Noble metal promoted $Ni_{0.03}Mg_{0.97}O$ solid solution catalysts for the reforming of CH_4 with CO_2

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Reforming of CH_4 with CO_2 to produce syngas was studied over $Ni_{0.03}Mg_{0.97}O$ solid solution catalyst and its bimetallic derivative catalysts which contained small amounts of Pt, Pd or Rh (the atomic ratio $M/(Ni+Mg)$ was about 2×10^{-4}, M = Pt, Pd or Rh). It was found that although the $Ni_{0.03}Mg_{0.97}O$ catalyst showed an excellent stability and activity at the reaction temperature of 1123 K, it lost its activity completely within 51 h when the reaction temperature was as low as 773 K. However, both the activity and the stability at 773 K were improved significantly by adding Rh, Pt, or Pd. This synergistic effect is rationally explained by the promoted reducibility of Ni. On all these catalysts, the amount of deposited carbon during the reaction was very low, suggesting that carbon deposition was not the main cause of the deactivation. Also, the catalytic activity of bimetallic catalysts increased gradually with the noble metal loading, but after passing through a maximum, it decreased with superfluous addition. The maximum was found to be located at around the atomic ratio of $M/(Ni+Mg) \approx 0.02\%$ (M = Pt, Pd and Rh). This phenomenon could most probably be attributed to the different composition of Pt–Ni alloy particles formed after the reduction.

Keywords: reforming of methane with carbon dioxide; nickel magnesia solid solution; magnesia supported nickel catalyst; platinum–nickel alloy; deposited carbon

1. Introduction

Extensive work has been done on the catalytic reforming of CH_4 with CO_2 to produce syngas in recent years considering the chemical utilization of natural gas and CO_2. Ni, Pd, Pt, Rh, Ru and Ir have been proved to be effective catalytic components for this reaction [1–10]. However, one of the major problems in conducting this reaction is the deactivation of catalyst caused by carbon formation probably via the Boudouard reaction ($2CO \rightarrow CO_2 + C$) and methane decomposition ($CH_4 \rightarrow C + 2H_2$). It has been reported that supported noble metal catalysts experienced less carbon formation than did Ni-based catalysts [1–5]. Despite that this conclusion is available for the conventional Ni-based catalysts, it does not suit our developed $Ni_{0.03}Mg_{0.97}O$ solid solution catalyst which retained its high activity for 3000 h at the reaction temperature of 1123 K with the used catalyst containing less than 1% carbon even under the condition of CO_2/CH_4 ratio of 1 [11]. This excellent anticoking performance of $Ni_{0.03}Mg_{0.97}O$ is at least comparable to that of noble metal catalysts [5]. As a solid solution, $Ni_{0.03}Mg_{0.97}O$ has a disadvantage over conventional Ni-based catalysts in its hard reducibility. Therefore, high temperature reduction is essential to generate the reduced state Ni and consequently to catalyze the reforming of CH_4 with CO_2. Also, the $Ni_{0.03}Mg_{0.97}O$ had a lower activity and poor stability at the low reaction temperature of 773 K. This is probably due to the low concentration of active sites and the partial oxidation of the active Ni species by CO_2 or H_2O during the reaction. It is well known that a small amount of noble metals can promote the reducibility of base metal, such as Ni, and stabilize their degree of reduction during the catalytic process [12,13]. Thus, we expect to improve the performances of the $Ni_{0.03}Mg_{0.97}O$ catalyst by adding small amounts of noble metals (Pt, Pd or Rh) to $Ni_{0.03}Mg_{0.97}O$. In this paper, the results on the additive effect of Pt, Pd and Rh are presented.

2. Experimental

$Ni_{0.03}Mg_{0.97}O$ solid solution catalyst was prepared by co-precipitating nickel acetate and magnesium nitrate aqueous solutions using potassium carbonate. The details of the catalyst preparation were described in a previous paper [6]. After being filtered and washed with hot water, the precipitate was dried overnight at 393 K, and then calcined at 1223 K for 10 h. The bimetallic catalysts containing Pt, Pd and Rh on $Ni_{0.03}Mg_{0.97}O$ were prepared by impregnating $Ni_{0.03}Mg_{0.97}O$ with acetone solutions of the corresponding metal acetylacetonate complexes, which have been reported to be suitable for the preparation of highly dispersed metal particles [14–16]. The loading of added metals ranged from 0.011 to 0.032% as the molar ratio of $M/(Ni+Mg)$ (M = Pt, Pd and Rh). The acetone was then removed in a water bath at 343 K. M/MgO catalysts were also prepared by substituting $Ni_{0.03}Mg_{0.97}O$

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Table 1
Preparation parameters of the catalysts

Sample	Preparation method	Precursor	Calcination temp. (K)	Calcination time (h)	BET surface area (m^2/g)
MgO	coprecipitation	$Mg(NO_3)_2 + K_2CO_3$	1223	10	27
$Ni_{0.03}Mg_{0.97}O$	coprecipitation	$Mg(NO_3)_2 + Ni(C_2H_3O_2)_2 + K_2CO_3$	1223	10	19
0.021 mol% M/MgO [a]	impregnation [b]	$M(C_5H_7O_2)_x$ [c]+MgO	– [d]	– [d]	28 [e]
0.021 mol% M/$Ni_{0.03}Mg_{0.97}O$ [a]	impregnation [b]	$M(C_5H_7O_2)_x$ [c]+$Ni_{0.03}Mg_{0.97}O$	– [d]	– [d]	20–25

[a] M = Pt, Pd and Rh.
[b] Impregnation with acetone solution of $M(C_5H_7O_2)_x$.
[c] For Pt and Pd, x equals 2, for Rh, x equals 3.
[d] Only dried at 393 K overnight.
[e] Pt-promoted catalyst.

with a home-made MgO support of which the preparation method was the same as that for $Ni_{0.03}Mg_{0.97}O$. Table 1 lists the preparation parameters. All these samples were pressed into tablets and the particles with the size of 20–40 mesh were obtained by crushing and sieving.

Activity measurements were carried out in a fixed-bed continuous-flow reactor made of 6 mm i.d. quartz tube. The catalysts were reduced in a flow of H_2 at 1123 K for 0.5 h before catalytic reactions were performed. The standard reaction conditions were: reaction temperature range 773–973 K, total pressure 0.1 MPa, $CH_4/CO_2 = 1/1$, $W/F = 1.2$ or 0.5 g-cat h/mol, the amount of catalysts 0.3 or 0.1 g. The effluent gas was analyzed with an on-line gas chromatograph using active carbon as the separating column. An ice bath was set between the reactor exit and the GC sampling valve to remove the water. The surface area was measured by BET method. The amount of deposited carbon on the catalysts was quantified in terms of the methane formation during the temperature-programmed reaction (TPR) of H_2 in the temperature range between 295 and 1123 K.

3. Results and discussion

We first examined the stability of the catalysts at 773 K (or 1123 K) and space velocity of 48000 h^{-1}, followed by measuring the amount of deposited carbon on these used samples. Results are illustrated in fig. 1 and table 2. Clearly, the high activity over the $Ni_{0.03}Mg_{0.97}O$ solid solution catalyst remained constant at 1123 K for 51 h. However, at reaction temperature of 773 K, the $Ni_{0.03}Mg_{0.97}O$ deactivated gradually with time-on-stream until its activity reached zero. This large difference in stability could not be explained by the carbon deposition, since the amount of carbon on the catalyst was almost zero after the reaction at 773 K for 51 h. An obvious change in the color of the catalyst was observed from gray before reaction to green after reaction. This result indicates that the deactivation of $Ni_{0.03}Mg_{0.97}O$

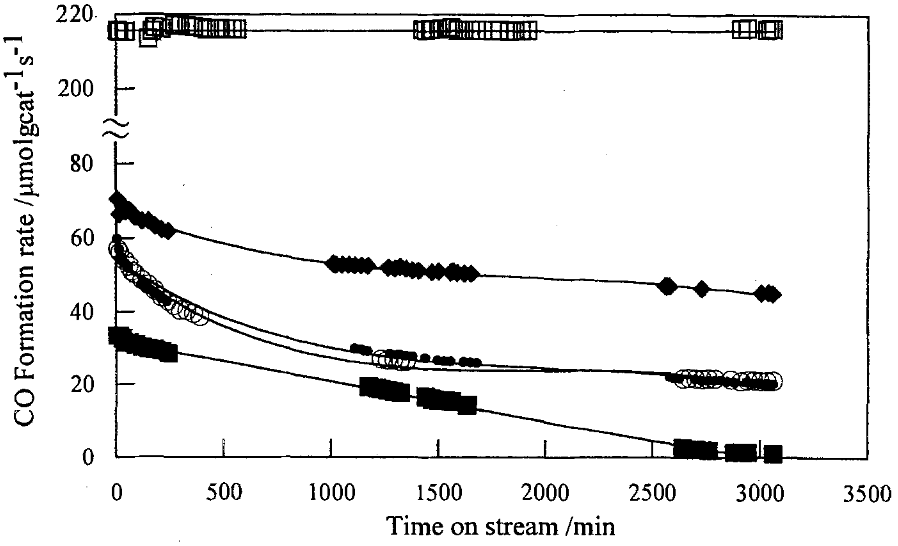

Fig. 1. Activity as a function of time-on-stream for CH_4–CO_2 reaction over $Ni_{0.03}Mg_{0.97}O$ and M/$Ni_{0.03}Mg_{0.97}O$ catalysts (M = Pt, Pd and Rh). (■) $Ni_{0.03}Mg_{0.97}O$, (○) 0.021 mol% Pt/$Ni_{0.03}Mg_{0.97}O$, (●) 0.021 mol% Pd/$Ni_{0.03}Mg_{0.97}O$, (◆) 0.021 mol% Rh/$Ni_{0.03}Mg_{0.97}O$, (□) $Ni_{0.03}Mg_{0.97}O$ (reaction at 1123 K). Reaction temperature: 773 K, $CH_4/CO_2 = 1/1$, total pressure: 0.1 MPa, $W/F = 0.5$ g-cat h/mol, weight of catalyst: 0.1 g.

Table 2
Amount of carbon deposited on various catalysts estimated by H_2 TPR after the reaction of reforming CH_4 with CO_2 for 51 h at 773 K[a]

Catalyst	Amount of carbon (10^{-4} g g-cat^{-1})
$Ni_{0.03}Mg_{0.97}O$[b]	3.1
$Ni_{0.03}Mg_{0.97}O$[c]	2.6
$Ni_{0.03}Mg_{0.97}O$	0.0
0.021 mol% Pt/$Ni_{0.03}Mg_{0.97}O$	1.4
0.021 mol% Pd/$Ni_{0.03}Mg_{0.97}O$	0.4
0.021 mol% Rh/$Ni_{0.03}Mg_{0.97}O$	2.1

[a] Reaction conditions: total pressure, 0.1 MPa; $CH_4/CO_2 = 1/1$; $W/F = 0.5$ g-cat h/mol; weight of catalyst, 0.1 g.
[b] Reaction temperature, 1123 K.
[c] Time on stream, 23.5 h.

may be ascribed to the oxidation of reduced state Ni during the reaction. At 773 K, the conversion of CH_4 and CO_2 was too low to maintain the reductive atmosphere surrounding the catalyst which was required to keep the degree of Ni reduction constant. In contrast, the high $(CO + H_2)/(CO_2 + H_2O)$ ratio in the product at 1123 K should be enough to keep Ni in the reduced state. Neither XRD nor XPS measurements could give direct evidence for the oxidation of reduced state Ni because of the low content of Ni in the catalyst. It can be seen from table 2 that, on all catalysts studied here, the amount of deposited carbon is much lower than that reported on other conventional Ni-based catalysts [7,8]. This fact reveals that both the $Ni_{0.03}Mg_{0.97}O$ solid solution catalyst and its bimetallic catalysts M/$Ni_{0.03}Mg_{0.97}O$ (M = Pt, Pd and Rh) have low activity in carbon formation. Note that there is a strong correlation between the catalyst activity and the amount of carbon formed. The greater the amount of carbon formed, the more active the catalyst (see table 2 and fig. 2). Similar results have already been reported by Chen and Ren [17]. This fact possibly implies a mechanism as suggested later that the catalyst with higher activity for the reforming of CH_4 with CO_2 should be more active for the CH_4 decomposition.

As shown in fig. 1, the initial activity for noble metal promoted $Ni_{0.03}Mg_{0.97}O$ catalysts was two times higher than that for the unpromoted catalyst. Simultaneously, the stability was also enhanced dramatically by the addition of Pt, Pd and Rh. Among these bimetallic catalysts, Rh/$Ni_{0.03}Mg_{0.97}O$ was the most effective. The relative activity, a, ($a = a_t/a_0$, where a_t and a_0 are respectively the activity at 51 h and 5 min) is 0.64 for Rh/$Ni_{0.03}Mg_{0.97}O$, 0.36 for Pt/$Ni_{0.03}Mg_{0.97}O$, 0.33 for Pd/$Ni_{0.03}Mg_{0.97}O$ and 0.02 for $Ni_{0.03}Mg_{0.97}O$.

The catalytic activity of bimetallic catalysts versus a range of M/(Ni + Mg) (M = Pt, Pd and Rh) atomic ratios is demonstrated in fig. 2. The activity over M/MgO (M/(Ni + Mg) = 0.021%) is also given for comparison. First, it is seen that, although each of the promoters is inactive for this reaction when it is used alone, the bimetallic catalysts show much higher activity than the original one. Second, the content of the promoter plays an important role in determining the activity for the bimetallic catalysts. The activity showed an initial increase followed by a decrease with increasing M/(Ni + Mg) atomic ratio for each bimetallic catalyst, with its maximum appearing at around 0.02% where the bimetallic catalysts have much higher activity than would be expected from the linear combination of $Ni_{0.03}Mg_{0.97}O$ and the corresponding M/MgO catalyst. These results suggest that a synergistic effect exists between Ni and promoter in a suitable range of M/(Ni + Mg) atomic ratio.

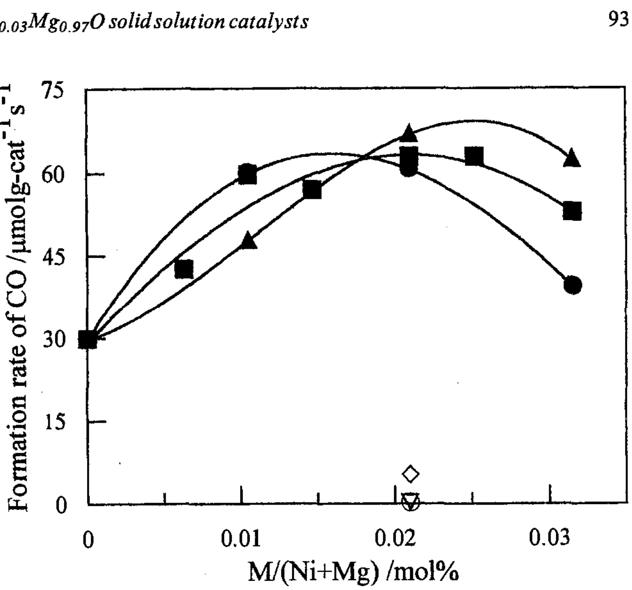

Fig. 2. Dependence of CO formation rate on the loading amount of M (M = Pt, Pd and Rh) over M/$Ni_{0.03}Mg_{0.97}O$ catalysts for CH_4–CO_2 reaction. (■) Pt/$Ni_{0.03}Mg_{0.97}O$, (●) Pd/$Ni_{0.03}Mg_{0.97}O$, (▲) Rh/$Ni_{0.03}Mg_{0.97}O$, (▽) Pt/MgO, (○) Pd/MgO, (◇) Rh/MgO. Reaction temperature: 773 K, $CH_4/CO_2 = 1/1$, total pressure: 0.1 MPa, $W/F = 0.5$ g-cat h/mol, weight of catalyst: 0.1 g.

The influence of reduction temperature on the initial catalytic activity was investigated for $Ni_{0.03}Mg_{0.97}O$ and Pt/$Ni_{0.03}Mg_{0.97}O$ catalysts (fig. 3). For $Ni_{0.03}Mg_{0.97}O$, a significant increase in activity with increasing reduction temperature was observed. The rate of CO formation varied from 0 to 30 μmol g-cat^{-1} s^{-1} as the reduction temperature increased from 923 to 1123 K. However, raising the reduction temperature from 923 to 1123 K scarcely affected the catalytic activity of Pt/$Ni_{0.03}Mg_{0.97}O$. The sufficient reduction temperature was at most 1023 K for Pt/$Ni_{0.03}Mg_{0.97}O$, at which the activity approached the saturation value. This result suggests that Ni^{2+} in $Ni_{0.03}Mg_{0.97}O$ is difficult to be reduced, which is consistent with the results reported by Parmaliana et al. [18] that the formation of a NiO–MgO solid solution lowers the reducibility of Ni^{2+}. Accordingly, it can be deduced that the addition of Pt dramatically promotes the reducibility of the $Ni_{0.03}Mg_{0.97}O$ by the spillover of hydrogen from Pt to $Ni_{0.03}Mg_{0.97}O$ surface [19]. It has been pointed out that a Pt–Ni alloy was formed during the reduction, and the

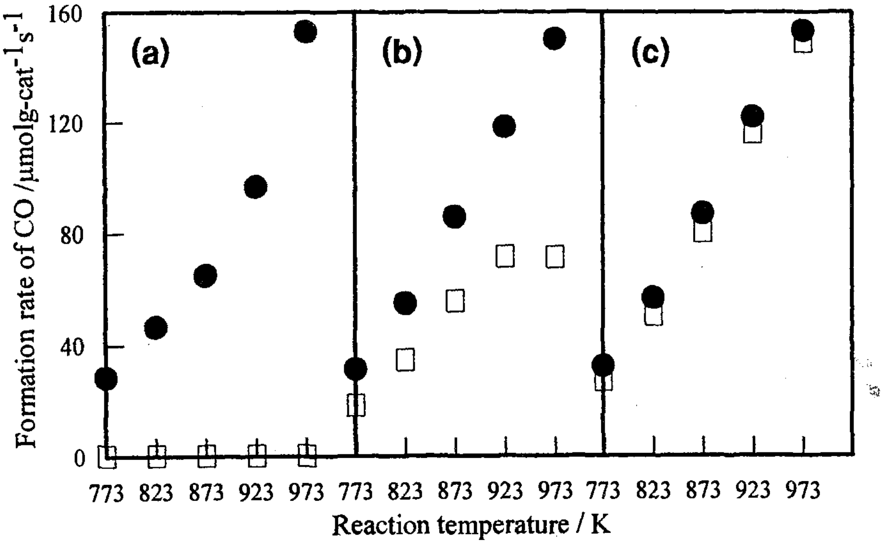

Fig. 3. Effect of the reduction temperature on CO formation rate for CH_4–CO_2 reaction over $Ni_{0.03}Mg_{0.97}O$ and 0.021 mol% Pt/$Ni_{0.03}Mg_{0.97}O$ catalysts. (□) $Ni_{0.03}Mg_{0.97}O$, (●) 0.021 mol% Pt/$Ni_{0.03}Mg_{0.97}O$. (a) H_2 reduction at 923 K, (b) H_2 reduction at 1023 K, (c) H_2 reduction at 1123 K. Reaction temperature: 773–973 K, $CH_4/CO_2 = 1/1$, total pressure: 0.1 MPa, $W/F = 1.2$ g-cat h/mol, weight of catalyst: 0.3 g.

presence of Pt facilitated the reduction of Ni^{2+} significantly [13]. Assuming that Pt and reduced Ni species had no intimate interaction, and that the activity was determined only by the amount of surface reduced Ni species, the catalytic activity of bimetallic catalyst would increase with the concentration of Pt until all reducible Ni^{2+} were reduced, and then it would level off at higher concentration of Pt. Together with the dependence of activity on the loading of promoter, the Pt–Ni alloy is very likely to be formed on the Pt/$Ni_{0.03}Mg_{0.97}O$ catalyst. The different surface composition of Pt–Ni alloy may be responsible for the observed catalytic performance, as Gauthier et al. suggested [20] that the activity and selectivity on an alloy is correlated with the surface composition of the alloy. At present, we have no direct evidence of the M–Ni (M = Pt, Pd and Rh) alloy formation. We tried to study the reduction behavior of the catalysts by means of temperature-programmed reduction, however, we could not get any evidence for the Pt–Ni alloy formation because the content of Pt was too low and the solid solution $Ni_{0.03}Mg_{0.97}O$ itself was very difficult to be reduced, thus no clear H_2 consumption peak was observed corresponding to the reduction of Pt and Ni. Therefore, further characterization is necessary to substantiate this suggestion. In addition, it was noted that the activity over the $Ni_{0.03}Mg_{0.97}O$ leveled off at reaction temperature higher than 923 K. As a result of the insufficient reduction of the $Ni_{0.03}Mg_{0.97}O$ at 1023 K, the formed Ni^0 might be in the pseudo-stable state and was easier to be oxidized in CH_4–CO_2 reactant gas. From fig. 3b, this deactivation due to the oxidation of Ni^0 is very likely to be related to the reaction temperature and time on stream, since the differences in activities between the two catalysts became larger as the reaction temperature increased. At the reduction temperature of 1123 K, the activity on both catalysts tended to be the same. This is because the CH_4 conversion reached the equilibrium level under this reaction condition ($W/F = 1.2$ g-cat h/mol).

The effect of partial pressure of CH_4 and CO_2 on the catalytic activity over $Ni_{0.03}Mg_{0.97}O$ and 0.021 mol% Pt/$Ni_{0.03}Mg_{0.97}O$ was also investigated under differential reaction conditions. The kinetic data are summarized in table 3. The fact that for $Ni_{0.03}Mg_{0.97}O$ the reaction order with respect to CH_4 is close to 1, and that of CO_2 is almost zero indicates that the decomposition of CH_4 is the rate-determining step. However, for Pt-promoted bimetallic catalyst, the reaction order of CH_4 decreases to 0.43 in company with the increase of that of CO_2 to 0.3. The different kinetic order between these two catalysts can be rationalized in the following way, taking account of the reaction mechanism proposed by Solymosi et al. [3]:

$$CH_4 \rightarrow CH_x + ((4-x)/2)H_2 \tag{1}$$

$$CO_2 \rightarrow CO_a + O_a \tag{2}$$

$$CH_x + O_a \rightarrow CO_a + (x/2)H_2 \tag{3}$$

Table 3
The reaction order of CH_4 and CO_2 in the reforming of CH_4 with CO at 773 K over $Ni_{0.03}Mg_{0.97}O$ and 0.021 mol% Pt/$Ni_{0.03}Mg_{0.97}O$ [a]

Catalyst	Kinetic order [b]	
	CH_4	CO_2
$Ni_{0.03}Mg_{0.97}O$	0.9	0.1
0.021 mol% Pt/$Ni_{0.03}Mg_{0.97}O$	0.4	0.3

[a] $W/F = 0.5$ g-cat h/mol, 0.0075 MPa $\leqslant P_{CH_4} \leqslant$ 0.0375 MPa, 0.0075 MPa $\leqslant P_{CO_2} \leqslant$ 0.0375 MPa, balance gas: Ar.
[b] Based on initial CO formation rate.

For $Pt/Ni_{0.03}Mg_{0.97}O$, the dissociation of CO_2 (eq. (2)) or the oxidation of the surface hydrocarbon species by adsorbed oxygen (eq. (3)) may become more rate-determining by the promotion of reaction (1) by added Pt. This promotion might be attributed to the enhancement of the catalyst reducibility. The activation energies for the reforming of CH_4 with CO_2 obtained at $W/F = 0.5$ g-cat h/mol were 17 (CH_4 conversion rate), 14 (CO_2 conversion rate), 20 (CO formation rate) and 20 (H_2 formation rate) kcal/mol for $Ni_{0.03}Mg_{0.97}O$, as well as 11 (CH_4), 18 (CO_2), 15 (CO) and 18 (H_2) kcal/mol for $Pt/Ni_{0.03}Mg_{0.97}O$.

4. Conclusion

(1) Although $Ni_{0.03}Mg_{0.97}O$ catalyst has a stable activity for the reforming of CH_4 with CO_2 at high reaction temperature (1123 K), the deactivation was observed at low reaction temperature (773 K), which is attributed to the oxidation of active Ni species.

(2) The catalytic activity and stability of $Ni_{0.03}Mg_{0.97}O$ was improved significantly by the addition of Pt, Pd or Rh. An apparent synergistic effect between Ni and the promoter was observed. This is partly due to the increased reducibility through hydrogen spillover from noble metal to $Ni_{0.03}Mg_{0.97}O$.

(3) The catalytic activity of bimetallic catalysts increased gradually with the noble metal loading, but after passing through a maximum, it decreased with superfluous addition. The maximum activity located at about $M/(Ni + Mg) = 0.02\%$ for each bimetallic catalyst was two times higher than that for $Ni_{0.03}Mg_{0.97}O$ catalyst.

(4) The reaction order of CH_4 and CO_2 for the reforming of CH_4 with CO_2 on $Ni_{0.03}Mg_{0.97}O$ was 0.9 and 0.1, while that on $Pt/Ni_{0.03}Mg_{0.97}O$ was 0.4 and 0.3, respectively. This means that the reaction mechanism or the rate-determining step was changed by the addition of Pt, suggesting that Pt–Ni alloy particles are formed.

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