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Promoting effect of Pt on self-activation over NiO–MgO solid solution in oxidative steam reforming of methane

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The addition of Pt on NiO–MgO solid solution enhanced the performance of oxidative steam reforming of methane, especially, the catalyst can be activated during the oxidative reforming of methane at low reaction temperature like 823 K. 0.1% Pt/$Ni_{0.2}Mg_{0.8}O$ exhibited much higher performance than 0.1% Pt/MgO and $Ni_{0.2}Mg_{0.8}O$. From the comparisons, the additive effect of Pt to $Ni_{0.2}Mg_{0.8}O$ is to promote both the activity of combustion and reforming of methane. This additive effect can be explained by the high combustion activity caused by the synergy of Pt with NiO–MgO solid solution and the high catalyst reducibility.

KEY WORDS: oxidative steam reforming of methane; NiO–MgO solid solution; additive effect; platinum; self activation.

1. Introduction

Steam reforming of natural gas on nickel-based catalyst is the most important process for the production of hydrogen and synthesis gas [1].

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

As described above, steam reforming of methane to synthesis gas is a highly endothermic reaction. Therefore, in the conventional steam reforming, the external heating process has been applied. On the other hand, for the purpose of highly energy efficiency, oxygen is added to the reactant gas to utilize the exothermic reactions such as methane combustion and partial oxidation of methane.

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

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

A most well-known process is ATR (autothermal reforming of methane) developed by Haldor Topsoe [2]. On the other hand, the catalysts for the combination of catalytic combustions with reforming have been developed [3–12].

It has been reported that NiO–MgO solid solution catalysts exhibited high performance in steam [13] and dry reforming of methane [14–18]. Especially, the catalysts had high resistance to coke deposition in dry reforming of methane. However, it is thought that solid solution catalysts can be easily oxidized and they are not suitable to reforming of methane with steam and O_2 (oxidative steam reforming of methane) [19].

In this letter, the additive effect of Pt on NiO–MgO is investigated for the development and design of suitable catalyst for the oxidative steam reforming of methane. Especially, when NiO–MgO solid solution is applied, the activation method is expected to be some problem since it has low reducibility and needs H_2 reduction at very high temperature [13]. Therefore, this letter focuses on the activation performance over Pt/NiO–MgO catalyst.

2. Experimental

NiO–MgO solid solution was prepared by the solid reaction method from NiO (Wako Pure Chemical Industries Ltd, Japan) and MgO (UBE Material Industries Ltd, Japan). The mixture of NiO with MgO was calcined in air at 1423 K for 12 h. The formation of NiO–MgO solid solution was identified by X-ray diffraction (XRD). The composition of solid solution prepared in this study was $Ni_{0.2}Mg_{0.8}O$. After the calcination, the BET surface area of $Ni_{0.2}Mg_{0.8}O$ was determined to be 3 m^2/g. As a reference, MgO was calcined at the same temperature. The loading of Pt on $Ni_{0.2}Mg_{0.8}O$ and MgO was performed by the impregnation of $Ni_{0.2}Mg_{0.8}O$ and MgO with $Pt(NO_2)_2(NH_3)_2$ aqueous solution. After removal of the solvent by heating, the catalysts were dried overnight at 383 K and then calcined in air at 773 K for 3 h. The loading amount of Pt was 0.1 wt%. Before use, all of these catalysts were pressed (500 kg/cm^2) into disks and then crushed to 60–100 mesh particles. These catalysts are

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denoted as $Ni_{0.2}Mg_{0.8}O$, 0.1% Pt/MgO and 0.1% Pt/$Ni_{0.2}Mg_{0.8}O$.

Oxidative steam reforming of methane was carried out in a fixed bed flow reaction system. A quartz tube (inner diameter, 4.4 mmø) was used as the reactor. At the outlet of the catalyst bed, the reaction temperature was monitored by the thermocouple, which was inserted into a thin quartz tube (thermowell). Catalyst reduction was carried out by hydrogen flow under atmospheric pressure at appropriate temperature if necessary. The pretreatment conditions are shown in each result. The partial pressure ratio of reactants was CH_4:H_2O:O_2 = 4:3:2, where H_2O was supplied by using the microfeeder. The total pressure was 0.1 MPa and 0.03 g catalyst was used for each experiment. The length of the catalyst bed was about 4 mm. Contact time W/F (W = catalyst weight/g and F = total flow rate of the introduced gases/mol/h) was 0.43 gh/mol. The equilibrium level of CH_4 conversion at each reaction temperature is indicated in figure 1(a). The effluent gas was analyzed with an FID gas chromatograph (GC) (column packing: Gaskuropack 54) equipped with a methanator for CH_4, CO, CO_2 and a TCD (column packing: Molecular Sieve 13×) was used for H_2 analysis. 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.

Methane conversion and CO selectivity on the NiO–MgO solid solution in oxidative steam reforming of methane were calculated as described below.

$$\text{Methane conversion (\%)} = (C_{CO} + C_{CO_2})/(C_{CH_4} + C_{CO} + C_{CO_2}) \times 100$$

$$\text{CO selectivity (\%)} = C_{CO}/(C_{CO} + C_{CO_2}) \times 100$$

C : concentration of each component in the effluent gas.

The amount of deposited carbon on all the catalysts after the activity tests for oxidative steam reforming of methane was estimated by thermogravimetric analysis method (TGA, Shimadzu, DTG-60). Sample weight was 10 mg, and TGA profiles were observed under air flowing (20 mL/min) at heating rate of 15 K/min. In the case that the carbon is present on the catalyst surface, the exothermic weight loss can be observed in the range of about 800–1000 K as reported previously [17]. However, this kind of weight loss was not observed at all in all these experiments, and it is found that the amount of carbon deposition was negligible here.

3. Results and Discussion

Figure 1 shows the behavior in oxidative reforming at increasing reaction temperature with time on stream over 0.1% Pt/$Ni_{0.2}Mg_{0.8}O$, 0.1% Pt/MgO and $Ni_{0.2}Mg_{0.8}O$. In this experiment, the reactant gas (CH_4/H_2O/O_2 = 4/3/2) was introduced without H_2 pretreatment. The procedures were as follows. At first, the catalyst was heated at 773 K under Ar flowing, and then the reactant gases (CH_4 + H_2O + O_2) for oxidative steam reforming of methane were introduced at 773 K. The performance was observed at the reaction temperature for 30 min. After 30 min, the temperature was increased to 823 K. Furthermore, the catalyst was heated stepwise up to 1073 K by 50 K. At each temperature, the performance was observed for 30 min. In the case of 0.1% Pt/ $Ni_{0.2}Mg_{0.8}O$ from figure 1(a), at 773 K, methane conversion (▲) was 25% and CO selectivity (○) was low, and this means that only methane combustion reaction proceeded under these conditions. This methane conversion was almost the same level as the dotted line in figure 1, which represents the methane conversion assigned to complete combustion of methane. This can also be supported by no H_2 formation, therefore, the H_2/CO (□) was not plotted here. At higher reaction temperature than 773 K, methane conversion was beyond 25%, and it was increased with increasing the reaction temperature, and at the same time, CO selectivity also increased and H_2/CO ratio decreased. These behaviors indicate that the reforming reaction proceeded and the synthesis gas was formed under these reaction conditions.

On the other hand, in the case of 0.1% Pt/MgO from figure 1(b), in the range of 773–973 K, methane conversion was much lower than 25%, and CO selectivity was also low. This indicates that 0.1% Pt/MgO has low activity of methane combustion and reforming. However, at 1023 K, methane conversion reached about 50%, although it was lower than that over 0.1% Pt/$Ni_{0.2}Mg_{0.8}O$. Furthermore, in the case of $Ni_{0.2}Mg_{0.8}O$ from figure 1(c), in all the temperature range, methane conversion did not reach 25%. In addition, CO selectivity on $Ni_{0.2}Mg_{0.8}O$ was a little higher than that on 0.1% Pt/MgO in low temperature range, although the formation of hydrogen was also very low and it can be neglected. This is why H_2/CO ratio is not shown in figure 1(c). From the comparisons, 0.1% Pt/$Ni_{0.2}Mg_{0.8}O$ exhibits much higher combustion activity than 0.1% Pt/MgO and $Ni_{0.2}Mg_{0.8}O$ catalysts. This can be due to the synergetic effect between Pt and NiO–MgO solid solution. An interesting result is that 0.1% Pt/ $Ni_{0.2}Mg_{0.8}O$ gave the high methane conversion and high formation rate of synthesis gas without H_2 pretreatment.

Figure 2 shows the reduction temperature dependence of oxidative steam reforming of methane over three catalysts at 1073 K. Even when the reduction temperature was as low as 773 K, 0.1% Pt/$Ni_{0.2}Mg_{0.8}O$ exhibited almost 100% methane conversion. The reduction temperature dependence was not observed on 0.1% Pt/ $Ni_{0.2}Mg_{0.8}O$. Similar behavior was observed over 0.1% Pt/MgO, although CH_4 conversion over 0.1% Pt/MgO was lower than that over 0.1% Pt/

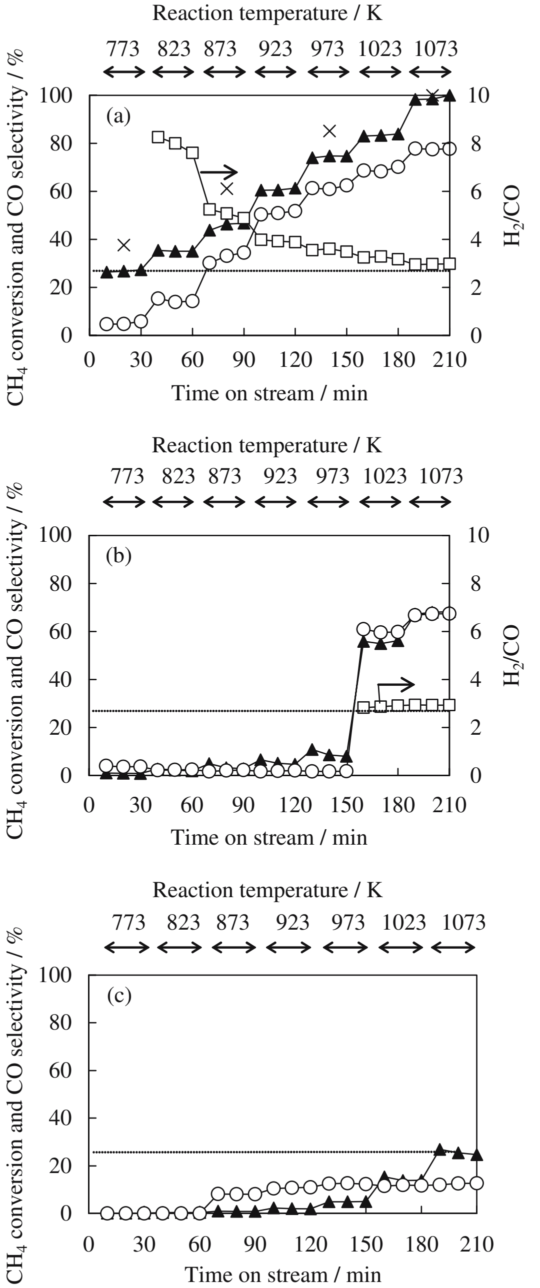

Figure 1. Results of CH_4 conversion, CO selectivity and H_2/CO ratio in oxidative steam reforming of methane during the reaction temperature increasing over the catalysts without H_2 pretreatment. (a) 0.1% Pt/ $Ni_{0.2}Mg_{0.8}O$, (b) 0.1% Pt/ MgO, (c) $Ni_{0.2}Mg_{0.8}O$ (▲) CH_4 conversion, (○) CO selectivity, (□) H_2/CO, (×) equilibrium level of CH_4 conversion at each reaction temperature. Reaction conditions: catalyst weight = 0.03 g, $CH_4:H_2O:O_2 = 4:3:2$, contact time, $W/F = 0.43$ gh/mol, total pressure = 0.1 MPa. Dotted line represents methane conversion due to methane combustion.

$Ni_{0.2}Mg_{0.8}O$. In contrast, significant reduction temperature dependence over $Ni_{0.2}Mg_{0.8}O$ was clearly observed. $Ni_{0.2}Mg_{0.8}O$ required the reduction temperature higher than 973 K. This result indicates that reduced $Ni_{0.2}Mg_{0.8}O$ solid solution has very high activity in oxidative reforming of methane. However, $Ni_{0.2}Mg_{0.8}O$, which is not reduced enough, was active for only methane combustion. On the basis of these results, it is found that the reason why $Ni_{0.2}Mg_{0.8}O$ exhibited very low methane conversion in figure 1(c) is that the catalyst in an oxidized state has very low catalytic activity of methane combustion and reforming. This is supported by our previous report [13]. From the comparisons of performance of these three catalysts, the additive effect of Pt on NiO–MgO solid solution is to promote the activity of methane combustion and methane reforming. Regarding methane combustion activity, 0.1% $Pt/Ni_{0.2}Mg_{0.8}O$ exhibited much higher activity than 0.1% Pt/MgO and $Ni_{0.2}Mg_{0.8}O$ as described in figure 1. According to the previous report on the structure of MgO supported on Pt by means of the extended X-ray absorption fine structure (EXAFS), Pt ions can be incorporated to the lattice of MgO with the substitution of Mg ion site in an oxidized state [20]. Therefore, it is expected that Pt ions can be incorporated to the lattice of NiO–MgO solid solution. In order to discuss the activity of methane combustion, it is necessary to consider the reactivity of the oxide ions (O^{2-}). In the case of 0.1% Pt/MgO, there are oxide ions between Pt and Mg ions, which is denoted as Pt–O–Mg. In the case of $Ni_{0.2}Mg_{0.8}O$, Ni–O–Mg structure is present. From the result of figure 1, it is thought that these structures can give low combustion activity. In contrast, Pt–O–Ni structure is present on 0.1% $Pt/Ni_{0.2}Mg_{0.8}O$ as well as Pt–O–Mg and Ni–O–Mg structures. It is expected that this can contribute to high methane combustion activity, although further investigations are necessary for the elucidation of active site for methane combustion over 0.1% $Pt/Ni_{0.2}Mg_{0.8}O$. On the other hand, the addition of Pt also promoted methane reforming reaction. As described in figure 2, NiO–MgO solid solution itself exhibited high methane reforming activity when it is sufficiently reduced, although the activity of reduced 0.1% Pt/MgO is not high. Since the active site of methane reforming to produce synthesis gas is metallic species such as Pt^0 and Ni^0, it is necessary to reduce the catalysts for the reforming reaction. Therefore, high reforming activity is related to high reducibility of 0.1% $Pt/Ni_{0.2}Mg_{0.8}O$ shown in the results of reduction temperature dependence (figure 2). This tendency has also been observed in our previous report [21]. From the catalyst characterization by means of temperature programmed reduction and the measurement of H_2 adsorption, the reduction degree of Ni on both $Ni_{0.2}Mg_{0.8}O$ and $Pt/Ni_{0.2}Mg_{0.8}O$ was 3.4%, on the other hand, the dispersion of metal particles over these two catalysts was 7.8% and 12.0%, respectively. The addition of Pt enhanced the dispersion. The molar ratio of Pt to the reduced Ni can be calculated to be as small as 0.04. The addition of Pt enhanced the dispersion, and it is related to high performance of $Pt/Ni_{0.2}Mg_{0.8}O$.

The behavior of 0.1% $Pt/Ni_{0.2}Mg_{0.8}O$ can be interpreted at present as follows: all the introduced oxygen can be consumed by combustion reaction near the

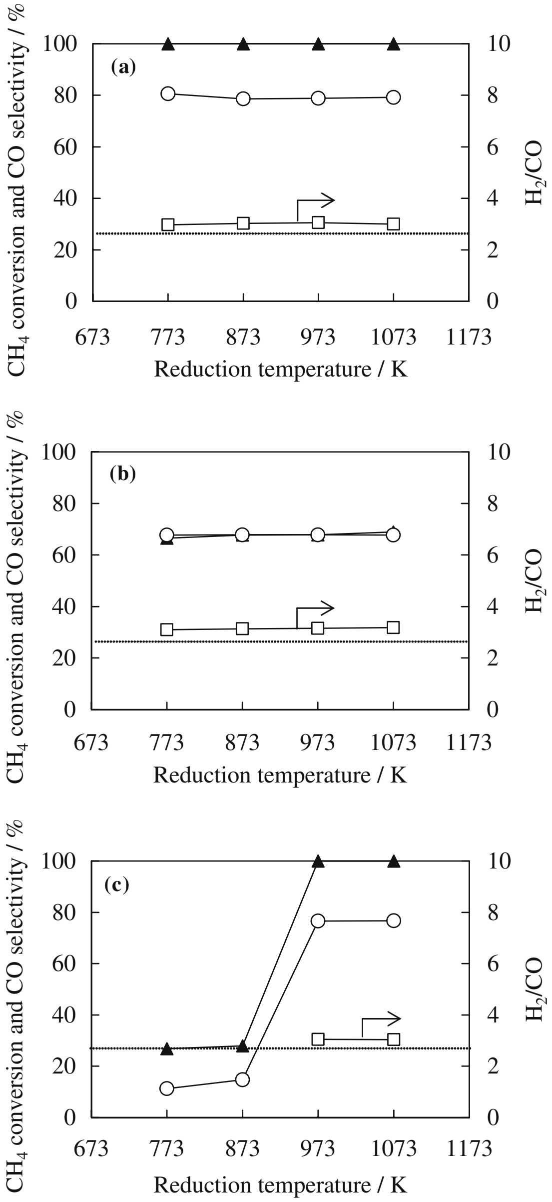

Figure 2. Reduction temperature dependence of CH_4 conversion, CO selectivity and H_2/CO ratio in oxidative steam reforming of methane over the catalysts at reaction temperature of 1073 K. (a) 0.1% Pt/ $Ni_{0.2}Mg_{0.8}O$, (b) 0.1% Pt/ MgO, (c) $Ni_{0.2}Mg_{0.8}O$ (▲) CH_4 conversion, (○) CO selectivity, (□) H_2/CO. Reaction conditions: catalyst weight = 0.03 g, $CH_4:H_2O:O_2 = 4:3:2$, contact time, $W/F = 0.43$ gh/mol, total pressure = 0.1 MPa. Dotted line represents methane conversion due to methane combustion.

catalyst bed inlet since the catalyst has high combustion activity. Therefore, the oxygen free region is present in the catalyst bed, where methane, steam, and CO_2 are exposed to the catalyst, and methane can reduce 0.1% Pt/$Ni_{0.2}Mg_{0.8}O$ at lower temperature such as 823 K. Once the catalyst reduction started, reduced species can promote methane reforming reaction to produce CO and H_2, which are stronger reducing agent than methane, and they can also promote the catalyst reduction more significantly. This phenomenon can be related to much lower oxygen affinity of Pt than that of Ni [22]. This interpretation will be able to be supported by the characterization of used catalysts near the catalyst bed inlet and outlet in the future. Furthermore, it is known that hydrogen spillover phenomenon from Pt to the support materials containing Ni species can enhance the reducibility of Ni. In addition, the behavior can be related to the alloy formation from Pt and Ni as reported previously [4, 21]. Therefore, 0.1% Pt/ $Ni_{0.2}Mg_{0.8}O$ exhibited high performance in oxidative reforming of methane without H_2 pretreatment, and this can be due to the self–activation caused by the synergy of Pt with NiO–MgO solid solution.

4. Conclusions

(1) $Ni_{0.2}Mg_{0.8}O$ solid solution exhibited high activity in oxidative steam reforming of methane when the catalyst was reduced sufficiently with H_2 at high temperature (973 K). $Ni_{0.2}Mg_{0.8}O$ in oxidized state showed low activity of methane combustion and reforming.

(2) 0.1% Pt/ $Ni_{0.2}Mg_{0.8}O$ catalyst showed much higher combustion activity than 0.1% Pt/MgO and $Ni_{0.2}Mg_{0.8}O$ catalysts. This is probably due to high reactivity of oxide ions located between Pt and Ni ions.

(3) The addition of Pt on $Ni_{0.2}Mg_{0.8}O$ enables high activity of oxidative reforming of methane without the activation by H_2 treatment. This can be due to the self-activation mechanism under the oxidative steam reforming atmosphere at low temperature like 823 K. This function can be related to high combustion activity, low oxygen affinity of Pt, and high catalyst reducibility.

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