

[Letter]

Initiation of Oxidative Reforming of Butane over Praseodymium Oxide Supported Ni Catalysts at Ambient Temperature

Katsutoshi Sato^{1,2)}, Katsutoshi Nagaoka^{1)*}, Hiroyasu Nishiguchi¹⁾, and Yusaku Takita¹⁾

1) Dept. of Applied Chemistry, Faculty of Engineering, Oita University, Dannoharu 700, Oita 870-1192, JAPAN

2) Research Fellow of the Japan Society for the Promotion of Science (DC)

(Received May 7, 2009)

The catalytic characteristics of various rare-earth oxide supports for Ni catalysts were investigated for the initiation of the oxidative reforming (OR) of C₄H₁₀ at ambient temperature. Ni/PrO_{1.83}, reduced at 873 K, successfully initiated the OR of C₄H₁₀ as previously reported for Ni/CeO₂. PrO_{1.83} undergoes reduction by H₂ at 873 K and subsequent oxidation at ambient temperature, so the catalyst is heated to initiate the auto-ignition temperature (633 K) of C₄H₁₀ OR over the catalyst.

Keywords: Oxidative reforming, Ambient temperature triggering, Rare-earth oxide, Praseodymium oxide, Nickel catalyst

Fuel cells (FC), which require hydrogen fuel, are expected to become an important type of next-generation power generators because of their high energy efficiency and low emissions of harmful effluent gases¹⁾. In recent years, the use of FC systems for domestic purposes has attracted considerable attention, but such an application would require repeated start-ups and shut-downs of the system. Therefore, an effective yet simple and rapid start-up process for the on-site reformer incorporated in FC systems is highly desirable. To develop such a system for FC systems, we have developed a new catalytic reforming process, which involves the initiation of oxidative reforming (OR) of C₄H₁₀ over partially reduced Rh/CeO₂ or Ni/CeO₂ catalyst at ambient temperature^{2,3)}. The reduced catalyst support, CeO_{2-x}, is oxidized spontaneously by O₂ present in the reaction mixture, resulting in the generation of heat⁴⁾, so that the temperature of the catalyst bed rapidly increases above 523 K (this temperature is referred to as the catalytic autoignition temperature over Rh/CeO₂) and the OR is initiated. This process allows a novel step-up approach, by which heat is generated internally, without requiring an external source of energy or a special start-up procedure.

The present study investigated new catalyst supports suitable for use in the OR of C₄H₁₀ at ambient temperatures using Ni catalyst supported on different types of rare-earth oxides such as CeO₂. In addition, desirable properties of the catalytic support required to trigger the OR at room temperature were investigated.

The supported Ni catalysts were prepared by the wet impregnation method with various rare-earth oxides and an aqueous solution of Ni(NO₃)₂·6H₂O (Wako Pure Chemicals Industries, Ltd., Japan). The loading of the catalyst metal was fixed at 20 wt%. The catalysts were calcined at 923 K for 5 h under an air stream. Activity tests on the catalysts were performed under nonadiabatic conditions. 100 mg of the catalyst

was loaded in a tubular quartz reactor. A K-type thermocouple was inserted in the catalyst bed to measure the catalyst bed temperature. The catalysts were reduced in pure H₂ at 873 K for 1 h, purged with pure Ar, and then cooled to ambient temperature. The furnace heater was then kept switched off throughout the test. A gas mixture of C₄H₁₀/O₂/Ar = 1/2/12 (SV = 333 L/(h·g)) was used as the feed and passed over each catalyst at ambient temperature. After allowing the reaction to take place for 30 min, the products obtained were analyzed using a GC-TCD. The reaction was terminated after 35 min by substituting the feed gas mixture with Ar. Details of the calculation (conversions and yields) and characterization methods were described previously^{2,3)}.

The conversion, yields of products, and the H₂ formation rate are summarized in **Table 1**. The Ni/PrO_{1.83} catalyst bed temperatures increased spontaneously above 873 K within 12 s after flow of the gas mixture was started following reduction. The Ni/PrO_{1.83} catalyst provided complete O₂ consumption and 86% C₄H₁₀ conversion after 30 min. The reaction products obtained were H₂, CO₂, CO, H₂O, and CH₄. H₂ and CO were the major products with yields of over 60%. In addition, the H₂ formation rate was above 70 L/(h·g). In contrast, the catalyst bed temperature of all other Ni catalysts did not increase even after flow of the reaction mixture was started. Additionally, the levels of the products from these catalysts after 30 min were below the detection limit of the thermal conductivity detector (TCD). Therefore, only Ni/PrO_{1.83} successfully catalyzed the OR of

Table 1 Catalytic Behavior of Ni Catalysts Supported on Rare-earth Oxides Reduced at 873 K

Catalyst	Conversion ^{a)} [%]		Yield ^{a)} [%]			H ₂ formation rate ^{a)} [L/(h·g)]	
	C ₄ H ₁₀	O ₂	H ₂	CO ₂	CO		CH ₄
Ni/PrO _{1.83}	86.0	100	65.8	12.3	64.0	4.4	73.0
Ni/TbO _{1.75}	0	0	-	-	-	-	0
Ni/YbO _{1.5}	0	0	-	-	-	-	0
Ni/HoO _{1.5}	0	0	-	-	-	-	0
Ni/GdO _{1.5}	0	0	-	-	-	-	0
Ni/SmO _{1.5}	0	0	-	-	-	-	0

a) measured after feeding reaction mixture for 30 min.

*酸化プラセオジウム担持Ni触媒を用いたブタンの酸化改質反応の常温駆動
佐藤勝俊^{1,2)}, 永岡勝俊^{1)*}, 西口宏泰¹⁾, 瀧田祐作¹⁾

1) 大分大学工学部応用化学科, 870-1192 大分市旦野原 700

2) 日本学術振興会 特別研究員 (DC)

*Corresponding author, E-mail: nagaoka@cc.oita-u.ac.jp

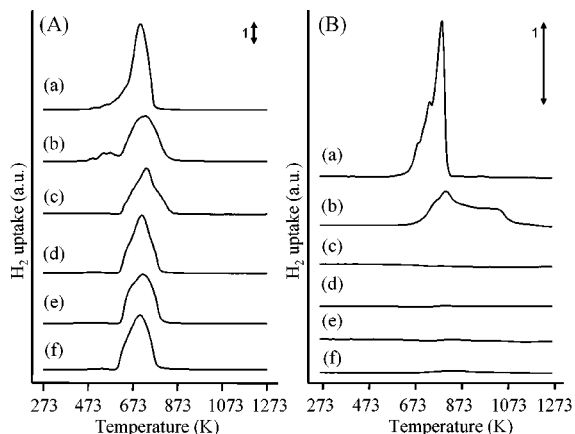


Fig. 1. TPR Profiles of Supported Ni Catalysts (A) and Rare-earth Oxides without Ni (B); (a): PrO_{1.83}, (b): TbO_{1.75}, (c): YbO_{1.5}, (d): HoO_{1.5}, (e): GdO_{1.5}, (f): SmO_{1.5}

C₄H₁₀ at temperature.

To investigate why only Ni/PrO_{1.83} successfully catalyzed the OR of C₄H₁₀ at ambient temperature, we further examined the character of the catalysts. As already mentioned, spontaneous oxidation by O₂ of the partially reduced catalyst support is the key step in triggering the OR of C₄H₁₀²⁾. To compare the reduction process of the catalysts, the temperature programmed reduction (TPR) profiles of all the catalysts were measured. **Figure 1(A)** shows the TPR profiles of the supported Ni catalyst. H₂ consumption was observed at approximately 500–800 K in the profiles of all catalysts. In the cases of Ni/YbO_{1.5}, Ni/HoO_{1.5}, Ni/GdO_{1.5}, and Ni/SmO_{1.5}, the amount of H₂ consumed coincided with the amount of H₂ required to completely reduce the supported NiO to Ni⁰. In contrast, in the cases of Ni/PrO_{1.83} and Ni/TbO_{1.75}, the amount of H₂ consumed was higher than that required for the complete reduction of NiO. These findings imply that the rare-earth oxides of the supports of Ni/PrO_{1.83} and Ni/TbO_{1.75} were reduced in addition to NiO. Assuming that complete reduction to Ni⁰ occurred, the stoichiometries of the supports were determined to be PrO_{1.54} and TbO_{1.58} after TPR measurements. **Figure 1(B)** shows the TPR profiles for the bare rare-earth oxides. The TPR profiles of PrO_{1.83} and TbO_{1.75} showed some peaks, whereas the profiles of other rare-earth oxides showed no such peaks. These results support the finding that only PrO_{1.83} and TbO_{1.75} were reduced by H₂ among the oxides studied. To evaluate the generation of heat by the oxidation of the reduced catalysts, an O₂-Ar mixture was passed over Ni/PrO_{1.83}, which was reduced at 873 K. The catalyst bed temperatures increased to above 753 K in contact with this gas mixture at ambient temperature, which higher than the autoignition temperature of Ni/PrO_{1.83} (633 K). This result indicates that catalyst bed was heated internally and initiates the oxidation of C₄H₁₀ and subsequent reforming. However, no increase in the catalyst bed temperature was observed, even if O₂-Ar mixture was passed over Ni/TbO_{1.75} reduced at 873 K.

X-ray diffraction was used to compare the structures of Ni/PrO_{1.83} and Ni/TbO_{1.75} before and after reduction followed by exposure to an O₂-Ar mixture (**Fig. 2**). The XRD spectra

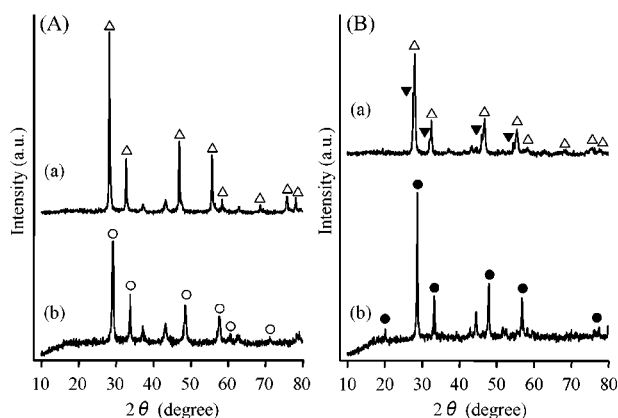


Fig. 2. XRD Patterns of Supported Ni Catalysts after Calcination (A) and after Reduction (B); (a): Ni/PrO_{1.83}, (b): Ni/TbO_{1.75}; (Δ): PrO_{1.83}, (▼): PrO_{1.5}, (○): TbO_{1.75}, (●): TbO_{1.5}

indicated fluorite-type structures for both PrO_{1.83} and TbO_{1.75}, which mainly contain Pr⁴⁺ and Tb⁴⁺, before reduction. The XRD spectra of Ni/PrO_{1.83} showed both the fluorite-type structure for PrO_{1.83} as well as the sesqui-oxide type structure for PrO_{1.5} containing Pr³⁺ after reduction followed by passing the O₂-Ar mixture. Therefore, the support of Ni/PrO_{1.83} was reduced to PrO_{1.54} by H₂ reduction, suggesting that about 90% of Pr⁴⁺ was reduced. Subsequently, the reduced praseodymium oxide (PrO_{1.54}) was more or less oxidized to PrO_{1.83} by exposure to O₂ and the catalyst bed was heated to 753 K, as observed for supported CeO₂ catalysts²⁾. On the other hand, the XRD spectrum of Ni/TbO_{1.75} after reduction followed by passing an O₂ mixture only showed peaks assignable to TbO_{1.5} containing only Tb³⁺, which is approximately in accordance with TPR results. These results suggest that TbO_{1.5} was not oxidized to TbO_{1.75} by O₂ at ambient temperature. Therefore, TbO_{1.5} was stable at ambient temperature and was not oxidized, so that the catalyst bed temperature did not increase to the autoignition temperature.

The present study found that the new catalyst, Ni/PrO_{1.83}, initiates the OR of C₄H₁₀ at ambient temperature, because of the intrinsic characteristics of reduction by H₂ at 873 K and easy oxidation at ambient temperature. These reduction and oxidation properties of the material are important for initiating the OR at ambient temperature.

References

- 1) Cheekatamarla, K. P., Finnerty C. M., *J. Power Sources*, **160**, 490 (2006).
- 2) Nagaoka, K., Sato, K., Fukuda, S., Nakashiki, S., Nishiguchi, H., Lercher, A. J., Takita, Y., *Chem. Mater.*, **20**, 4176 (2008).
- 3) Sato, K., Adachi K., Nagaoka, K., Nishiguchi, H., Takita, Y., *Catal. Commun.*, **10**, 1478 (2009).
- 4) Ruckenstein, E., Wang, Y. H., *J. Catal.*, **187**, 151 (1999).
- 5) Sata, T., Yoshimura, M., *J. Ceramic Assoc. Japan*, **76**, 116 (1968).

Acknowledgments: This study was partly supported by a Grant for Research from The Japan Petroleum Institute, Grant in Aid for JSPS Fellows, the Nippon Sheet Glass Foundation for Materials Science and Engineering and Linking mechanism of research results to practical application from Japan Science and Technology Agency.