

Promoting Effect of Pd Addition to $\text{Ni}_{0.2}\text{Mg}_{0.8}\text{Al}_2\text{O}_4$ in Oxidative Steam Reforming of Methane

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Addition of Pd to $\text{Ni}_{0.2}\text{Mg}_{0.8}\text{Al}_2\text{O}_4$ promoted oxidative steam reforming of methane, and it gave high activity under high partial pressure of steam and low W/F , where $\text{Ni}_{0.2}\text{Mg}_{0.8}\text{Al}_2\text{O}_4$ showed very low activity. The $\text{Ni}_{0.2}\text{Mg}_{0.8}\text{Al}_2\text{O}_4$ requires the H_2 reduction pretreatment; however, Pd/ $\text{Ni}_{0.2}\text{Mg}_{0.8}\text{Al}_2\text{O}_4$ can be activated automatically by the reactant gases of oxidative reforming of methane.

Oxidative steam reforming of methane is one of attractive methods for the production of hydrogen for fuel cells and the synthesis gas for gas-to-liquid process because the oxidative reforming is more energy efficient than conventional steam reforming of methane.¹⁻⁷ This difference can be mainly due to the heating methods: The oxidative reforming is internal-heating and the conventional reforming is external-heating. On the other hand, in the oxidative reforming of methane, it has been reported that the Ni catalysts can be deactivated by the oxidation of Ni metal species.^{5,8} In this letter, we report that the addition of Pd to $\text{Ni}_{0.2}\text{Mg}_{0.8}\text{Al}_2\text{O}_4$ spinel enhanced the catalyst reducibility, and this can be related to high activity in oxidative steam reforming of methane. Furthermore, $\text{Ni}_{0.2}\text{Mg}_{0.8}\text{Al}_2\text{O}_4$ modified with Pd can be activated easily with the reactant gases of the oxidative reforming, although the activation of $\text{Ni}_{0.2}\text{Mg}_{0.8}\text{Al}_2\text{O}_4$ needs H_2 reduction at high temperature.

$\text{Ni}_{0.2}\text{Mg}_{0.8}\text{Al}_2\text{O}_4$ was prepared by the solid reaction method from NiO (Wako Pure Chemical Industries Ltd., Japan), MgO (UBE Material Industries Ltd., Japan), and Al_2O_3 (Nippon Aerosil Corporation, Japan). The mixture of NiO, MgO, and Al_2O_3 with the appropriate composition was calcined in air at 1423 K for 12 h. As a reference, MgAl_2O_4 and NiAl_2O_4 were also prepared by the calcinations at 1423 K for 12 h. The loading of Pd on $\text{Ni}_{0.2}\text{Mg}_{0.8}\text{Al}_2\text{O}_4$ and MgAl_2O_4 was performed by the impregnation of $\text{Ni}_{0.2}\text{Mg}_{0.8}\text{Al}_2\text{O}_4$ and MgAl_2O_4 with aqueous solutions of $\text{Pd}(\text{NO}_3)_2$ (N.E. Chemcat Corp, Japan). The loading amount of Pd was 0.1 mass% (9.4×10^{-6} mol/g-cat), and BET surface areas of these catalysts are listed in Table 1.

Oxidative steam reforming of methane was carried out in a fixed bed flow reaction system. In usual case, the catalysts were pretreated by hydrogen under atmospheric pressure at 1123 K for 0.5 h. In the self-activation test, the catalysts were used without hydrogen reduction pretreatment. The partial pressure ratio of reactants was $\text{CH}_4/\text{H}_2\text{O}/\text{O}_2 = 2/1.5/1$ and $2/4/1$. The operating total pressure was 0.1 MPa; 30 mg of catalyst was used. Contact time W/F was used as 0.43 and 0.13 g h mol^{-1} . The effluent gas was analyzed with a gas chromatograph. CH_4 conversion and CO selectivity were estimated on the basis of our previous report.⁸ The methods of temperature programmed reduction with H_2 (H_2 -TPR) and H_2 chemisorption were described in our previ-

Table 1. Properties of the catalysts

Catalysts	BET / $\text{m}^2 \text{g}^{-1}$	Ni	Pd	H_2 cons ^a / 10^{-6} mol g^{-1}	D_{red}^b /%	H_2 ad ^c / 10^{-6} mol g^{-1}	D_{disp}^d /%
		content / 10^{-4} mol g^{-1}	content / 10^{-6} mol g^{-1}				
$\text{Ni}_{0.2}\text{Mg}_{0.8}\text{Al}_2\text{O}_4$	23.9	13.4	0	816	61	20.4	5.0
Pd/ $\text{Ni}_{0.2}\text{Mg}_{0.8}\text{Al}_2\text{O}_4$	23.9	13.4	9.4	1222	90	56.2	9.2
Pd/ MgAl_2O_4	29.9	0	9.4	21	—	4.2	39.3

^aTotal amounts of hydrogen consumption in TPR profiles (283–1123 K).

^bReduction degree of Ni: the ratio of reduced Ni to total Ni.

^cTotal amount of hydrogen adsorption at 298 K.

^dDispersion: $(2 \times \text{H}_2 \text{ adsorption})/(\text{Pd} + \text{reduced Ni}) \times 100$. The loading amount of Pd was 0.1 mass%, and it is assumed that all Pd atoms were reduced as $\text{Pd}^{2+} + \text{H}_2 \rightarrow \text{Pd}^0 + 2\text{H}^+$.

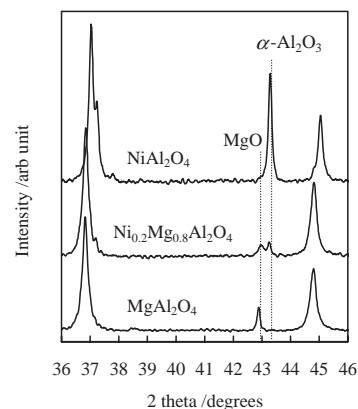


Figure 1. XRD patterns of the samples after the calcination at 1423 K for 12 h.

ous report.⁹ The amount of deposited carbon during the reaction was negligible in all the cases. Characterization results are also listed in Table 1.

Figure 1 shows the XRD patterns of the MgAl_2O_4 , $\text{Ni}_{0.2}\text{Mg}_{0.8}\text{Al}_2\text{O}_4$, and NiAl_2O_4 . The peaks around 43° can be assigned to MgO and $\alpha\text{-Al}_2\text{O}_3$ found as impurities. According to the X-ray powder diffraction data file, it is found that MgAl_2O_4 ¹⁰ and NiAl_2O_4 ¹¹ have a spinel structure. The peaks of $\text{Ni}_{0.2}\text{Mg}_{0.8}\text{Al}_2\text{O}_4$ were positioned between those of MgAl_2O_4 and NiAl_2O_4 . This indicates that $\text{Ni}_{0.2}\text{Mg}_{0.8}\text{Al}_2\text{O}_4$ also has a spinel structure. Table 2 represents the effect of partial pressure ratios in oxidative steam reforming of methane. In the case of $\text{Ni}_{0.2}\text{Mg}_{0.8}\text{Al}_2\text{O}_4$, methane conversion decreased remarkably with increasing steam pressure. This behavior indicates that Ni metal species was oxidized under high steam partial pressure at this W/F condition. Similar tendency has been observed in

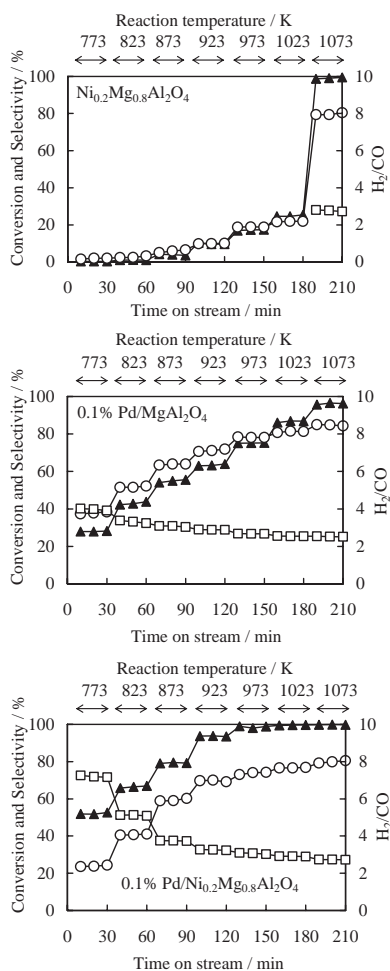


Figure 2. Results of CH₄ conversion, CO selectivity, and H₂/CO ratio in oxidative steam reforming of methane during the reaction temperature increasing over the catalysts without H₂ pretreatment. (▲) CH₄ conversion, (○) CO selectivity, (□) H₂/CO. Reaction conditions: catalyst weight = 30 mg, CH₄/H₂O/O₂ = 2/1.5/1, W/F = 0.43 g h mol⁻¹.

our previous report.⁶ On the other hand, in the case of Pd/MgAl₂O₄ and Pd/Ni_{0.2}Mg_{0.8}Al₂O₄, methane conversion was almost constant under both partial pressure conditions. Another important point is that Pd/Ni_{0.2}Mg_{0.8}Al₂O₄ exhibited much higher methane conversion than Ni_{0.2}Mg_{0.8}Al₂O₄ and Pd/MgAl₂O₄ under all the partial pressure conditions.

Figure 2 shows the results of self-activation test in oxidative steam reforming of methane. In this experiment, the reactant gas (CH₄/H₂O/O₂ = 2/1.5/1) was introduced to the catalyst bed without H₂ pretreatment, and the reaction temperature increased. In the case of Ni_{0.2}Mg_{0.8}Al₂O₄, methane conversion was very low in the temperature range between 773 and 1023 K. This indicates that Ni_{0.2}Mg_{0.8}Al₂O₄ catalyst cannot be activated with the reactant gases (CH₄ + H₂O + O₂) in this range, and higher temperature such as 1073 K is necessary for the activation. In contrast, in the case of Pd/MgAl₂O₄ at 773 K, methane conversion was beyond 25%, CO selectivity and H₂/CO ratio suggest that the reforming reaction can proceed even at this low temperature. In this profile, Pd/MgAl₂O₄ can be activated with the reactant gases at 773 K, and the methane conversion increased

Table 2. Effect of partial pressure ratios on methane conversion, CO selectivity, and H₂/CO ratio in oxidative steam reforming of methane^a

Catalysts	CH ₄ /H ₂ O/O ₂	CH ₄ conv. /%	CO sel. /%	H ₂ /CO
Ni _{0.2} Mg _{0.8} Al ₂ O ₄	2/1.5/1	93	87	2.4
	2/4/1	12	5	0
Pd/MgAl ₂ O ₄	2/1.5/1	72	93	1.8
	2/4/1	69	90	2.2
Pd/Ni _{0.2} Mg _{0.8} Al ₂ O ₄	2/1.5/1	94	87	2.6
	2/4/1	94	76	3.3
Equilibrium	2/1.5/1	>99	79	2.8
	2/4/1	>99	59	4.1

^aReaction conditions: catalyst weight = 30 mg, W/F = 0.13 g h mol⁻¹, reaction temperature = 1073 K, H₂ reduction pretreatment = 1123 K.

with increasing reaction temperature. Similar behavior was also observed on Pd/Ni_{0.2}Mg_{0.8}Al₂O₄ and, moreover, methane conversion was much higher than that of Pd/MgAl₂O₄ in all reaction temperature range. This behavior indicates that the Pd/Ni_{0.2}Mg_{0.8}Al₂O₄ can be activated by the CH₄ + H₂O + O₂ at 773 K and the reduction of Ni species in Ni_{0.2}Mg_{0.8}Al₂O₄ can be also promoted by the addition of Pd drastically. Equilibrium conversion and selectivity were almost the same as the obtained results on Pd/Ni_{0.2}Mg_{0.8}Al₂O₄ at each reaction temperature in Figure 2. In addition, this is also related to much higher activity of Pd/Ni_{0.2}Mg_{0.8}Al₂O₄ than those reported.⁶ High activity of Pd/Ni_{0.2}Mg_{0.8}Al₂O₄ can be related to higher reduction degree of Ni and larger amount of hydrogen adsorption than Ni_{0.2}Mg_{0.8}Al₂O₄ (Table 1). Furthermore, the previous results suggest that the alloying of Pd with Ni can influence the catalytic performance.^{12,13} In the present case, we have already confirmed the Pd–Ni alloy formation by EXAFS analysis.¹⁴

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