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# Autothermal $CO_2$ reforming of methane over NiO–MgO solid solution catalysts under pressurized condition

## Effect of fluidized bed reactor and its promoting mechanism

Yuichi Matsuo, Yusuke Yoshinaga, Yasushi Sekine,
Keiichi Tomishige*, Kaoru Fujimoto[1]

*Department of Applied Chemistry, School of Engineering, The University of Tokyo, Bunkyo-ku, 7-3-1 Hongo, Tokyo 113-8656, Japan*

## Abstract

The effect of fluidized bed reactor in autothermal $CO_2$ reforming of methane over NiO–MgO solid solution catalysts was investigated by comparing with fixed bed reactor. Methane conversion to syngas was drastically enhanced by using a fluidized bed reactor. The catalyst was reduced and oxidized repeatedly in fluidized bed reactor during the reaction. The enhancement of methane conversion is related to the catalyst reducibility. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Autothermal reforming; NiO–MgO solid solution; Fluidized bed reactor

## 1. Introduction

$CO_2$ reforming of methane ($CH_4 + CO_2 \rightarrow 2CO + 2H_2$, $\Delta H = 247\,\mathrm{kJ/mol}$) is suitable to the production of CO-rich syngas which can be utilized to Fischer–Tropsch, methanol and dimethyl ether synthesis [1]. Pressurized syngas is more required because the synthesis reactions have been carried out under more pressurized condition. The problem in $CO_2$ reforming of methane is carbon deposition on the catalysts surface, and this problem becomes more serious under higher total pressure. Therefore, it is necessary to develop the catalyst with higher resistance to carbon deposition [2]. NiO–MgO solid solution catalysts reduced at high temperature (>1073 K) exhibited higher resistance to carbon deposition in $CO_2$ reforming of methane [3–11]. In addition, another problem is that $CO_2$ reforming of methane is a highly endothermic reaction. Combination of the reforming reaction with methane combustion ($CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$, $\Delta H = -861\,\mathrm{kJ/mol}$) is one of the solution to supply the heat effectively [12–16].

Some researches about autothermal reforming of methane [$CH_4 + O_2 + (CO_2 \text{ or } H_2O)$] using the fixed bed reactor have been carried out [12,13]. It has been insisted that methane combustion is followed by $CO_2$ and $H_2O$ reforming of methane and water–gas shift reaction. In that case, highly exothermic combustion and considerably endothermic reforming caused significant temperature gradient in the catalyst bed. Groote and Froment [12] simulated temperature gradient of catalyst bed in partial oxidation of methane using the fixed bed reactor. They pointed out that the temperature of the beginning part of the catalyst bed partially increases up to 1700 K though the reactor was controlled at about 1223 K by thermo-controller. In addition, at the beginning of the catalyst bed, cat-

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* Corresponding author. Tel.: +81-3-5841-7258;
fax: +81-3-5841-8578.
*E-mail address:* tomi@appchem.t-tokyo.ac.jp (K. Tomishige).

[1] Co-corresponding author.

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alysts were oxidized and exhibited little activity in reforming. Dissanayake et al. [13] have reported that the catalyst bed was divided into three parts in partial oxidation of methane over $Ni/Al_2O_3$ using fixed bed reactor. The first part was composed of $NiAl_2O_4$, and the second part consisted of $NiO/Al_2O_3$. It is found that oxygen reached these two parts in the fixed bed reactor. The catalyst in these parts contributed to combustion of methane. However in the third part, surface nickel was in the metallic state, which is active for selective formation of $H_2$ and CO.

Several researches on autothermal reforming of methane using the fluidized bed reactor have been reported [14–16]. It has been insisted that the high rates of heat transfer and stability of the operation were obtained by using the fluidized bed reactor. Combustion proceeded in the front part of the catalyst bed and reforming did in the rear part in both cases of fixed and fluidized bed. It is thought that both combustion and reforming proceeds on one catalyst particle in fluidized bed reactor. Santos et al. [14] have reported partial oxidation of methane over Ni/MgO and Co/MgO using fluidized bed reactor. It has been discussed that Ni and Co changes between oxidized and reduced state, and these continuous redox cycles may affect the stability and catalytic behavior of these solids in the long run.

In this study, we evaluated the effect of the fluidized bed reactor in autothermal reforming of methane over NiO–MgO catalysts. Especially the catalytic properties under pressurized condition of this reaction over the NiO–MgO solid solution catalysts were investigated by the comparison between fluidized bed and fixed bed reactor.

## 2. Experimental

$Ni_xMg_{1-x}O$ ($x = 0.03, 0.07, 0.15$) catalysts were prepared by the co-precipitation method from aqueous solution of $Ni(CH_3COO)_2\cdot4H_2O$ (Kanto Chemical; >98.0%) and $Mg(NO_3)_2\cdot6H_2O$ (Kanto Chemical; >99.0%) using $K_2CO_3$ (Kanto Chemical; >99.5%) as the precipitant. After being filtered and washed with hot water, the precipitate was dried at 393 K for 12 h, and then pre-calcined in air at 773 K for 3 h. Furthermore, they were pressed into disks at 600 kg/m$^2$, and then calcined at 1423 K for 20 h.

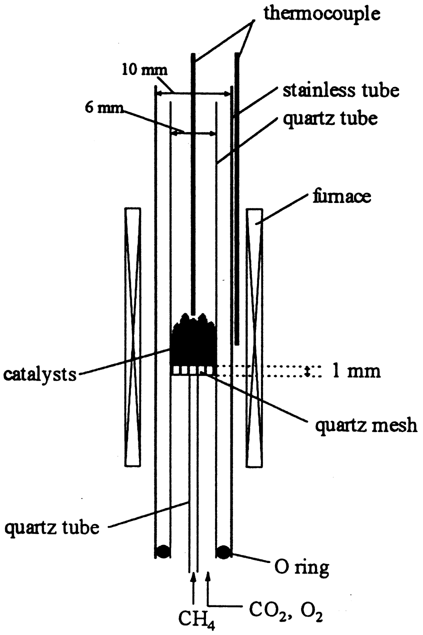

Fig. 1. Illustration of the fluidized bed reactor for autothermal reforming of methane.

$Pt/Ni_{0.03}Mg_{0.97}O$, Pt/MgO, Ni/MgO catalysts were prepared by impregnating support with an acetone solution of $Pt(C_5H_7O_2)_2\cdot H_2O$ (Soekawa Chemicals; >99%) or $Ni(C_5H_7O_2)_2\cdot H_2O$ (Soekawa Chemicals; >99%). The catalyst was dried at 393 K after impregnation in air for 12 h. MgO support was prepared by almost the same precipitation method as $Ni_xMg_{1-x}O$. Pre-calcination, press and calcination conditions were the same as those of solid solution catalysts. The catalysts were crushed and sieved to particles with 80–150 or 150–250 μm diameter. Surface area of catalysts was measured by BET method.

Autothermal reforming of methane was carried out in a fluidized and fixed bed flow reaction system under pressurized condition. The illustration of the fluidized bed reactor is shown in Fig. 1. The reactor had the quartz tube (6 mm i.d.) inside stainless steel tube (10 mm i.d.). A sintered quartz mesh was used as a distributor in fluidized bed reactor. In the fixed bed reactor, quartz wool was put on catalyst bed so as to prevent catalysts from moving. Pretreatment of catalysts was $H_2$ reduction at 1173 K for 0.5 h under hydrogen flow at atmospheric pressure. $CH_4$ was introduced to the reactor through the thin quartz tube, whose outlet was located just before the distributor. $CO_2$ and $O_2$ were introduced into the reactor outside the $CH_4$ feed tube. The partial pressure of the reactant gases was $CH_4/CO_2/O_2 = 50/20/30$, and the total pressure was 1.0 MPa. Reaction temperature was monitored inside and outside the reactor. The reaction temperature was controlled by monitoring the thermocouple at the inside of the reactor. Reaction temperature was 673–1173 K, and 0.2-g catalyst was used for each experiment. A space velocity GHSV = 19 000–110 000 $cm^3/g\,h$ and this corresponds to apparent 1.4–8.6 cm/s. The effluent gas was analyzed with FID gas chromatograph (GC) (column packing: Gaskuropack 54) equipped with methanator for $CH_4$, CO, $CO_2$ and TCD (column packing: Molecular Sieve 13X) for $H_2$. An ice bath was set between the reactor exit and a sampling port for GC analysis in order to remove water in the effluent gas. $CH_4$ (99.9%), $O_2$ (99%), $CO_2$ (99.9%), and $H_2$ (99%) were purchased from Takachiho and were used without further purification.

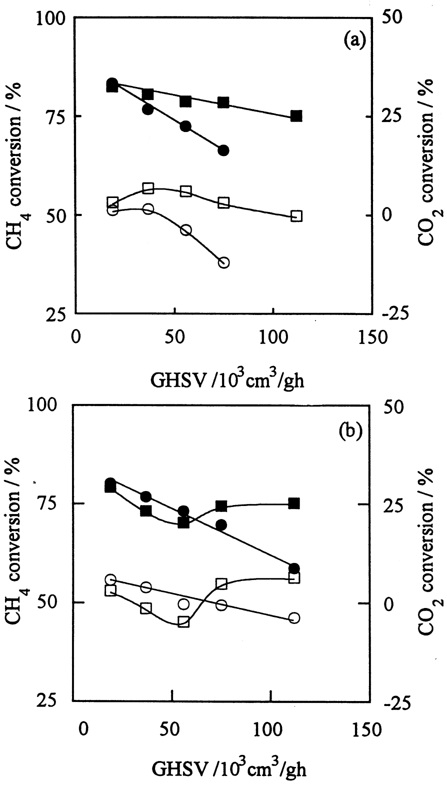

Fig. 2. Dependence of (■, ●) $CH_4$ and (□, ○) $CO_2$ conversion on the space velocity of reactant gas in autothermal $CO_2$ reforming of methane over $Ni_{0.15}Mg_{0.85}O$ catalyst using (■, □) fluidized and (●, ○) fixed bed reactor: (a) particle size, 80–150 μm; (b) particle size, 150–250 μm. Reaction conditions: temperature, 1073 K; total pressure, 1.0 MPa; feed gas $CH_4/CO_2/O_2 = 50/20/30$; $H_2$ pretreatment, 1173 K; catalyst weight, 0.2 g.

## 3. Results and discussion

Comparison between fluidized and fixed bed reactor in autothermal reforming of methane over $Ni_{0.15}Mg_{0.85}O$ with two kinds of particle size is shown in Fig. 2. These activity tests were carried out continuously from lower to higher space velocity (SV). The activity was measured for 0.5 h at each SV. At low SV, the conversion and the mole ratio $H_2/CO$ in both fluidized and fixed bed were almost the same on catalyst with 150–250 μm. This indicated that catalyst particles did not fluidize under this flow condition even in the fluidized reactor, and the state in the reactor was similar to that in fixed bed reactor. On the other hand, at high SV, the large difference between the two reactors in $CH_4$ and $CO_2$ conversion was observed. In the fixed bed reactor, the conversion decreased monotonously with SV simply because the contact time became shorter. In contrast, in the fluidized bed reactor, the conversion jumped at about GHSV = 60 000 $cm^3/g\,h$. Equilibrium conversion of methane was about 82% under the reaction condition. In all cases, oxygen conversion was 100%. On the other hand, in the case of the catalyst with 80–150 μm, the fluidized bed reactor also gave higher $CH_4$ conversion than the fixed bed reactor. However, different behavior was observed on each catalyst. On the catalyst with the small particle size (80–150 μm), the conversion gap between two reactors was observed at higher SV than 40 000 $cm^3/g\,h$. Minimum space velocity, where different levels of conversion for $CH_4$ and $CO_2$ was observed, was found to be strongly influenced by the particle size of the catalyst in fluidized bed reactor. This can be explained by the tendency that smaller particle can fluidize more easily. In addition, methane conversion was almost the same on the catalysts with different particle size in the fixed bed flow reactor. This indicates that the catalytic activity was not influenced by the particle size of the catalyst. This shows that reforming activity is not controlled

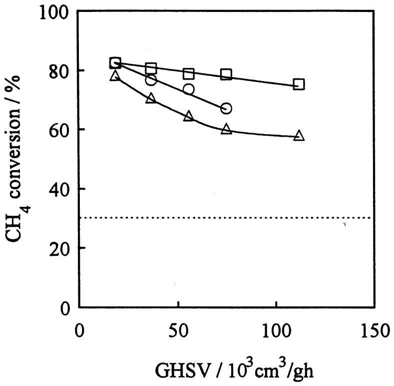

Fig. 3. Effect of Ni content in $Ni_xMg_{1-x}O$ catalysts on $CH_4$ conversion in autothermal reforming of methane using fluidized bed reactor: (□) $Ni_{0.15}Mg_{0.85}O$; (○) $Ni_{0.07}Mg_{0.93}O$; (△) $Ni_{0.03}Mg_{0.97}O$; (dotted line) $CH_4$ conversion due to combustion. Reaction conditions: temperature, 1073 K; total pressure, 1.0 MPa; feed gas $CH_4/CO_2/O_2 = 50/20/30$; $H_2$ pretreatment, 1173 K; catalyst weight, 0.2 g; granule size, 80–150 μm.

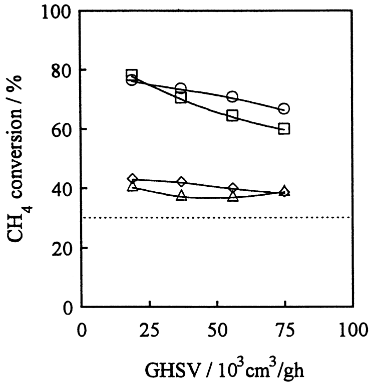

Fig. 4. Effect of addition of Pt to NiO–MgO catalyst on $CH_4$ conversion in autothermal reforming of methane using fluidized bed reactor: (○) 0.04 wt.% Pt/$Ni_{0.03}Mg_{0.97}O$; (□) $Ni_{0.03}Mg_{0.97}O$; (△) 0.04 wt.% Pt/MgO; (◇) MgO; (dotted line) $CH_4$ conversion due to combustion. Reaction condition: temperature, 1073 K; total pressure, 1.0 MPa; feed gas $CH_4/CO_2/O_2 = 50/20/30$; $H_2$ pretreatment, 1173 K; catalyst weight, 0.2 g; granule size, 80–150 μm.

by the gas diffusion inside the catalyst particles. Considering from the above results, it is clarified that the enhancement of conversion in autothermal $CO_2$ reforming is given by using fluidized bed reactor.

Fig. 3 shows the dependence of conversion on the space velocity in autothermal reforming of methane over $Ni_xMg_{1-x}O$ ($x = 0.03$, 0.07 and 0.15) using the fluidized bed reactor. In each catalyst, methane conversion decreased with increasing SV. However, on NiO–MgO catalyst with higher Ni content, the smaller was the gradient of $CH_4$ conversion decrease. The difference of methane conversion among $Ni_xMg_{1-x}O$ catalysts was considerably large in the case of the fluidized bed reactor. Methane conversion in $CO_2$ reforming of methane under pressurized condition is listed in Table 1. From these data, it was found that the difference of methane conversion among $Ni_xMg_{1-x}O$ catalysts was not so large in the fixed bed reactor and in $CO_2$ reforming reaction. The difference in the case of fluidized bed reactor cannot be explained by the difference of reforming activity on each catalyst.

Fig. 4 shows dependence of $CH_4$ conversion on SV in autothermal reforming of methane using the fluidized bed reactor over $Ni_{0.03}Mg_{0.97}O$, 0.04 wt.% Pt/$Ni_{0.03}Mg_{0.97}O$, MgO and 0.04 wt.% Pt/MgO. It was found that MgO and Pt/MgO exhibited almost the same conversion level. This is probably because the amount of Pt was so small (molar ratio $Pt/Ni = 3 \times 10^{-3}$). On the other hand, significant increase in conversion was observed by loading Pt into $Ni_{0.03}Mg_{0.97}O$. Authors have reported that the addition of the small amount of noble metal modified

Table 1
BET surface area and results of $CO_2$ reforming of $CH_4$[a]

| Catalyst | BET ($m^2/g$) | $CH_4$ conversion (%) | Carbon deposition (mg/g-catalyst)[b] |
|---|---|---|---|
| $Ni_{0.03}Mg_{0.97}O$ | 3 | 51 | 0 |
| $Ni_{0.07}Mg_{0.93}O$ | 3 | 57 | 90 |
| $Ni_{0.15}Mg_{0.85}O$ | 3 | 57 | 130 |
| 0.04 wt.% Pt/$Ni_{0.03}Mg_{0.97}O$ | 3 | 55 | 0 |

[a] Reaction condition: 1.0 MPa, $CH_4/CO_2 = 1/1$, 1123 K, GHSV = 37 000 $cm^3/g\,h$, fixed bed reactor.

[b] Carbon deposition was estimated by TG method. Reaction condition: 1.0 MPa, $CH_4/CO_2 = 1/1$, 1123 K, GHSV = 19 000, 25 000, 37 000, 75 000 $cm^3/g\,h$, each GHSV for 45 min, fixed bed reactor. Samples were located in the inlet of catalyst bed.

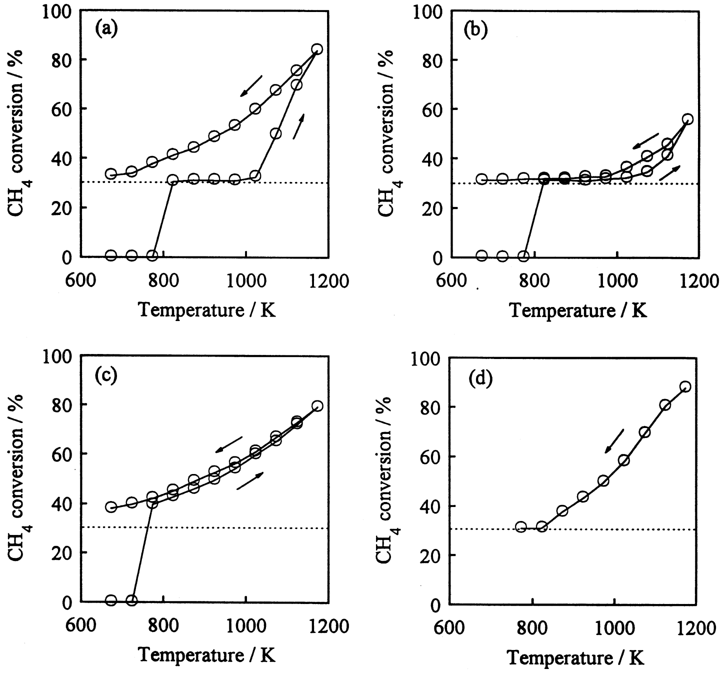

Fig. 5. The heating and cooling profile of methane conversion in autothermal $CO_2$ reforming of methane over: (a) $Ni_{0.15}Mg_{0.85}O$, (b) $Ni_{0.03}Mg_{0.97}O$, (c) 0.04 wt.% $Pt/Ni_{0.03}Mg_{0.97}O$ and (d) $Ni_{0.03}Mg_{0.97}O$ with $H_2$ pretreatment at 1173 K for 30 min. Reaction condition: catalyst weight, 0.2 g; particle size, 80–150 μm; 1.0 MPa; GHSV = 56000 $cm^3/g\,h$; $CH_4/CO_2/O_2$ = 50/20/30; fluidized bed reactor. Catalysts were used without $H_2$ pretreatment except (d), dotted line: $CH_4$ conversion due to combustion.

$Ni_{0.03}Mg_{0.97}O$ catalyst in $CO_2$ reforming of methane [4,10]. According to the report, the addition of noble metal dramatically enhanced the reducibility of $Ni_{0.03}Mg_{0.97}O$ by the spillover effect of hydrogen from noble metal to $Ni_{0.03}Mg_{0.97}O$ surface. Under pressurized condition, the catalytic activity itself in the fixed bed reactor on $Pt/Ni_{0.03}Mg_{0.97}O$ was almost the same as that on $Ni_{0.03}Mg_{0.97}O$. From the results of Fig. 3 and Fig. 4, methane conversion did not seem to be dependent on the reforming activity itself of each catalyst, but it is related to catalyst reducibility.

We investigated the dependence of methane conversion on the reaction temperature over $Ni_{0.15}Mg_{0.85}O$, $Ni_{0.03}Mg_{0.97}O$, 0.04 wt.% $Pt/Ni_{0.03}Mg_{0.97}O$ by changing the temperature stepwise in the $O_2$-added $CO_2$ reforming of methane, in order to evaluate the reduction and oxidation profile during the catalytic reaction, as shown in Fig. 5. In this experiment, the reactant gas was fed to the catalyst bed without $H_2$ pretreatment. At first, reactant gas was fed to the reactor and the pressure becomes higher up to 1.0 MPa at room temperature. The catalyst was heated stepwise up to 1173 K by 50 K and after that, it was cooled stepwise. In Fig. 5, the dotted line represents the methane conversion due to combustion. The contribution of the reforming reaction corresponded to the conversion above this dotted line. Since catalysts were used without the reduction pretreatment, catalysts were in the oxidation state at first. Methane combustion started at 773 K, and the reforming reaction started to proceed at 1023 K over $Ni_{0.15}Mg_{0.85}O$ and $Ni_{0.03}Mg_{0.97}O$. The temperature where combustion and reforming started to proceed was almost the same as on $Ni_{0.03}Mg_{0.97}O$ and $Ni_{0.15}Mg_{0.85}O$. In contrast, the increase in the methane reforming activity on $Ni_{0.15}Mg_{0.85}O$ was much higher than that on $Ni_{0.03}Mg_{0.97}O$ in heating process. These results indicated that $Ni_{0.15}Mg_{0.85}O$ had higher reducibility than $Ni_{0.03}Mg_{0.97}O$, and this is consistent with the previous report [17]. In addition, $Ni_{0.15}Mg_{0.85}O$

exhibited much large difference between heating and cooling processes. On the other hand, the addition of Pt to $Ni_{0.03}Mg_{0.97}O$ changed the profile drastically. Methane combustion started at lower temperature and that of methane reforming started at much lower temperature than other catalysts. This indicated that Pt gave high reducibility to $Ni_{0.03}Mg_{0.97}O$ solid solution catalyst. Further, the difference between heating and cooling process on Pt/$Ni_{0.03}Mg_{0.97}O$ became very small. This also indicated that the reducibility of the catalyst was drastically enhanced. The conversion in cooling process on Pt/$Ni_{0.03}Mg_{0.97}O$ was higher than that on $Ni_{0.03}Mg_{0.97}O$ reduced at 1173 K as shown in Fig. 5(d). This indicated that the addition of Pt gave the anti-oxidation ability to the catalyst.

Table 2
Activity of autothermal $CO_2$ reforming of methane using fluidized and fixed bed reactor[a]

| Catalyst | Reactor | Conversion (%) | | $H_2$/CO |
|---|---|---|---|---|
| | | $CH_4$ | $CO_2$ | |
| $Ni_{0.15}Mg_{0.85}O$ | Fluidized | 78 | 3 | 1.4 |
| | Fixed | 66 | −12 | 1.4 |
| 3 mol.% Ni/MgO | Fluidized | 64 | −19 | 1.4 |
| | Fixed | 65 | −12 | 1.3 |

[a] Reaction condition: temperature, 1073 K; total pressure, 1.0 MPa; GHSV = 75 000 $cm^3$/g h; $CH_4/CO_2/O_2$ = 50/20/30; catalyst weight, 0.2 g.

Methane conversion and the molar ratio $H_2$/CO in autothermal reforming over 3 mol.% Ni/MgO and $Ni_{0.15}Mg_{0.85}O$ using the fluidized and fixed bed reactor are listed in Table 2. The conversion level on the 3 mol.% Ni/MgO was lower than that on the $Ni_{0.15}Mg_{0.85}O$ solid solution catalyst using fluidized bed reactor. In contrast, no difference in methane conversion was observed between fluidized and fixed bed on 3 mol.% Ni/MgO. It has been reported that the dispersion of nickel metal particle is considerably low on Ni/MgO [4]. The reducibility of $Ni^{2+}$ is related to the Ni concentration on the catalyst surface and near-surface. The order of surface Ni concentration is as follows: 3 mol.% Ni/MgO $\gg$ $Ni_{0.15}Mg_{0.85}O$ > $Ni_{0.03}Mg_{0.97}O$ [6]. Therefore the 3 mol.% Ni/MgO catalyst has very high reducibility and the low ability to be oxidized. These suggest that the utilization of fluidized bed reactor in the autothermal $CO_2$ reforming of methane is very effective when the catalyst has medium ability to be reduced and oxidized. This strongly suggests that the catalyst in the fluidized bed reactor is in the cycle of reduction–oxidation. Fig. 6 shows the model scheme of NiO–MgO solid solution catalyst in autothermal reforming of methane in the fluidized bed and fixed bed reactor. Methane combustion proceeds on the catalyst at the beginning part of catalyst bed, followed by the reforming of methane. Therefore, since the inlet part of bed is the oxidizing atmosphere, surface nickel of the catalyst is oxidized ($Ni^{2+}$). Oxidized NiO–MgO solid solution catalyst showed no reforming activity as shown in Fig. 5. The atmosphere of upper part of catalyst bed is composed of produced syngas and residual reactants containing

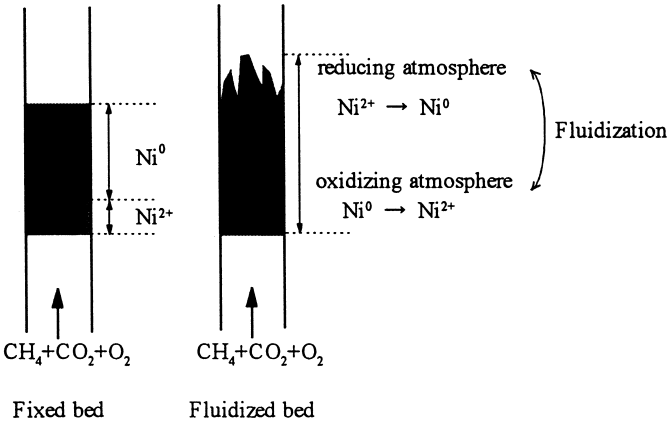

Fig. 6. Model scheme of autothermal reforming of methane on NiO–MgO catalysts using fluidized and fixed bed reactor.

no oxygen. In this region, oxygen is absent because all of the oxygen is consumed. The upper part is reducing atmosphere. Therefore surface nickel of catalyst is reduced to be $Ni^0$. In this way, the catalyst bed can be divided to two parts in fixed bed. This is similar to the previous report [13]. On the other hand, in a fluidized bed reactor, the catalyst oxidized by oxygen in the front region can transfer to the rear part where it is re-reduced and exhibits reforming activity. This decreases the amount of oxidized catalyst, and increases the amount of reduced catalyst. Enhancement of methane reforming activity by using fluidized bed reactor can be explained by the model described above. On the 3 mol.% Ni/MgO in fixed bed and fluidized bed, methane conversion was almost the same. Since the oxidation rate of large nickel metal particle may be low, the amount of oxidized catalyst should be much smaller than NiO–MgO solid solution catalyst. No enhancement of methane conversion by using fluidized bed reactor on the 3 mol.% Ni/MgO can be explained by this concept.

## 4. Conclusion

1. It was found that high reforming conversion can be attained by using a fluidized bed reactor in autothermal reforming of methane on NiO–MgO solid solution catalysts under pressurized condition.
2. Fluidization of the catalysts could reduce and activate the catalyst which was oxidized by oxygen near the inlet of the catalyst bed with the produced syngas.
3. Since NiO–MgO solid solution catalyst with higher Ni content had higher reducibility, they exhibited high conversion in autothermal reforming of methane using fluidized bed reactor.

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