O\(_2\) (77 %) was higher than that of Rh/CeO\(_2\) (58 %). Therefore, the low reduction temperature of Rh/Ce\(_{0.5}\)Zr\(_{0.5}\)O\(_2\) for triggering OR at ambient temperature was not connected to the reduced catalytic auto-ignition temperature of OR over the catalyst.

Next, we analysed the oxidation process at 323 K of Rh/Ce\(_{0.5}\)Zr\(_{0.5}\)O\(_2\) after reduction. Even if Rh/Ce\(_{0.5}\)Zr\(_{0.5}\)O\(_2\)
was reduced at 373 K, as much as 288 μmol g⁻¹ of O₂ was absorbed on the catalyst, which indicates that 25.7 % of Ce⁴⁺ was reduced to Ce³⁺. This O₂ absorption amount was 70 % of that observed for Rh/CeO₂ reduced at 873 K. Note that the composition of the support was determined as Ce⁰.5Zr⁰.5O¹.94 after reduction at 373 K. Such enhancement of the reducibility of Ce⁴⁺ with the incorporation of Zr⁴⁺ in the fluorite structure is in agreement with earlier findings. Therefore, the characteristic of Rh/Ce⁰.5Zr⁰.5O₂ to trigger OR is attributed to the properties of reduction and re-oxidation at low temperature.

We performed cycle tests of OR under non-adiabatic conditions. Prior to the first cycle, Rh/Ce⁰.5Zr⁰.5O₂ was reduced at 373 K. Then the feed gas was supplied to the catalyst under non-adiabatic conditions, where the insulation materials for the quasi-adiabatic reactor were removed from the system. Not only after H₂ reduction but also after Ar purge, OR of n-C₄H₁₀ was triggered repeatedly at ambient temperature. For all cycles, the H₂ yields were identical and the catalyst exhibited similar levels of activity. These results indicate that Rh/Ce⁰.5Zr⁰.5O₂ was reduced both in H₂ at 373 K and in-situ by the H₂ formed during OR even under non-adiabatic conditions. On the other hand, in the case of Rh/CeO₂ reduced at 873 K, OR was triggered after H₂ reduction (1st cycle), but not after Ar purge (2nd cycle). We assume that in-situ reduction of CeO₂ was insufficient under the conditions where heat losses occur. Furthermore, the activity of the Rh/Ce⁰.5Zr⁰.5O₂ catalyst was relatively stable for more than 100 h with only minor amounts of coke deposition (0.6 wt%) (Fig. 13). Apparently, the excellent redox property of the Ce⁰.5Zr⁰.5O₂ inhibits carbon formation on the catalyst. The application of Ni with the substitution of Rh and other hydrocarbons such as methane and ethanol is now under investigation.

6. Potential of the New Oxidative Reforming Process in the Fuel Cell System

Application of the proposed OR of hydrocarbons to the reformer of the PEFCs system will add steam to the process and reduce the flow rate of oxygen, which leads to more efficient usage of the excess heat for steam reforming and better heat integration. Application of the proposed OR of hydrocarbons to the reformer of solid oxide fuel cells (SOFC), which is called the pre-reformer and used for converting hydrocarbons to C₁ compounds, will use the heat produced in the reformer for heating the SOFCs rapidly, i.e. the starter of the SOFCs.

7. Conclusion

Cold-start process of hydrogen production by oxidative reforming (OR) of hydrocarbon was developed with the use of supported Rh catalysts. In this process, the catalyst is rapidly heated from ambient temperature to the catalytic auto-ignition temperature of OR by the heat generated by self-oxidation of the carrier as well as Rh. Among three Rh catalysts supported on different rare earth oxides with redox properties, i.e. CeO₂, Pr₆O₁₁ and Tb₄O₇, only Rh/CeO₂ triggered OR through oxidation of the CeO₁.⁹¹ produced by reduction at 873 K. On the other hand, OR was not triggered over reduced Rh/Pr₆O₁₁ and Rh/Tb₄O₇ due to insufficient re-oxidation of the reduced carriers. Therefore, the re-oxidation process at ambient temperature of the reduced catalyst, especially the carrier, was very important. The temperature for reducing the catalyst must...
be reduced for utilizing this new catalytic OR process. To enhance the redox property of the Ce$^{4+}$, CeO$_2$ was modified by addition of other elements, i.e., Zr$^{4+}$. Then OR was triggered repeatedly at ambient temperature over Rh/Ce$^4$/Zr$^0$:Zr$^2$:O$_2$ even under non-adiabatic conditions, in which heat losses occur, after reduction at 373 K or after in-situ reduction during the OR. Operation under non-adiabatic conditions may allow heat integration of the total system. Our proposed catalytic oxidative reforming process represents an innovative step in the development of new generation self-sufficient reforming processes. In addition, our findings demonstrate that highly localized energy produced by self-heating of the catalyst is useful for initiating the rapid cold start of various other types of reactions.

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要  旨
燃料電池への応用を志向したn-ブタンの酸化改質に用いるコールドスタートプロセスの開発

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Redox能を有する触体にRhを担持した触媒を用いることで、炭化水素の酸化改質による水素製造反応のコールドスタートプロセスの構築に成功した。このプロセスは還元した触媒の酸化により発生した熱で、触媒を常温から酸化改質の反応開始温度まで急速に加熱することで、結果的に酸化改質を常温から駆動するものである。873 K で水素処理した Rh/CeO2 ではn-ブタンの酸化改質の常温駆動が可能であったが、還元態の常温での再酸化性に劣る Rh/PtO2 と Rh/TbO2 では常温駆動ができなかった。そのため、このプロセスに用いる触媒の担体には還元性はもちろんのこと、常温での酸化性が強く求められることが明らかとなった。そこで、低温での酸化還元特性に優れた Ce0.5Zr0.5O2 を Rh 接触の担体に用いたところ、373 K での還元、および酸化改質の生成物である水素による in-situ 還元によって担体が還元され、熱損失の起こる非断熱条件であっても、繰り返しの常温駆動が可能となった。この新規酸化改質プロセスは近未来の自立型燃料電池の実装に寄与するものであると期待される。