Oxidative Reforming of *n*-Butane Triggered by Spontaneous Oxidation of CeO_{2-x} at Ambient Temperature

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The oxidative catalytic reforming of liquid hydrocarbon fuels (e.g., liquefied petroleum gas, gasoline, and diesel) to produce a hydrogen-rich reformate gas is a topic of great interest because such reforming could enable these fuels to be used as a reducing medium for NO_x abatement in diesel engine exhaust gases or as a fuel for fuel cells.[1] Oxidative reforming (OR) is a combination of exothermic (combustion) and endothermic (reforming) reactions; therefore, OR is more advantageous for start-up procedures and transient performance than conventional steam reforming (SR).[2] Furthermore, because of its exothermic and endothermic characteristics, OR is expected to be the preferred approach to produce hydrogen locally in hydrogen filling stations and for on-site reformers for domestic fuel cells, for which start-up and shut-down processes are frequently repeated.

The criteria that have been deemed crucial for the efficient start-up process of a reformer include start-up time, overall energy efficiency, and catalyst stability.[3] The most critical parameter, however, is the catalytic autoignition temperature, which is normally greater than 473 K in the presence of noble metal catalysts.[1] To reach such temperatures, researchers have explored several strategies, including electrical heating of catalysts[4] and homogeneous combustion.[5] Electrical heating is favored from a practical viewpoint since this method is safer than combustion and does not require a complex start-up procedure. However, this method requires external energy for heating the catalysts from ambient temperature to at least 473 K, as well as adequate time for heating, and this time lapse delays the onset of hydrogen production.

Here we describe a new step-up approach that generates heat internally without requiring a specialized start-up procedure (Figure 1). For this approach, we developed a new catalyst consisting of highly dispersed Rh nanoparticles (~3 nm) supported on partially reduced CeO_2 (CeO_{2-x}), and we tested the catalyst by studying the OR of *n*-butane (*n*-C_4H_{10}). Prior to use, the catalyst was reduced in a hydrogen atmosphere at least at 873 K and the OR of a gas mixture containing *n*-C_4H_{10} was then triggered in the presence of the catalyst at ambient temperature (~300 K). For subsequent cycles, the OR process could be repeatedly triggered at ambient temperature, provided that the catalyst was cooled without exposure to air.

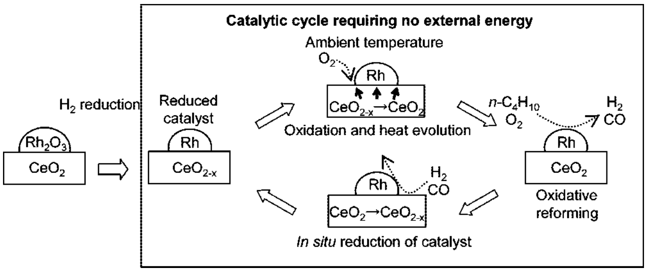

Figure 1. Schematic of the catalytic system developed for *n*-C_4H_{10} OR.

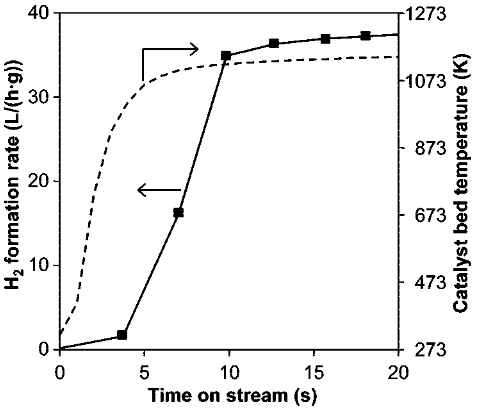

Figure 2. H_2 formation rate and catalyst bed temperature during OR vs time on stream over Rh/CeO_2. Reaction conditions: reduction (873 K), *n*-$C_4H_{10}/O_2/Ar/N_2$ (1/2/7/1), SV (122 L/(h·g)), initial temperature (ambient temperature).

Figure 2 shows the amount of H_2 that was evolved over Rh/CeO_2 reduced at 873 K. These tests were performed under quasi-adiabatic conditions (i.e., the power of the furnace was switched off during the reaction; see Figure S1, Supporting Information). As shown in Figure 2, the H_2 concentration increased drastically over Rh/CeO_2 with increasing time on stream. This concentration increase occurred simultaneously with the rise in catalyst bed temperature observed after the reactant gas mixture was fed into the system (Figure 2), indicating that the OR (combustion and subsequent reforming) was triggered at ambient temperature. After 10 s, the H_2 production rate increased to 35 L/(h·g), and the catalyst bed temperature rose to 1123 K. Thus, the heat was fully balanced between exothermic and endothermic reactions, including external heat losses. Though we note that atomic hydrogen formed during the reduction might contribute to the OR triggering mechanism, H_2 temperature-programmed desorption revealed that atomic hydrogen desorbed below

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[†] Oita University.
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(1) Williams, K. A.; Schmidt, L. D. *Appl. Catal., A* **2006**, *299*, 30.
(2) Ahmed, S.; Krumpelt, M. *Int. J. Hydrogen Energy* **2001**, *26*, 291.
(3) Borup, B. L.; Inbody, M. A.; Semelsberrger, T. A.; Tafoya, J. I.; Guidry, D. R. *Catal. Today* **2005**, *99*, 263.
(4) Jung, H.; Yoon, W. L.; Lee, H.; Park, J. S.; Shin, J. S.; LA, H.; Lee, J. D. *J. Power Sources* **2003**, *124*, 76.
(5) (a) Leclerc, C. A.; Redenius, J. M.; Schmidt, L. D. *Catal. Lett.* **2002**, *79*, 39. (b) Schmidt, L. D.; Klein, E. J.; Leclerc, C. A.; Krummenacher, J. J.; West, K. N. *Chem. Eng. Sci.* **2003**, *58*, 1037.

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Table 1. Catalytic Activity at Ambient Temperature and O_2 Absorption Capacity at 323 K

catalyst	reduction temperature[a] (K)	H_2 formation rate[b] (L/(h•g))	O_2 absorption at 323 K (μmol/g)
Rh/CeO_2	673	0	87
	873	37	303
	1073	35	721
Rh/Al_2O_3	673	0	62
	873	0	63
	1073	0	46

[a] Following H_2 reduction at the temperatures listed here, the catalysts were cooled in Ar to the appropriate temperature for each measurement. [b] Measured after 20 s. Reaction conditions: n-$C_4H_{10}/O_2/Ar/N_2$ (1/2/7/1), SV (122 L/(h•g)), initial temperature (ambient temperature).

773 K, a temperature lower than the purge temperature (873 K) after H_2 reduction.

We now address the mechanism of OR reaction triggering at such low temperatures. Thermodynamic calculations show that complete O_2 conversion and corresponding n-C_4H_{10} consumption by combustion (eq 1) can be achieved at any desired temperature.[6]

$$n\text{-}C_4H_{10} + 6.5O_2 \rightarrow 4CO_2 + 5H_2O \qquad \Delta H(323\ K) = -2660\ kJ\ mol^{-1} \quad (1)$$

However, the oxidation reaction requires a minimum temperature, that is, the triggering temperature, to proceed at such a rate that more heat is produced than is removed from the system by convection from the flowing gas. Once triggered, the exothermic reaction rapidly reaches the operation point, which is given by the sum of the heat flux produced by exothermic and endothermic chemical reactions and the removal of heat through convection and transmission through the reactor walls.

Notably, OR could not be triggered at ambient temperature with Rh/Al_2O_3 reduced at 673, 873, or 1073 K or with Rh/CeO_2 reduced at 673 K (Table 1). The temperature of these catalyst beds rose only briefly and to a minimal extent upon exposure to the reaction mixture, indicating that only minor oxidation of a catalyst component had occurred. Neither oxidation nor reforming of n-C_4H_{10} was observed under these conditions. These results indicate that the heat produced by the oxidation of metallic Rh alone was insufficient to initiate the combustion and subsequent reforming of n-C_4H_{10} at ambient temperature. Thus, for Rh/CeO_2 reduced at 873 and 1073 K, an additional reaction that triggered the temperature rise, the combustion of n-C_4H_{10}, or both, must have occurred. In this context, Sata and Yoshimura reported that Ce_2O_3 prepared from CeO_2 by H_2 reduction at 1673 K ignited spontaneously upon exposure to air at ambient temperature.[7] The oxidation is strongly exothermic:

$$Ce_2O_3 + (1/2)O_2 \rightarrow 2CeO_2 \qquad \Delta H(323K) = -381\ kJ/mol \quad (2)$$

Thus, we concluded that the oxidation of the partially reduced CeO_2, that is, CeO_{2-x}, provided the additional heat that triggered n-C_4H_{10} combustion and reforming. As a test of this conclusion, an O_2/Ar mixture was passed over Rh/CeO_2 that was reduced at 873 K. Upon addition of this gas mixture, the temperature of the catalyst bed increased to 513 K within 4 s (Figure S2, Supporting Information). The rapid increase indicates that the oxidation of CeO_{2-x} provided sufficient heat in the catalyst bed to trigger the oxidation of n-C_4H_{10} and its subsequent reforming.

To better understand the oxidation process, we determined the O_2 absorption on the reduced catalysts by pulsing O_2 into the catalyst bed at 323 K. The results of this study are presented in Table 1. In the case of Rh/Al_2O_3 reduced at 673 and 873 K, the O_2 absorption was nearly equal to the theoretical amount of O_2 uptake for oxidation of Rh to Rh_2O_3 (73 μmol/g). A slightly smaller amount of O_2 was taken up on the catalyst reduced at 1073 K. On the basis of these results, we speculated that Rh atoms located in the bulk of large Rh particles were not oxidized. The amount of O_2 absorption on Rh/CeO_2 reduced at 673 K was similar to that observed for Rh/Al_2O_3, but much larger amounts of O_2 were absorbed on Rh/CeO_2 reduced at 873 and 1073 K than were absorbed on Rh/Al_2O_3 reduced at those temperatures (Table 1). These results indicate that CeO_2 was reduced to CeO_{2-x} at 873 and 1073 K and that the oxidation of CeO_{2-x} at 323 K increased the amount of O_2 absorption. After the O_2 absorption measurements on Rh/CeO_2 reduced at 873 K were obtained, the catalyst was heated to 723 K in Ar, and the sample was again exposed to O_2 pulses. For this second exposure to O_2, only trace amounts of O_2 (11 μmol/g) were taken up. This result demonstrates that Rh and CeO_{2-x} were nearly fully oxidized to CeO_2 at 323 K and that the resulting material was thermally stable. Assuming that a complete oxidation to CeO_2 and Rh_2O_3 occurred, the CeO_{2-x} in Rh/CeO_2 that was reduced at 873 and 1073 K was determined to have average stoichiometries of $CeO_{1.91}$ and $CeO_{1.77}$, respectively. We have also revealed that such reduction and oxidation behavior of the CeO_2 was not influenced by supporting Rh on CeO_2. By combining the results of O_2 absorption and activity tests, we have concluded that critical value in CeO_{2-x} for triggering OR is $1.91 \le (2 - x) < 2.00$. To trigger the OR, care must be taken to prevent the catalyst being exposed to too much water vapor, CO_2, or O_2 in purge gases, which induce reoxidation of prereduced CeO_2.

To study the role of CeO_2 and Rh deeply, an activity test was performed on bare CeO_2 reduced at 873 K. The complete conversion of O_2 and 89% n-C_4H_{10} conversion were obtained; nevertheless, yields of CO, CO_2, CH_4 and C_2-C_3 hydrocarbons were 50, 17, 9, and 20%, respectively (see Figure 3 for comparison with Rh/CeO_2). This indicates that combustion and cracking of n-C_4H_{10} are triggered at ambient temperature on CeO_2. Hence, the essential role of Rh was ascribed to catalysis of n-C_4H_{10} reforming.

Finally, the catalytic system described in Figure 1 was tested in terms of n-C_4H_{10} OR. Prior to the first cycle, Rh/CeO_2 was reduced in H_2 at 873 K and OR was triggered from ambient temperature (Figure 3). After 35 min, the reaction was terminated by substitution of the n-$C_4H_{10}/O_2/Ar/N_2$ feed gas with Ar, and the catalyst was cooled to ambient temperature. This feed−purge sequence was repeated three more times. In all experiments, H_2 was produced

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(6) Thermodynamic calculations were carried out with help of the computer program HSC Chemistry for Windows 4.1, Outokumpu Research Oy, Finland.

(7) Sata, T.; Yoshimura, M. *J. Ceram. Soc. Japan (Yogyo-Kyokai-Shi)* **1968**, *76*, 116.

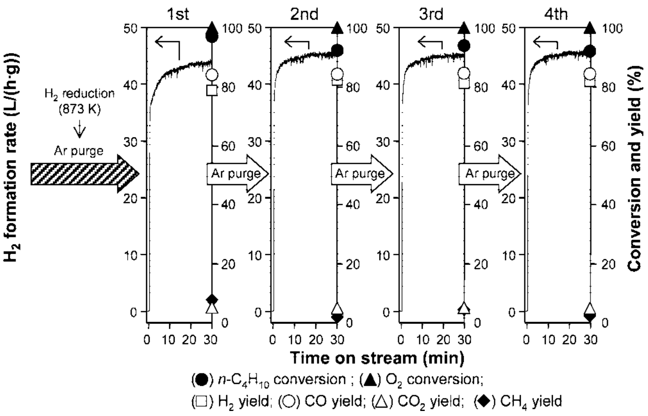

Figure 3. Catalytic activity for Rh/CeO$_2$ reduced at 873 K during OR. Reaction condition: reduction (873 K), n-C$_4$H$_{10}$/O$_2$/Ar/N$_2$ (1/2/7/1), SV (122 L/(h·g)), initial temperature (ambient temperature).

immediately after the reactant gas mixture was fed into the catalyst bed, and H$_2$ levels reached stable values after several minutes (Figure 3). The complete conversion of O$_2$ and a 90% conversion of n-C$_4$H$_{10}$ were achieved at all times, as well. The reaction products obtained were H$_2$, CO$_2$, CO, H$_2$O, and CH$_4$. We speculate that the slightly lower reaction rate with increase in cycle number is related to minor sintering of Rh and CeO$_2$. After the second cycle, Rh/CeO$_2$ was apparently reduced in situ during OR. It is interesting that CeO$_2$ was reduced under the reaction conditions in the presence of O$_2$. However, all of the O$_2$ was consumed at an inlet of the catalyst by combustion. Even if 50 mg of the catalyst (one-quarter of other conditions) was loaded in the reactor, O$_2$ conversion achieved 100%. Therefore, most of the catalyst in the current condition was not exposed to O$_2$ and reduced by H$_2$, and CO formed from OR. The catalyst bed temperature exceeded 1073 K during the OR, which was a temperature sufficient for reduction of CeO$_2$ to CeO$_{2-x}$.

Though the experiments presented here were conducted at ambient temperature (near 300 K), the OR reaction was triggered at 273 K as well (see "Table of Contents"). Immediately after the n-C$_4$H$_{10}$/O$_2$/Ar/N$_2$ gas mixture was fed into a reactor immersed in an ice bath, the catalyst turned red, indicating that the OR of n-C$_4$H$_{10}$ was triggered. H$_2$ formation was confirmed as well with a quadrupole mass spectrometer. Therefore, the catalytic system is available even in colder climates. Furthermore, the catalyst showed relatively stable activity for 150 h (Figure S3, Supporting Information), with only minor amounts of coke deposition (1.9 wt %).

To summarize, we have demonstrated that the OR of n-C$_4$H$_{10}$ was triggered at ambient temperature through the heat produced by the spontaneous oxidation of the CeO$_{2-x}$ catalytic support in a Rh/CeO$_2$ catalyst. Our results demonstrate that highly localized energy produced by the oxidation of CeO$_{2-x}$ drove the overall reaction to rapidly reach an operation point sufficient for reforming 90% of the provided n-C$_4$H$_{10}$. Furthermore, the oxidized CeO$_2$ was reduced in situ by H$_2$ and CO formed during the OR process. Therefore, the present research is a starting point from which the reforming of hydrocarbons can be realized without external energy input and with a minimum complexity of operation, allowing the development of self-sufficient reforming systems for a new generation of fuel cell applications.

Supporting Information Available: Preparation of catalyst, setup, experimental procedure, and a figure of catalytic test are included (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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