

High combustion activity of methane induced by reforming gas over Ni/Al₂O₃ catalysts

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Abstract

During the reactions related to oxidative steam reforming and combustion of methane over α -alumina-supported Ni catalysts, the temperature profiles of the catalyst bed were studied using an infrared (IR) thermograph. IR thermographical images revealed an interesting result: that the temperature at the catalyst bed inlet is much higher under CH₄/H₂O/O₂/Ar = 20/10/20/50 than under CH₄/H₂O/O₂/Ar = 10/0/20/70; the former temperature is comparable to that over noble metal catalysts such as Pt and Pd. Based on the temperature-programmed reduction and oxidation measurements over fresh and used catalysts, the metallic Ni is recognized at the catalyst bed inlet under CH₄/H₂O/O₂/Ar = 20/10/20/50, although it is mainly oxidized to NiAl₂O₄ under CH₄/H₂O/O₂/Ar = 10/0/20/70. This result indicates that the addition of reforming gas (CH₄/H₂O = 10/10) to the combustion gas (CH₄/O₂ = 10/20) can stabilize Ni species in the metallic state even under the presence of oxygen in the gas phase. This would account for its extremely high combustion activity.

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1. Introduction

Oxidative steam reforming of methane and hydrocarbons has attracted much attention in terms of hydrogen production for fuel cells as well as synthesis gas production for C1 chemistry [1–3]. Conventional steam reforming and dry reforming of methane (CH₄ + H₂O → CO + 3H₂, $\Delta H^\circ = 206$ kJ/mol; CH₄ + CO₂ → 2CO + 2H₂, $\Delta H^\circ = 247$ kJ/mol) are highly endothermic reactions, and these processes necessitate severe external heating [4–8]. In contrast, the oxidative steam reforming, an internal heating system, which is a combination of an exothermic combustion or partial oxidation reaction with an endothermic reforming reaction [9–23], is expected to be more energy-efficient than an external heating system like the conventional reforming process uses [24]. However, this process generally has some problems related to hot spot formation and a large

temperature gradient in the catalyst bed [25]. Because the combustion reaction occurs more rapidly than the reforming reaction, in the usual cases it proceeds near the catalyst bed inlet, and the reforming reaction takes place after the complete consumption of oxygen [26–29]. When Ni catalyst is utilized, it can easily be oxidized in the presence of oxygen and can lose its reforming activity. This will reasonably result in a very large temperature gradient because the exothermic and the endothermic regions are separated.

Recently, our group reported that Rh/Al₂O₃ and Pt/Al₂O₃ gave flat temperature profiles in oxidative steam reforming of methane. This phenomenon can be interpreted by the overlap of combustion zone with reforming zone. On the other hand, the Pd/Al₂O₃ catalyst showed very large temperature gradient in the catalyst bed; this was due to its high combustion activity and low reforming activity [30].

In this research, we investigated the temperature profile of the catalyst bed over Ni/ α -Al₂O₃ catalyst in oxidative steam reforming and combustion of methane, as compared with results for Pt/ α -Al₂O₃ and Pd/ α -Al₂O₃ catalysts. It is

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found that Ni catalyst showed high combustion activity comparable to that of a noble metal catalyst under specific reaction conditions, especially under $\text{CH}_4/\text{H}_2\text{O}/\text{O}_2/\text{Ar} = 20/10/20/50$. We also characterized Ni catalysts by means of temperature-programmed reduction (TPR) and oxidation (TPO) in order to understand the state of Ni species. This result is of vital importance for the elucidation of the mechanism of the hot spot formation in oxidative reforming of methane and other hydrocarbons over Ni catalysts.

2. Experimental

2.1. Catalyst preparation

The alumina support was prepared by the calcination of JRC-ALO-1 (provided by Catalysis Society of Japan, diameter of 2–3 mm, $143 \text{ m}^2/\text{g}$) in air at 1473 K for 3 h.

After the calcination, the microstructure of the support material was changed from $\gamma\text{-Al}_2\text{O}_3$ to $\alpha\text{-Al}_2\text{O}_3$, though the spherical shape was maintained; this structural change was confirmed by X-ray diffraction, as shown in our previous paper [30]. The surface area of the calcined alumina was determined to be $6 \text{ m}^2/\text{g}$. $\text{M}/\alpha\text{-Al}_2\text{O}_3$ ($\text{M} = \text{Ni}, \text{Pt}, \text{Pd}$) catalysts were prepared by the conventional impregnation method of the alumina support with the aqueous solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Wako Pure Chemical Industries Ltd. 99.9%), $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (Wako Pure Chemical Industries Ltd. 99.9%) and PdCl_2 (Wako Pure Chemical Industries Ltd. 99.9%), respectively. After impregnation, the solvent was evaporated at 353 K and then completely dried in an oven at 383 K overnight. Subsequently, the resulting product was calcined in air at 773 K for 3 h. The calcined catalyst was crushed and sieved to 180–250 μm . The metal loading amount in the catalyst is denoted in the parentheses, for example, Ni (0.2), which means that the weight percent of Ni catalyst is 0.2 wt.%.

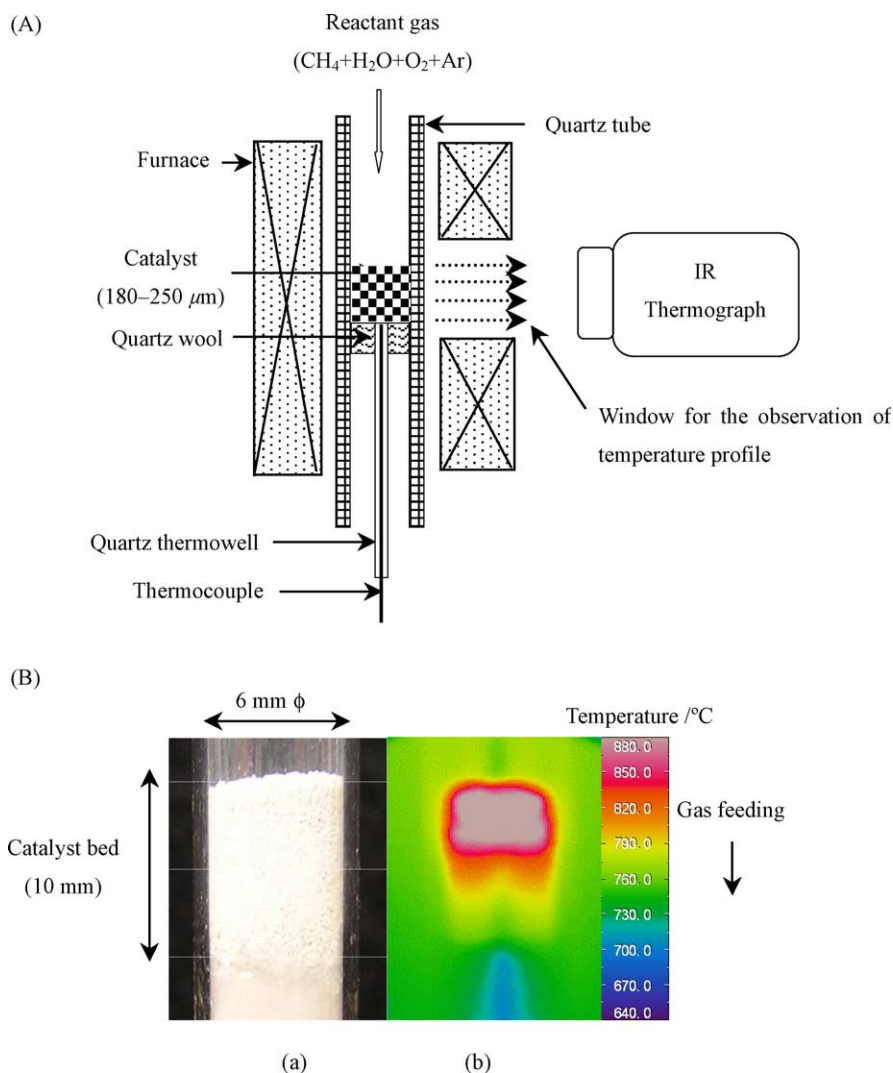


Fig. 1. (A) Schematic diagram of the fixed-bed reactor in the reforming of methane and the method of temperature profile observation. (B) Picture of catalyst granules in the quartz glass tube (a) before reaction and (b) one example of thermographical image.

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