Catalyst design of Pt-modified Ni/Al_2O_3 catalyst with flat temperature profile in methane reforming with CO_2 and O_2

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$Pt(0.3)/Ni(10)/Al_2O_3$, prepared by a sequential impregnation method, exhibited a more excellent performance in methane reforming with CO_2 and O_2 in terms of the catalytic activity and the temperature profile of the catalyst bed than $Pt(0.3) + Ni(10)/Al_2O_3$ prepared by a coimpregnation method, $Ni(10)/Al_2O_3$, $Pt(0.3)/Al_2O_3$, and $Pt(10)/Al_2O_3$. It is thought that this is because the surface Pt atoms on Ni catalyst can contribute to the enhancement of the catalyst reducibility.

KEY WORDS: methane; reforming; combustion; heat supply; Pt–Ni bimetallic catalyst.

1. Introduction

Reforming of methane with CO_2 (1) is a promising method for the production of CO-rich synthesis gas from natural gas; such synthesis gas can be utilized for hydrocarbon, methanol, and dimethyl ether production, and for oxo-syntheses:

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \quad \Delta H = 247\,\mathrm{kJ/mol}. \qquad (1)$$

One of the problems of methane reforming to synthesis gas is the heat requirement since the reaction is highly endothermic, as shown above. In contrast, partial oxidation of methane (2) is a totally exothermic reaction, as described below. However, it has been reported that the synthesis gas is produced by a two-step path consisting of highly exothermic methane combustion (3) to give H_2O and CO_2, followed by the endothermic reforming of methane with H_2O (4) and CO_2 (1) [1–7]:

$$CH_4 + 1/2O_2 \rightarrow CO + 2H_2 \quad \Delta H = -36\,\mathrm{kJ/mol} \qquad (2)$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad \Delta H = -803\,\mathrm{kJ/mol} \qquad (3)$$

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad \Delta H = 206\,\mathrm{kJ/mol}. \qquad (4)$$

In this case, the reaction rate of methane combustion is so high that the combustion proceeds near the inlet of the catalyst bed, and therefore the temperature becomes very high within a very small thickness [8,9]. On the other hand, the temperature in the catalyst bed for methane reforming becomes lower. It has been reported that this causes a large temperature difference of the catalyst bed in partial oxidation of methane [6,8–12]. This hot spot in the catalyst bed is one of the main difficulties in operating the partial oxidation. In addition, Dissanayake *et al.* have reported that the catalyst bed was divided into three parts in the partial oxidation of methane over Ni/Al_2O_3 using a fixed-bed reactor [2]. Several research works on the partial oxidation and reforming of methane to synthesis gas using a fluidized-bed reactor have also been reported [13–19]. It has been claimed that the high rates of heat transfer and the stability of the operation were obtained by using the fluidized-bed reactor.

The effects of CO_2 and H_2O addition on partial oxidation of methane or of O_2 addition on CO_2 and/or steam reforming of methane have been investigated [20–24]. When the endothermic CO_2 reforming of methane was combined with the exothermic partial oxidation of methane, it was observed that the hot spots in the catalyst bed were reduced significantly [20,21]. In this reaction, it is possible to achieve a thermoneutral reaction by manipulating the $CH_4{:}CO_2{:}O_2$ ratio [22]. Furthermore, little or no coking was found in the combination process [23], though coke formation is a serious and general problem in CO_2 reforming of methane [25]. It has been reported that the heat transfer between exothermic oxidation and endothermic reforming is responsible for the better performance of the system [26]. In the autothermic conversion of methane to hydrogen, when two catalyst functions are available on the same support, optimal performance was achieved [26]. In the case of Ni catalyst, Ni is oxidized under the presence of oxygen as reported previously [2]. The oxidized Ni species shows high activity for combustion, but it has no activity for reforming. Maintenance of the metallic surface is thought to be very important when methane

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combustion and reforming proceed on the same catalyst surface. In contrast, the metallic state is very stable for noble metals like Pt even under the presence of oxygen [27]. Recently it has been reported that the temperature profile of the catalyst bed of Pt/Al_2O_3 in methane reforming with CO_2 and O_2 is much flatter than that of Ni/Al_2O_3 [28]. From this result, it is strongly suggested that methane combustion and reforming can proceed on the same zone in the catalyst bed over Pt/Al_2O_3 (Pt loading: 1.5×10^{-4} mol/g-cat). This can enhance the efficiency of heat supply from exothermic combustion and endothermic reforming. However, in terms of the cost and limited availability of noble metals, the development of a Ni-based catalyst is necessary. This letter reports that $Pt–Ni/Al_2O_3$ catalyst with low loading of Pt is prepared by a sequential impregnation method, and this catalyst exhibits the rather flat temperature profile like Pt/Al_2O_3 with much higher loading of Pt.

2. Experimental

Supported monometallic Pt and Ni catalysts were prepared by the impregnation method. The precursors of Pt and Ni were $H_2PtCl_6{\cdot}6H_2O$ (Soekawa Chemical Co. Ltd.) and $Ni(NO_3)_2{\cdot}6H_2O$ (Soekawa Chemical Co. Ltd.), respectively. The Al_2O_3 (Aerosil, Aluminum Oxide C, $100\,m^2/g$) was used as the support material. The catalyst was prepared by impregnating the support material with an aqueous solution of precursor. After removal of the solvent by heating, catalysts were dried at 393 K for 12 h and then calcined in air at 773 K for 3 h. Furthermore, the catalysts were crushed and sieved to granules with 60–100 mesh after each sample was pressed into a disk at $600\,kg/cm^2$. Loading of Ni is 1.5×10^{-4} mol/g-cat (0.9 mass%), and this catalyst is denoted as $Ni(10)/Al_2O_3$. Loading of Pt is 1.5×10^{-4} mol/g-cat (2.9 mass%) and 4.5×10^{-6} mol/g-cat (0.09 mass%), and these catalysts are denoted as $Pt(10)/Al_2O_3$ and $Pt(0.3)/Al_2O_3$. Bimetallic Pt–Ni catalysts were prepared by two methods. One is the sequential impregnation method. $Ni(10)/Al_2O_3$ granules are reduced at 1123 K for 0.5 h under H_2 flowing. After that, Pt is added by the impregnation of reduced $Ni(10)/Al_2O_3$ with $Pt(C_5H_7O_2)_2{\cdot}H_2O$ (Soekawa Chemicals) acetone solution. The added amount of Pt is 4.5×10^{-6} mol/g-cat. After removal of the solvent by heating, the catalyst was dried at 393 K for 12 h and then calcined in air at 573 K for 3 h. This catalyst is denoted as $Pt(0.3)/Ni(10)/Al_2O_3$. The other preparation method is the coimpregnation method. The precursor is the mixed aqueous solution of $H_2PtCl_6{\cdot}6H_2O$ and $Ni(NO_3)_2{\cdot}6H_2O$. The loading amount of Pt and Ni is 4.5×10^{-6} mol/g-cat (0.09 mass% Pt) and 1.5×10^{-4} mol/g-cat (0.9 mass% Ni), respectively. This catalyst is denoted as $Pt(0.3) + Ni(10)/Al_2O_3$. The preparation method of this catalyst is just the same as that of monometallic catalysts after the impregnation. All the catalysts are reduced at 1123 K for 0.5 h before the reaction.

Methane reforming with CO_2 and oxygen was carried out in a fixed-bed flow reaction system under atmospheric pressure. The illustration of the reactor is shown in figure 1. A quartz tube (outer diameter: 8 mm; inner diameter: 6 mm) was used as the reactor, and a thin quartz tube (outer diameter: 3 mm; inner diameter: 1.5 mm) was used as the thermocouple-well. This reactor is equipped with two thermocouples. The thermocouple outside the quartz reactor (denoted as wall temperature) is connected to the thermo-controller. The temperature of the catalyst bed (denoted as bed temperature) is measured by the other thermocouple in the reactor. This thermocouple can be moved from the inlet to the outlet through the catalyst bed. The moving part of this thermocouple is adjusted to the center of the reactor tube. In the figures of temperature measurement, the position of the catalyst bed corresponds to $0 \sim 4$ mm and the temperature of $-5 \sim 0$ and $4 \sim 8$ mm was also measured. In our experiments, the partial pressure ratio of inlet gas is $CH_4/CO_2/O_2 = 40/40/20$. The total pressure was 0.1 MPa. 0.07-g catalysts were used for each experiment. Contact time W/F (W/g = catalyst weight, $F/mol\,h^{-1}$ = total flow rate of the introduced gases) was in the range of 0.13–0.4 gh/mol. The wall temperature was controlled at 1123 K. The lengths of the catalyst bed were 4 mm. The effluent gas was analyzed with an FID gas chromatograph(GC) equipped with a methanator for CH_4, CO, CO_2 (column packing: Porapak N) and with a TCD GC for H_2 (column packing: active carbon).

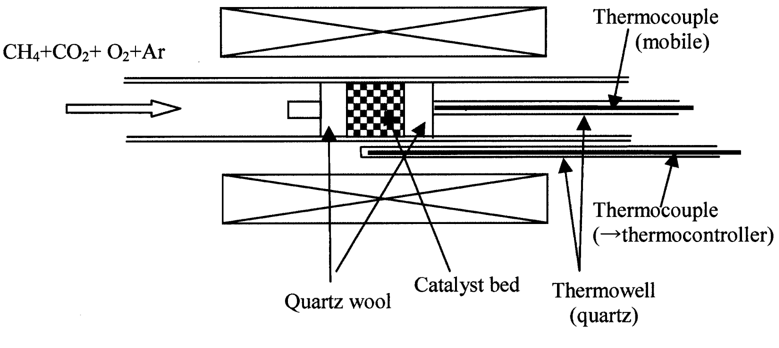

Figure 1. Schematic diagram of the fixed-bed reactor in methane reforming with CO_2 and O_2.

An ice bath was set up between the reactor exit and a sampling port in order to remove water from the effluent gas for GC analysis. Research-grade gases (CH_4, CO_2, O_2) were purchased from Takachiho Trading and were used without further purification. Conversion of oxygen in the experiment was 100%. The CO_2 conversion can be calculated by {1-(the amount of CO_2 effluent)/(CO_2 introduced)}. When the formation of CO_2 due to methane combustion is larger than CO_2 consumption due to methane reforming, CO_2 conversion is below zero. The activity test was carried out for 30 min, and all the catalysts under all the reaction conditions described here were stable.

The activity test of methane combustion was also carried out using air containing 2% CH_4 as the reactant gas. 0.2-g catalyst was used and the contact time was $W/F = 0.4$ gh/mol. Wall temperature is in the range of 473–1123 K. The temperature was increased by 50 K. The analysis method of the effluent gas in methane combustion was the same as that in the methane reforming.

3. Results and discussion

Conversion and H_2/CO in methane reforming with CO_2 and O_2 over various catalysts are listed in table 1. $Pt(0.3)/Ni(10)/Al_2O_3$ exhibited higher activity than $Pt(0.3) + Ni(10)/Al_2O_3$, $Ni(10)/Al_2O_3$ and $Pt(0.3)/Al_2O_3$. The activity of $Pt(0.3)/Ni(10)/Al_2O_3$ was comparable to $Pt(10)/Al_2O_3$. From the comparison between $Pt(0.3) + Ni(10)/Al_2O_3$ and $Ni(10)/Al_2O_3$, the additive effect of Pt is significant at low W/F (0.13–0.27 gh/mol), but the effect is not observed at high W/F (0.33–0.40 gh/mol). Totally, the additive effect of Pt is very small. These results indicate that the addition of Pt by the sequential impregnation method is much more effective than that by the coimpregnation method in terms of the catalytic activity.

Table 1

Catalytic performance of methane reforming with CO_2 and O_2 over various catalysts: dependence of W/F.

Catalyst	W/F/gh mol^{-1}	Conversion (%)		H_2/CO
		CH_4	CO_2	
$Pt(0.3)/Ni(10)/Al_2O_3$	0.13	68	34	0.80
	0.27	79	37	0.84
	0.33	90	40	0.92
	0.40	96	47	0.96
$Pt(0.3) + Ni(10)/Al_2O_3$	0.13	48	26	0.56
	0.27	62	32	0.66
	0.33	75	36	0.81
	0.40	88	44	0.90
$Ni(10)/Al_2O_3$	0.13	37	17	0.48
	0.27	52	25	0.62
	0.33	72	34	0.75
	0.40	86	43	0.87
$Pt(0.3)/Al_2O_3$	0.13	60	31	0.81
	0.27	68	34	0.84
	0.33	78	39	0.88
	0.40	83	41	0.91
$Pt(10)/Al_2O_3$	0.13	73	37	0.82
	0.27	84	42	0.86
	0.33	98	50	0.99
	0.40	99	50	1.00

Reaction conditions: wall temperature 1123 K, $CH_4/CO_2/O_2 = 40/40/20$, total pressure 0.1 MPa, catalyst weight 0.07 g, H_2 pretreatment at 1123 K.

Figure 2 shows the dependence of W/F on the temperature profile of the reactor in methane reforming with CO_2 and O_2 over various catalysts. The temperature profile of $Ni(10)/Al_2O_3$ (figure 2(c)) indicates that the bed temperature of the inlet (position: 0 mm) was very high and the temperature of the position ($-5 \sim 0$ mm) was also higher than the wall temperature. When the quartz sand was used in place of catalysts and $CH_4/CO_2/O_2 = 40/40/20$ was introduced to the reactor, methane combustion did not proceed at all and the increase of the bed temperature was not observed at all. In this case, the bed temperature (1123 ± 2 K) was almost the same as the wall temperature (1123 K). The highest temperature in figure 2(c) was about 1220 K. This is much lower than the hot-spot temperature which is expected from the simulation [10]. The temperature of the catalyst particles seems to be higher than that of the gas phase [12]. In our experiment, the gas-phase temperature is measured by means of the thermocouple. Therefore, our temperature measurement is qualitative. From this consideration, it is suggested that the increase of the temperature of the position ($-5 \sim 0$ mm) is related to the hot-spot formation.

On the other hand, the flat temperature profile on $Pt(10)/Al_2O_3$ (figure 2(e)) in the range of $W/F = 0.33$–0.40 gh mol^{-1} suggests that the hot spot does not seem to be formed. At $W/F = 0.27$ and 0.13 gh mol^{-1}, the temperature near the catalyst bed inlet became higher; however, the temperature on $Pt(10)/Al_2O_3$ was much lower than that on $Ni(10)/Al_2O_3$. The oxygen affinity of Ni is much higher than that of Pt [27]. Pt metal is much more stable than Ni metal under oxygen atmosphere. Under the presence of oxygen in the gas phase, nickel exists as Ni^{2+}. The Ni ion does not have the reforming activity [28], though it has high combustion activity. Only methane combustion proceeds over $Ni(10)/Al_2O_3$ catalyst at the inlet of the catalyst bed and the methane reforming can proceed over $Ni(10)/Al_2O_3$ after oxygen is consumed. The exothermic and endothermic reaction zones are separated on the Ni catalyst. In contrast, it is thought that the Pt can exist as Pt^0 even in the presence of oxygen under the reaction condition. Therefore, methane combustion and reforming can proceed simultaneously on the same catalyst surface [29]. Much shorter distances between the exothermic and the endothermic zone can be realized in this case, and it can give efficient heat transfer. This can explain that the temperature of $Pt(10)/Al_2O_3$ was

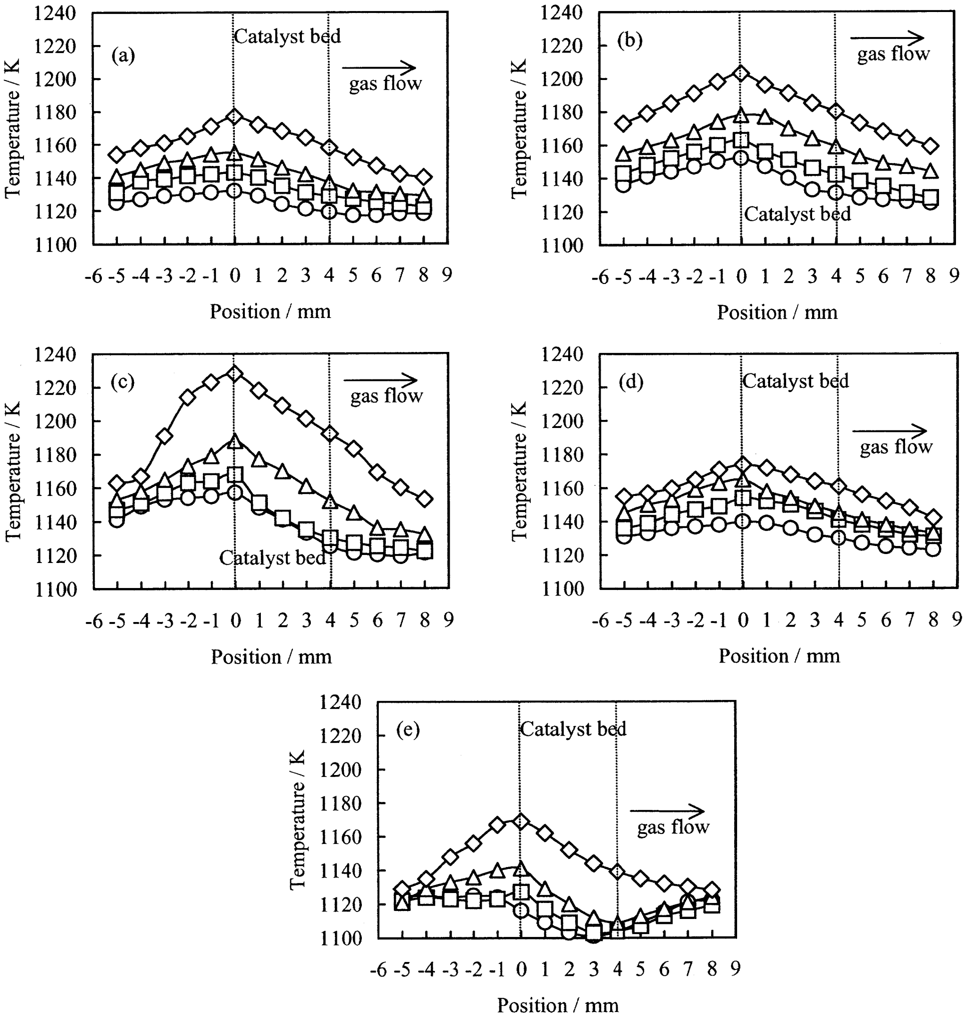

Figure 2. Dependence of W/F on the temperature profile of the reactor in methane reforming with CO_2 and O_2. (a) Pt(0.3)/Ni(10)/Al_2O_3, (b) Pt(0.3) + Ni(10)/Al_2O_3, (c) Ni(10)/Al_2O_3, (d) Pt(0.3)/Al_2O_3 and (e) Pt(10)/Al_2O_3. W/F/gh mol^{-1} = 0.13 (◇), 0.27 (△), 0.33 (□), 0.40 (○). Reaction conditions: wall temperature 1123 K, $CH_4/CO_2/O_2 = 40/40/20$, total pressure 0.1 MPa, catalyst weight 0.07 g, H_2 pretreatment at 1123 K.

much lower than that of Ni(10)/Al_2O_3 in methane reforming with CO_2 and O_2.

The temperature of Pt(0.3)/Al_2O_3 (figure 2(d)) was considerably higher than that of Pt(10)/Al_2O_3 and the wall temperature. The temperature profile of Pt(0.3)/Al_2O_3 suggests that a hot spot can be formed. The conversion of Pt(0.3)/Al_2O_3 is rather close to that of Ni(10)/Al_2O_3 (table 1) in the range of W/F = 0.33–0.4 gh/mol; however, the bed temperature of Pt(0.3)/Al_2O_3 is much lower than that of Ni(10)/Al_2O_3. This is also related to the properties of Pt itself as described above. As listed in table 1, methane conversion on Pt(0.3)/Al_2O_3 was lower than that on Pt(10)/Al_2O_3 because of the much lower loading of Pt. When methane conversion due to the reforming decreases, the bed temperature increases. In contrast, at W/F = 0.13 gh/mol, the highest temperature of Pt(0.3)/Al_2O_3 was almost the same as that of Pt(10)/Al_2O_3. This can be explained by both the higher reforming and combustion activity of Pt(10)/Al_2O_3 than those of Pt(0.3)/Al_2O_3. This result indicates that the catalyst with too low loading of Pt cannot exhibit high conversion and an efficient heat supply in methane reforming with CO_2 and O_2. In order to develop an excellent catalyst with low loading of Pt, Pt–Ni bimetallic catalysts are investigated.

Figure 2(b) shows the results of Pt(0.3) + Ni(10)/Al_2O_3 prepared by the coimpregnation method. In the range of W/F = 0.13–0.27 gh/mol, Pt(0.3) + Ni(10)/Al_2O_3 gave higher conversion than Ni(10)/Al_2O_3. Under this condition, the temperature at the inlet of the catalyst bed decreased significantly. On the other hand, the temperature of the inlet of the catalyst bed on Pt(0.3) + Ni(10)/Al_2O_3 in the range of W/F = 0.33–0.40 gh/mol was almost the same as that of Ni(10)/Al_2O_3. In addition, the conversion of both catalysts was also almost the same. This indicates that the effect of Pt added by the coimpregnation method is not so significant.

On the other hand, the effect of Pt added by the sequential impregnation method is remarkable. Figure

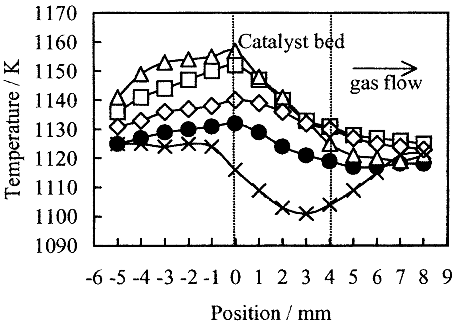

Figure 3. Comparison of temperature profile of the catalyst bed in methane reforming with CO_2 and O_2 over various catalysts. Pt(0.3)/Ni(10)/Al_2O_3 (●), Pt(0.3) + Ni(10)/Al_2O_3 (□), Ni(10)/Al_2O_3 (△), Pt(0.3)/Al_2O_3 (◇) Pt(10)/Al_2O_3 (×). Reaction conditions: wall temperature 1123 K, $CH_4/CO_2/O_2 = 40/40/20$, W/F = 0.4 gh/mol, total pressure 0.1 MPa, catalyst weight 0.07 g, H_2 pretreatment at 1123 K.

2(a) shows the result of Pt(0.3)/Ni(10)/Al_2O_3 prepared by the sequential impregnation method. In the entire range of W/F = 0.13–0.40 gh/mol, the temperature of the catalyst bed inlet on Pt(0.3)/Ni(10)/Al_2O_3 was much lower than that on Ni(10)/Al_2O_3. Furthermore, the addition of Pt also enhanced the methane conversion. These results indicate that the additive effect of Pt by the sequential impregnation method is much more significant than that by the coimpregnation method.

Figure 3 shows the comparison of the temperature profile in methane reforming with CO_2 and O_2 at W/F = 0.4 gh/mol. Ni(10)/Al_2O_3 gave much higher temperature than the wall temperature. Pt(0.3) + Ni(10)/Al_2O_3 exhibited a similar behavior to Ni(10)/Al_2O_3. Pt(0.3)/Ni(10)/Al_2O_3 gave a lower temperature than monometallic Pt(0.3)/Al_2O_3 and Ni(10)/Al_2O_3. The bed temperature on Pt(0.3)/Ni(10)/Al_2O_3 is a little higher than that on Pt(10)/Al_2O_3; however, the total profile of Pt(0.3)/Ni(10)/Al_2O_3 is much flatter than that of Pt(10)/Al_2O_3.

Figure 4 shows the relation between methane conversion and the temperature difference in methane reforming with CO_2 and O_2 at W/F = 0.4 gh/mol. Ni(10)/Al_2O_3 showed a medium conversion and large temperature difference. Pt(0.3) + Ni(10)/Al_2O_3 gave a similar tendency. Pt(0.3)/Al_2O_3 was located at low conversion and small temperature difference. Pt(10)/Al_2O_3 exhibited a high conversion and medium temperature difference. This temperature difference is also caused by the endothermic part. Pt(0.3)/Ni(10)/Al_2O_3 exhibited a high conversion and small temperature difference. Pt(0.3)/Ni(10)/Al_2O_3 is an excellent catalyst for an effective heat supply from combustion to reforming.

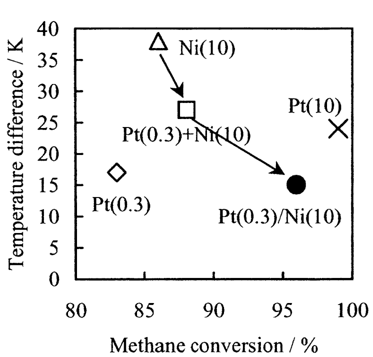

Figure 4. Relation between methane conversion and the temperature difference in the reactor in methane reforming with CO_2 and O_2 over various catalysts. Pt(0.3)/Ni(10)/Al_2O_3 (●), Pt(0.3) + Ni(10)/Al_2O_3 (□), Ni(10)/Al_2O_3 (△), Pt(0.3)/Al_2O_3 (◇), Pt(10)/Al_2O_3 (×). Reaction conditions: wall temperature 1123 K, $CH_4/CO_2/O_2 = 40/40/20$, W/F = 0.4 gh/mol, total pressure 0.1 MPa, catalyst weight 0.07 g, H_2 pretreatment at 1123 K. Temperature difference = highest temperature–lowest temperature.

Table 2
Results of the activity test of methane combustion.

Catalyst	Temperature (K)[a]
Pt(0.3)/Ni(10)/Al_2O_3	973
Pt(0.3) + Ni(10)/Al_2O_3	1073
Ni(10)/Al_2O_3	1123
Pt(0.3)/Al_2O_3	1023
Pt(10)/Al_2O_3	873

[a] Reaction temperature at which methane conversion is beyond 90%. Reaction conditions: CH_4/Air = 2/98, W/F = 0.4 gh/mol, total pressure 0.1 MPa, catalyst weight 0.2 g, H_2 pretreatment at 1123 K for 0.5 h, reaction temperature = wall temperature.

Methane combustion activity is listed in table 2. On Pt(10)/Al_2O_3, methane conversion became higher than 90% at much lower temperature than that on other catalysts. Therefore, the combustion zone on Pt(10)/Al_2O_3 seems to be smaller than other catalysts. In the case of Pt(10)/Al_2O_3, the temperature of part of the catalyst bed is below the wall temperature. This can be because the exothermic zone is so small that the heat transfer to the endothermic zone is not enough. On the other hand, the exothermic zone on Pt(0.3)/Ni(10)/Al_2O_3 can be larger, and this can be related to the flat temperature profile of the catalyst, as shown in figure 3.

In our results, the additive effect of a small amount of Pt is very dependent on the preparation method. It is though the position of added Pt is different in these two catalysts. In the case of the coimpregnation method, Pt is located on the surface and inside of Ni metal particles because Pt and Ni are reduced in the same procedure. In contrast, when Pt is added by the sequential impregnation method, Pt can be mainly located on the surface of Ni metal particles. This is because Ni is reduced at first and then Pt is reduced. This kind of structural character of bimetallic catalysts has also been reported [29]. Since the reaction temperature is very high, Pt may migrate from bulk to surface or vice versa. If the migration takes place, then the activity should be independent of the preparation method. However, the activity and temperature profile are very dependent on the preparation method, and this indicates that migration of Pt does not occur. The addition of Pt enhances the reducibility of Ni catalysts for methane reforming [30,31]. This is because of the formation of the alloy particles and/or hydrogen spillover effect. In our system, since surface Pt is much more effective, it is thought that Pt(0.3)/Ni(10)/Al_2O_3 shows a more excellent performance. Catalyst characterization is necessary for the elucidation of the location of Pt atoms in Pt–Ni bimetallic catalysts and the effect of the preparation method.

4. Conclusions

1. In methane reforming with CO_2 and O_2 over Ni(10)/Al_2O_3, the bed temperature of the inlet was very high. In the reaction over Pt(10)/Al_2O_3 and Pt(0.3)/Al_2O_3, the bed temperature was much lower than Ni(10)/Al_2O_3. This indicates that the heat of methane combustion is effectively and directly supplied to methane reforming over monometallic Pt/Al_2O_3 catalysts.
2. The activity of Pt(0.3)/Al_2O_3 in methane reforming with CO_2 and O_2 was lower than Ni(10)/Al_2O_3 and Pt(10)/Al_2O_3. Monometallic Pt/Al_2O_3 with low loading of Pt cannot show an excellent performance.
3. The addition of a small amount of Pt to Ni(10)/Al_2O_3 was carried out by coimpregnation and sequential impregnation methods. Pt(0.3)/Ni(10)/Al_2O_3, prepared by a sequential impregnation method, exhibited higher performance in methane reforming with CO_2 and O_2 in terms of the catalytic activity and the temperature profile of the catalyst bed than Pt(0.3) + Ni(10)/Al_2O_3, prepared by the coimpregnation method. It is thought that this sequential method is very effective for locating Pt atoms on the surface. The surface Pt atoms in bimetallic catalysts can contribute to the enhancement of the catalyst reducibility *via* alloying and/or hydrogen spillover effect.

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