

Steam Reforming of CH₄ over Ni/Mg-Al Catalyst prepared by *spc*-Method from Hydrotalcite

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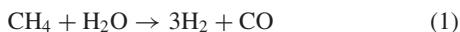
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The catalytic activity and stability for steam reforming of CH₄ was studied on Ni/Mg-Al prepared by the solid phase crystallization (*spc*-) method. *spc*-Ni/Mg-Al showed higher activity than those prepared by the conventional impregnation method such as Ni/MgO or Ni/Al₂O₃. This catalyst also showed high stability even under a low steam to carbon ratio. The high and stable activity of *spc*-Ni/Mg-Al is caused by the formation of highly dispersed and stable Ni metals.

The conversion of hydrocarbon to hydrogen will play an important role in 21st century, especially for providing hydrogen for fuel cell. Actually one of the most reliable processes for this purpose seems to be the steam reforming of CH₄ (eq (1)).¹



In the small units providing hydrogen for fuel cell in vehicles or domestic supplies, the reformer must be far smaller, cheaper and stronger than in the classic steam reforming. For this purpose, the catalysts must have far higher activity as well as stability compared to those for synthesis gas production for methanol or Fischer-Tropsch synthesis, and therefore a new concept of the catalysts preparation should be required. We have proposed the *spc*-method for preparing the highly dispersed and stable metal particle-supported catalysts, starting from the crystalline precursors containing active metal species in the structure.² In this report, we prepared *spc*-Ni/Mg-Al starting from Mg-Al hydrotalcite (HT) precursors and tested for the steam reforming of CH₄.

Catalysts were prepared by the *spc* method by using the Mg-Al HT ([Mg₃Al₁(OH)₈1/2CO₃²⁻]₂·2H₂O) anionic clays as the precursors. A part of Mg²⁺ was replaced by Ni²⁺ for preparing the precursor of the catalyst. The HT precursor was prepared by co-precipitation at pH = 10.0 and at room temperature by adding slowly an aqueous solution containing the nitrates of the metal components to an aqueous solution containing NaOH and Na₂CO₃, followed by aging for 12 h at 383 K. The precipitate was washed with distilled water, followed by drying at 383 K for 12 h to give an HT precursor. The catalysts were obtained by calcining the precursors at 1123 K in air, followed by reducing at 1073 K in 10 vol% H₂ in N₂ stream. The *imp*-Ni/Mg-Al, *imp*-Ni/MgO and *imp*-Ni/Al₂O₃ catalysts were prepared by the impregnation method (*imp*) and finally calcined at 1123 K in air for 5 h. α - and γ -Al₂O₃ (Kanto and JRC-ALO-4) and MgO "smoke" powder (JRC-MgO-4) were used as the support and impregnated in Ni nitrate aqueous solution. In the case of *imp*-Ni/Mg-Al, Mg-Al mixed oxide prepared from Mg-Al HT was used as the support. The catalytic test was carried out using a fixed-bed flow reactor of a quartz tube (8 mm i.d.). The catalyst (24–42 mesh) was diluted by 1.0 g of quartz sand and was put between two quartz wool plugs in the reactor. The products were analyzed by three on-line TCD

gas chromatographs with Porapak-Q and Molecular Sieve 5A columns. The catalysts were characterized by ICP (Perkin Elmer ICP OPTIMA3000), XRD (Rigaku RINT2550VHF), H₂ adsorption, and TEM (JEM3000F) analysis.

The XRD pattern of the Ni-containing precursor after drying at 393 K showed the diffraction lines of well-crystallized hydrotalcite phase (JCPDS 22-700) alone, suggesting that Ni²⁺ is incorporated in the Mg²⁺ site and dispersed uniformly in Brucite layer of hydrotalcite structure. After the calcination at 1123 K, XRD pattern showed the collapse of hydrotalcite structure and the strong diffraction lines of MgO (JCPDS 45-948) and NiO (JCPDS 47-1049), which overlapped each other, strongly suggesting the formation of Ni-Mg-O solid solution. Very weak diffraction lines due to spinel phase (MgAl₂O₄; JCPDS 33-853) were also observed, indicating that the spinel phase was segregated during the calcination. After the reduction at 1073 K, the weak lines of Ni metal were observed together with MgO, indicating that a part of Ni²⁺ was reduced to Ni metal and segregated from Ni-Mg-O cubic lattice during the reduction.

Figure 1 shows the CH₄ conversion obtained over both *spc*- and *imp*-catalysts in the steam reforming of CH₄ at the ratio of steam to carbon of 2.0 at 1073 K when the space velocity was increased. Activity was evaluated by CH₄ conversion (eq (2)).

$$\text{CH}_4 \text{ conversion (\%)} = (\text{CH}_4 \text{ in} - \text{CH}_4 \text{ out})/\text{CH}_4 \text{ in} \times 100 \quad (2)$$

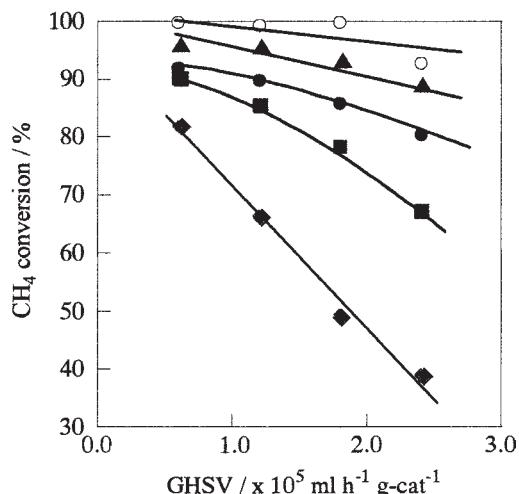


Figure 1. Effect of space velocity on steam reforming of CH₄. Reaction temp.: 1073 K, CH₄/H₂O/N₂ = 1/2/2, total pressure: 0.1 MPa, Ni loading: 6.3 wt%; (○) *spc*-Ni_{0.25}/Mg_{2.75}-Al, (▲) *imp*-6.3 wt%Ni/γ-Al₂O₃, (●) *imp*-6.3 wt%Ni/Mg-Al, (■) *imp*-6.3 wt%Ni/MgO and (◆) *imp*-6.3 wt%Ni/α-Al₂O₃.

The carbon balance was in the range of 95–100%. The equilibrium conversion of CH_4 under this reaction condition was above 99%. The Ni content in *spc*-Ni_{0.25}/Mg_{2.75}-Al was equal to that in *imp*-6.3 wt% Ni-supported catalysts. Evidently, *spc*-Ni/Mg-Al showed the highest activity among the catalyst tested, including *imp*-Ni catalysts loaded on various supports, at the space velocity of $6.0 \times 10^4 \text{ ml h}^{-1} \text{ g-cat}^{-1}$ ($\text{CH}_4/\text{H}_2\text{O}/\text{N}_2 = 1/2/2$). In the case of *spc*-Ni_{0.25}/Mg_{2.75}-Al, CO selectivity and H_2/CO ratio were 51.3% and 7.9, respectively. As the space velocity increased, CH_4 conversion significantly decreased on the *imp*-6.3 wt%Ni/MgO and *imp*-6.3 wt%Ni/ α -Al₂O₃. In the cases of *imp*-6.3 wt%Ni/Mg-Al and *imp*-6.3 wt%Ni/ γ -Al₂O₃, CH_4 conversion gradually decreased with increasing the space velocity. *spc*-Ni/Mg-Al showed the highest activity even at high space velocity of $2.4 \times 10^5 \text{ ml h}^{-1} \text{ g-cat}^{-1}$ ($\text{CH}_4/\text{H}_2\text{O}/\text{N}_2 = 1/2/2$). The formation rate of hydrogen over *spc*-Ni/Mg-Al was quite high (ca. $1.8 \times 10^5 \text{ ml h}^{-1} \text{ g-cat}^{-1}$) under this reaction condition. This result clearly suggests that the *spc*-Ni/Mg-Al is preferable for the on site providing of a large amount of hydrogen to the fuel cell. When γ -Al₂O₃ (JRC-ALO-4) was used as the support, spinel structure NiAl₂O₄ formed on the catalyst surface, probably resulting in the high dispersion of Ni. Nonetheless such preferable effect expected on *imp*-6.3 wt%Ni/ γ -Al₂O₃, its activity was still lower than *spc*-Ni_{0.25}/Mg_{2.75}-Al.

Figure 2 shows the activity changes with time on stream at the low steam to carbon ratio of 1.0 and at the space velocity of $2.4 \times 10^5 \text{ ml h}^{-1} \text{ g-cat}^{-1}$. The low ratio of steam to carbon caused a lowering of equilibrium CH_4 conversion to around 92% at 1073 K. *imp*-12.6 wt%Ni/ α -Al₂O₃ showed a drastic decline in the activity during 50 h of the reaction. The activities of both *imp*-12.6 wt%Ni/MgO and *imp*-12.6 wt%Ni/Mg-Al were also lower than that of *spc*-Ni_{0.5}/Mg_{2.5}-Al and decreased gradually during the time course. The best one among the *imp*-catalysts was *imp*-12.6 wt%Ni/ γ -Al₂O₃, but its activity still decreased along the time for 50 h even though the activity was enough high at the

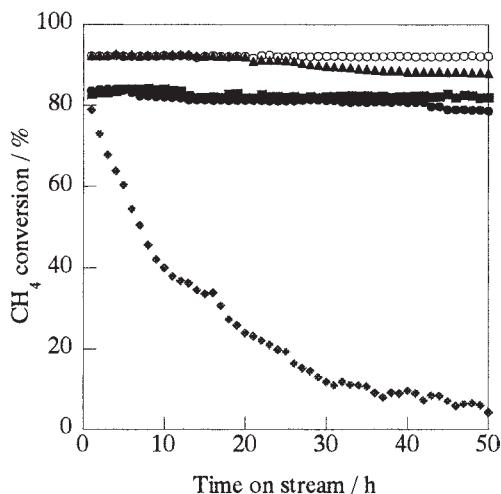


Figure 2. Stability of Ni-supported catalysts at 1073 K, $\text{CH}_4/\text{H}_2\text{O}/\text{N}_2 = 1/1/2$, GHSV = $2.4 \times 10^5 \text{ ml h}^{-1} \text{ g-cat}^{-1}$, total pressure: 0.1 MPa, Ni loading: 12.6 wt%; (○) *spc*-Ni_{0.5}/Mg_{2.5}-Al, (▲) *imp*-12.6 wt%Ni/ γ -Al₂O₃, (●) *imp*-12.6 wt%Ni/Mg-Al, (■) *imp*-12.6 wt%Ni/MgO and (◆) *imp*-12.6 wt%Ni/ α -Al₂O₃.

Table 1. Amount of H_2 adsorption over Ni supported catalysts

Catalysts	Amount of adsorbed $\text{H}_2^a/\mu\text{mol g}^{-1}$	Dispersion /%
<i>spc</i> -Ni _{0.5} /Mg _{2.5} -Al	136.4	12.7
<i>spc</i> -Ni _{0.25} /Mg _{2.75} -Al	38.4	7.2
<i>imp</i> -12.6 wt%Ni/Mg-Al	72.5	6.8
<i>imp</i> -6.3 wt%Ni/Mg-Al	17.5	3.3
<i>imp</i> -12.6 wt%Ni/MgO	30.4	2.8
<i>imp</i> -6.3 wt%Ni/MgO	7.1	1.3
<i>imp</i> -12.6 wt%Ni/ γ -Al ₂ O ₃	103.0	9.6
<i>imp</i> -6.3 wt%Ni/ γ -Al ₂ O ₃	36.2	6.8
<i>imp</i> -6.3 wt%Ni/ α -Al ₂ O ₃	15.7	2.9

^aReduced at 1073 K.

beginning of the reaction. It is thus demonstrated that *spc*-Ni/Mg-Al was enough sustainable in the steam reforming of CH_4 compared to the *imp*-catalysts even under a low $\text{H}_2\text{O}/\text{CH}_4$ molar ratio.

The activity of *spc*-Ni/Mg-Al was higher than *imp*-Ni/Mg-Al at the same Ni loading, strongly suggesting that the dispersion of Ni metal is important for the catalytic activity. Table 1 shows the amount of H_2 adsorbed on Ni metal on the catalysts measured by the H_2 pulse method. The amount of H_2 adsorbed increased in the order of *imp*-Ni/ α -Al₂O₃ < *imp*-Ni/MgO < *imp*-Ni/Mg-Al < *imp*-Ni/ γ -Al₂O₃ < *spc*-Ni/Mg-Al, and inevitably the dispersion of Ni metal on the catalyst was calculated in the same order. This order well agrees with the order of catalytic activity. TEM observation also showed that *spc*-Ni/Mg-Al afforded rather sharp distribution of small size of Ni metal, while *imp*-Ni/Mg-Al showed a broad distribution of relatively large size of Ni metal. These results strongly suggest that the high activity due to the highly dispersed Ni metal species. In the *spc*-preparation starting from hydrotalcite as the precursors, Ni^{2+} replaces well the Mg^{2+} sites in the hydrotalcite precursor, followed by the formation of Ni-Mg-O solid solution after the calcination. Parmaliana et al.³ reported that NiO-MgO system forms solid solutions over the whole molecular fraction range and was successfully used as the catalyst for the steam reforming of CH_4 . Fujimoto and co-workers reported that a Ni-Mg-O solid solution was reduced at high temperature (>1073 K) to form an active and stable catalyst for steam or CO_2 reforming of CH_4 .⁴ It is likely that the formation of a Ni-Mg-O solid solution is a key step for bestowing the high activity on the Ni/MgO. The formation of a Ni-Mg-O solid solution is also reason for the formation of stable and highly dispersed Ni metal particles on the *spc*-catalyst after the reduction. We conclude that the high and stable activity observed on *spc*-Ni/Mg-Al is due to the stable and highly dispersed Ni metal particles.

References and Notes

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