

## 수소 스테이션 적용을 위한 LPG 수증기 개질 촉매

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### Steam Reforming Catalyst of LPG for Hydrogen Station Applications

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#### **Introduction**

Fuel cell technology, the most effective method using hydrogen, has recognized and has expected as the key opening the hydrogen economy society. Also, hydrogen infrastructure is essential for commercializing fuel cell and fuel cell powered vehicles. Hydrogen can be extracted by reforming various available hydrocarbons, such as methanol, natural gas, gasoline, and diesel. Reforming has been intensively developed for both on board vehicles, and off board (stationary, residential) applications [1,2]. The major process technologies for reforming hydrocarbons and alcohols into hydrogen and carbon monoxide are catalytic steam reforming (SR), partial oxidation (POX) and partial oxidation reforming(autothermal reforming, ATR) [3].

Steam reforming producing higher H<sub>2</sub> concentration of 70~80% in the crude reformat gas is a desirable process for hydrogen station. It was known that nickel has been the most suitable metal for SR of hydrocarbons. The SR catalysts are mainly nickel supported on refractory alumina and ceramic magnesium aluminate. These supports provide high mechanical strength and stability. However, coke formations [4] and sulfur poisoning [5] are two major problems associated with nickel catalyst. Coking is an even more serious problem when heavy hydrocarbon fuels such as gasoline and diesel were reformed. Recently, it was known that MgO supported catalyst is more effective to prevent the carbon deposition than conventional catalyst for steam reforming of hydrocarbons.

In this work, SR of LPG was carried out to evaluate the feasibility of using various oxide catalyst for hydrogen station and fuel processor applications. Especially, the effect of support on the catalytic performance and stability was investigated.

## Experimental

The supported nickel catalysts (12wt% Ni/S, S=Al<sub>2</sub>O<sub>3</sub>, MgO and CeO<sub>2</sub>) were prepared by impregnation method. Commercial  $\gamma$ -alumina (S.A. = 155m<sup>2</sup>/g, Aldrich Chemical Co.), MgO (~30 mesh, Aldrich Chemical Co.), CeO<sub>2</sub> (<5 micron, Aldrich Chemical Co.) were used in the preparation of Ni-based catalysts [6]. The prepared catalyst was characterized by N<sub>2</sub> physisorption (Quantachrome, Autosorb-1C), CO chemisorption (Micrometrics, Autochem II), XRD (Shimadzu Co., XRD-6000), TEM (CM30, Philips, US), TPR and XPS (CRATOS Analytical XSAM 800cpi, ESCA).

The catalytic performance for steam reforming of LPG was measured in a fixed bed reactor system. The preheater and LPG steam reforming reactor were made of an Inconel 600 tube (0.095 m I.D. and 0.20 m length), respectively. The unreacted H<sub>2</sub>O was removed by an ice trap and then gas effluent was analyzed by GC (HP 5890 Series II, TCD). All runs were conducted at the temperature range of 600 ~ 850°C, space velocity of 5000 ~ 25,000 h<sup>-1</sup> and feed molar ratio of H<sub>2</sub>O/C = 1.5 ~ 2.0 and atmospheric pressure.

## Results and Discussion

The characteristics of the Ni-based catalysts prepared in this work are shown in Table 1. It was found that BET surface area of Ni/Al<sub>2</sub>O<sub>3</sub> catalyst was higher than these of the other catalysts.

Table 1. Characteristics of the catalysts prepared in this work

	BET(g/m <sup>2</sup> )	Pore volume(cc/g)	Pore Size Distribution (Å)
Ni/Al <sub>2</sub> O <sub>3</sub>	91.3	0.211	92.4
Ni/CeO <sub>2</sub>	6.8	0.050	297.9
Ni/MgO <sup>a</sup>	16.3	0.251	617.1
Ni/MgO <sup>b</sup>	39.0	0.537	551.3
Ni/MgO <sup>a*</sup>	93.9	0.480	204.6
Ni/MgO <sup>a*</sup>	47.3	0.229	194.5

a : Aldrich Chemical reagent, b : Pure Chemical reagent, \* : After reaction

The effect of temperature on the product distribution in the steam reforming of LPG over Ni/Al<sub>2</sub>O<sub>3</sub> and Ni/MgO catalysts was represented in Figure 1. It was found that the H<sub>2</sub> concentration over Ni/MgO catalyst did not changed under the tested conditions, but that over Ni/Al<sub>2</sub>O<sub>3</sub> slowly decreased at less than 700°C. It was also found that methane over Ni/MgO catalyst was produced at less than 650°C, but that over Ni/Al<sub>2</sub>O<sub>3</sub> was formed under 750°C.

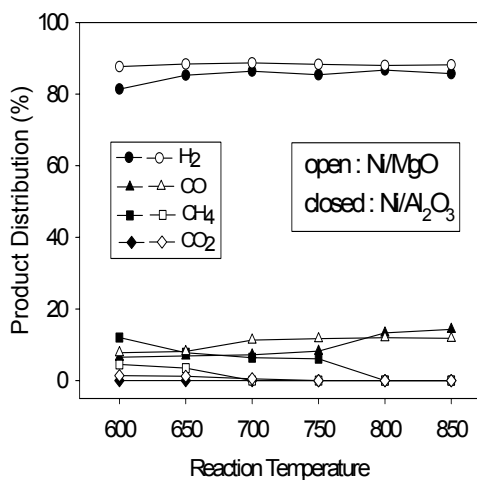


Figure 1. The effect of temperature on the product distribution for SR of LPG over Ni/MgO and Ni/Al<sub>2</sub>O<sub>3</sub> catalysts (SV = 5000 h<sup>-1</sup>, the ratio of S/C = 2.0).

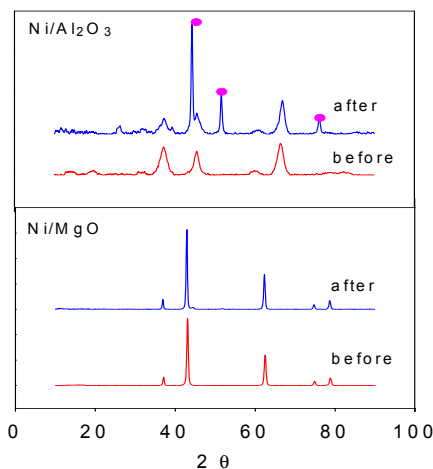


Figure 2. The XRD patterns of Ni-based catalysts before and after the reaction. The used catalysts were recovered after the reaction for 12 h (● : NiC).

X-ray diffraction patterns of the Ni-based catalysts before and after the reaction were presented in Figure 2. It could not be observed any major changes in the phase patterns of Ni/MgO catalyst but nickel carbide (NiC) peak on the surface of Ni/Al<sub>2</sub>O<sub>3</sub> catalyst after SR reaction was confirmed. It was concluded that Ni/MgO catalyst is a promising candidate for the production of hydrogen by the steam reforming of LPG.

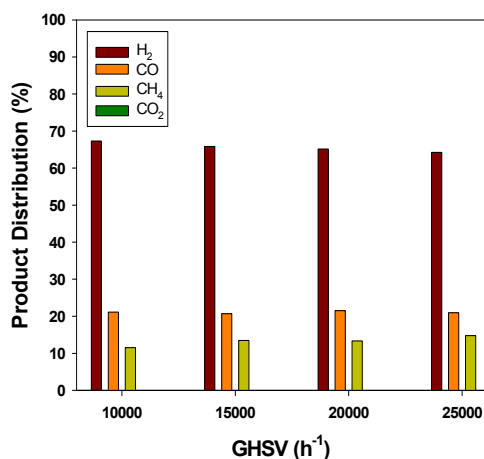


Figure 3. The effect of GHSV on the product distribution for SR of LPG over Ni/MgO catalyst (SV = 10000 ~ 25000h<sup>-1</sup>, the ratio of S/C = 1.5, reaction temperature = 800°C).

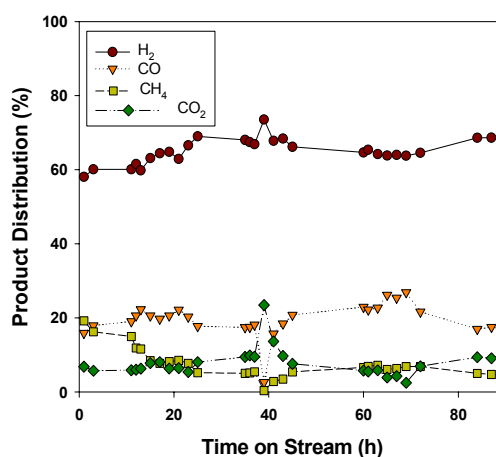


Figure 4. The product distribution in SR of LPG over Ni/MgO catalyst for 90h (Space velocity = 20000 h<sup>-1</sup>, the ratio of S/C = 2.0, reaction temperature = 850°C).

The effect of various space velocities on the product distribution in the steam reforming of LPG over Ni/MgO catalyst was shown in Figure 3. It was found that the H<sub>2</sub> and CO concentrations over Ni/MgO catalyst did not change with the increasing GHSV from 10,000 to 25,000 h<sup>-1</sup>.

The steam reforming of LPG over Ni/MgO<sup>b</sup> catalyst was carried out for 90 h, and the results were presented in Figure 4. The H<sub>2</sub> and CO concentrations did not change for 90 h. This stability of Ni/MgO catalyst is probably due to the reduction of Ni strongly held in Ni-MgO solid solutions. The unreacted CH<sub>4</sub> of LPG SR over Ni/MgO catalyst in the S/C = 2.0 showed lower than that in S/C = 1.5.

### Conclusions

It was identified that there was no major change in the X-ray diffraction patterns of Ni/MgO catalyst, however nickel carbide (NiC) peak was existed on the surface of Ni/Al<sub>2</sub>O<sub>3</sub> catalyst after SR reaction. With increasing GHSV, the H<sub>2</sub> and CO concentrations over Ni/MgO<sup>b</sup> catalyst hardly changed. Also the H<sub>2</sub> and CO concentrations over Ni/MgO<sup>b</sup> catalyst did not change for 90 h. It was suggested that Ni/MgO catalyst is a promising candidate for the production of hydrogen by the steam reforming of LPG.

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