DEVELOPMENT OF PRECIOUS METAL MODIFIED *spc*-Ni/MgAl CATALYST FOR HYDROGEN STATION APPLICATION

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Introduction

Fuel cell (FC) technology has been recognized as the most effective method using hydrogen to produce energy and expected as the key opening sustainable hydrogen economy society. Hydrogen as the fuel for the fuel cell can be prepared by the reforming of hydrocarbons such as methane, methanol, ethanol, liquefied petroleum gas (LPG), gasoline, diesel and other oil derivatives [1, 2]. Among the above hydrocarbon fuels, LPG is a commercial gas that is easily transported and stored on-site. This gas was proposed to be an attractive fuel for residential power generation (RPG) systems in remote areas where pipeline natural gas is not available. LPG, a mixture of propane and butane, can also be used for auxiliary power units (APU) based on solid oxide fuel cell (SOFC) systems [3].

The steam reforming (SR) process, which produces high H_2 concentration of 70~80% in the crude reformate gas, has widely been used to produce hydrogen from LPG. The steam reforming catalysts are made of mainly nickel which is supported on the alumina and 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 a heavy hydrocarbon and a gas mixture such as gasoline, diesel and LPG were reformed. For solving these problems, steam reforming of LPG has been studied by a few researchers [3, 6~11]. Recupero et al. [11] reported that Pt/CeO_2 provides high reforming activity with low carbon formation. Suzuki et al. [6] found that $Ru/CeO_2\text{-}Al_2O_3$ can reform LPG with a low inlet steam requirement at 450 ^oC. Autothermal reforming process was reported to provide great benefits in terms of catalyst stability and low coke formation [7, 8]. However, the yield of hydrogen production could be reduced due to the oxidation of hydrogen by oxygen. Although the noble metals such as Pt, Rh and Ru have been reported by several researchers to provide high reactivity for the reforming reactions and excellent resistant to coke formation [12 ~ 14]. However, these catalysts did not completely solve the problems of coke formation and sintering of active metal.

The anionic clays based hydrotalcite-like compounds have been researched as the catalyst for various reactions such as hydrogenation, polymerization and reforming, or the antiacid, antipeptin and stabilizer in the medicinal chemistry. The hydrotalcites or hydrotalcite-like compounds after calcinations have the properties; high surface area, basic properties, formation of homogeneous mixtures of oxides with very small crystal size, “Memory effect”, which allows the reconstruction of the original hydrotalcite structure when contacting the product of the thermal treatment with water solutions containing various anions under mild conditions [15]. K. Takehira et. al reported that the Ni-loaded catalyst prepared from Mg-Al hydrotalcite-like anionic clay has shown high and stable activity for CO_2 reforming, steam reforming and autothermal reforming (ATR) of CH_4 [16 ~ 18]. The reforming of LPG over catalyst of Ni-loaded hydrotalcite-like has not been reported yet.

In this work, steam reforming of LPG, a gas mixture of propane (C_3H_8) and butane (C_4H_{10}) with molar ratio of 30 : 70, was executed in a fixed bed reactor to evaluate the performance of noble metal modified Ni-based catalysts for solving of coke formation and sintering of active metal.

Experimental

1. Preparation of catalyst

Nickel nitrate [$Ni(NO_3)_2 \cdot 6H_2O$], Aluminum nitrate [$Al(NO_3)_3 \cdot 9H_2O$], Magnesium nitrate [$Mg(NO_3)_2 \cdot 6H_2O$],□Al_2O_3 and MgO with the purity of about 98 ~ 99% (Aldrich and High Pure Chemical Co.) were used without additional purification. The distilled and deionized water was used throughout whole the experiment. The propane and butane used in this work were supplied from Duck Yang Gas Co. (Seoul, Korea) with purity of 99.5%. The Ni/MgO and Ni/Al_2O_3 were prepared by a conventional incipient wetness method. The Ni/MgAl oxide catalysts using modified hydrotalcite were prepared by a co-precipitation method. An aqueous solution of the nitrates of Al(III) was added slowly with vigorous stirring into an aqueous solution of sodium carbonate. After disappearing the white power, an aqueous solution of the nitrates of Mg(II) and Ni(II) was orderly added. The atomic ratio of Ni/Mg was fixed at 1.0/2.5. Upon adjusting the pH of this solution to 10 with an aqueous solution of sodium hydroxide, fine greenish slurry precipitated. The crystal growth took place by aging the solution at 60^{o}C for 8 h. After the solution was cooled to room temperature, the precipitate was filtered and washed with distilled water until the hydroxide ion vanished, and then dried in air at 80^{o}C for 2h. The obtained Mg(Ni)-Al hydrotalcite-like precursors were calcined in a furnace in an air atmosphere by increasing the temperature from ambient temperature to 850^{o}C at a rate of 5 ^{o}C/min followed by keeping at 850 ^{o}C for 5 h to form the precursor of solid phase crystallization (spc)-Ni/MgAl.

2. Characterization of catalyst

Specific surface area of the prepared catalyst was determined by physisorption analyzer [Quantachrome Co., Autosorb-1C]. The active metal surface area was measured by chemisorption of CO with a sorption analyzer [Micromeritics Co., Autochem II]. Temperature programmed reduction (TPR) of catalyst was performed at a heating rate of 10□/min using a 5 vol% H_2/Ar as a reducing gas in the sorption analyzer. The X-ray Diffraction patterns of powdered samples were acquired at an ambient temperature under air using the XRD [Shimazdu Co., XRD-6000] with a Cu-Kα irradiation source (λ = 1.54056 Å) at voltage of 40kV and current of 30 mA.

3. Steam reforming of LPG

The steam reforming of LPG was performed in a fixed bed reactor system [19]. The preheater (0.008 m O.D. and 0.15 m length) and steam reforming reactor (0.014 mm O.D. and 0.25 m length) were made of an Inconel 600 tube, respectively. Before the reactions, the Ni-based catalysts were reduced at 750 ^{o}C for 3 h in the hydrogen atmosphere. The unreacted H_2O was removed by a cold trap and then a gas effluent was analyzed by an on-line gas chromatograph (HP 6890 Series II, TCD) with carbosphere column and GC/MS (HP 5890 Series/MS detector) with HP-FFAP capillary column. All runs were carried out at a temperature range of 600 ~ 850 ℃, a space velocity of 10,000 ~ 30,000 h^{-1}, atmospheric pressure, and feed molar ratio of H_2O/C ranging 1.0 ~ 3.0.

Results and Discussion

The nomenclature and the characteristics of the catalysts used in this work are shown in Table 1. BET surface area of spc-Ni/MgAl catalysts using modified hydrotalcite was higher than those of the other catalysts.

Table 1. Characteristics of the prepared and commercial ICI catalysts used in this work

Catalyst	Noble metal loading[a] (wt%)	Ni loading[a] (wt %)	BET[b] (m^2/g)	Active Metal Surface Area[c] (m^2/g)
Ni/Al_2O_3	-	12.96	91.3	7.46 (Ni)
Ni/MgO	-	11.96	39.0	3.62 (Ni)
spc-Ni/MgAl	-	20.0	197.7	6.68 (Ni)
Rh-Ni/MgAl	0.31	19.7	105.4	2.39 (Rh)
Ru-Ni/MgAl	0.30	19.8	106.2	2.45 (Ru)
ICI	-	21.97	13.8	-

a : measured by ICP/AES, b : measured by Quntachrome Co., c : measured by Micromeritics Co.

The TPR profiles of pure NiO and prepared catalysts were showed in Fig. 1. In TPR measurements of Rh-Ni/MgAl, spc-Ni/MgAl, Ni/MgO and Ni/Al_2O_3 catalysts, peak of H_2 consumption due to Ni reduction was observed depending on the nature of Ni species on each catalyst. The pure NiO (a) as a reference showed this peak at 452 ℃. Ni/Al_2O_3 (d) showed a peak at 867 ℃, while spc-Ni/MgAl catalyst (c) displayed a peak at 806 ℃. Ni/MgO (e) showed no peak of Ni reduction, due to too strong interaction between Ni and MgO by forming stable Mg–Ni–O solid solutions. Rh-Ni/MgAl (b) catalyst displayed two peaks due to the reduction of Rh metal at 230℃ and 425℃. These results reveal that reduction and oxidation of Rh metal is easier than that of Ni metal. This concludes that Rh metal react with the oxygen source easier than Ni metal due to low reduction temperature and finally suppresses the sintering of Ni metal during the SR of LPG.

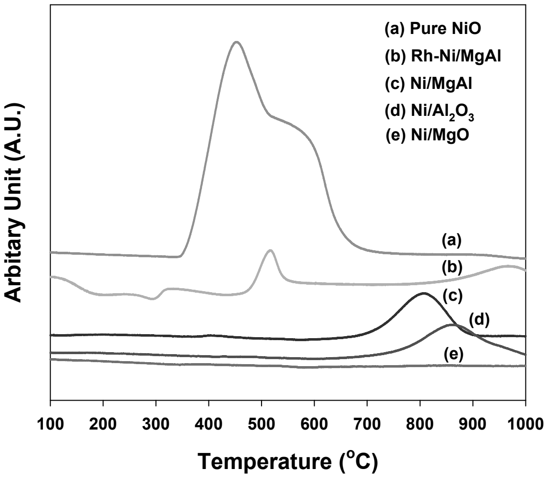

Fig. 1. The TPR profiles of prepared Ni-based catalysts (Heating rate : 5 ℃/min, Reducing gas : 5 vol% H_2/Ar balance).

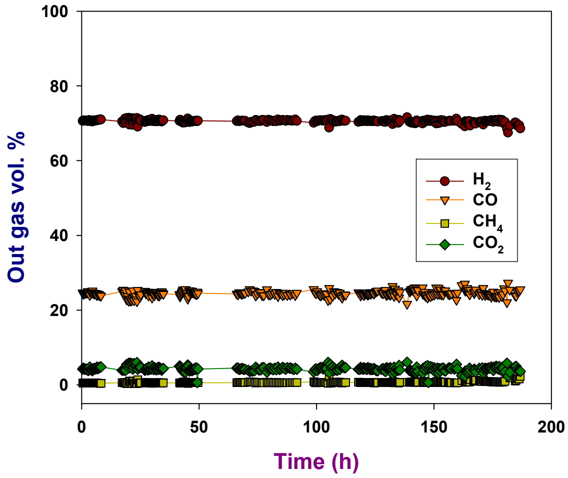

Fig. 2. Out gas distribution for SR of LPG over spc-Ni/MgAl catalyst for 186h (S/C = 2.0, GHSV = 20,000 h^{-1}, temp. = 800°C).

Fig.2 shows the product distribution in the steam reforming of LPG over spc-Ni/MgAl catalyst. The steam reforming of LPG was carried out at a temperature of 800 ℃, feed molar ratio of $H_2O/C = 2$ and GHSV of 20,000 h^{-1}. No C_{2+} components such as C_2H_4, C_2H_6, and C_3H_6 were detected in the product stream. However, a small amount of CH_4 was produced by the decomposition of feed gas or methanation of carbon. The concentration of products during the SR of LPG on spc-Ni/MgAl catalyst was maintained for 186 h under our operational conditions. However, that on ICI CH_4 SR catalyst was fluctuated for same reaction time [20, 21].

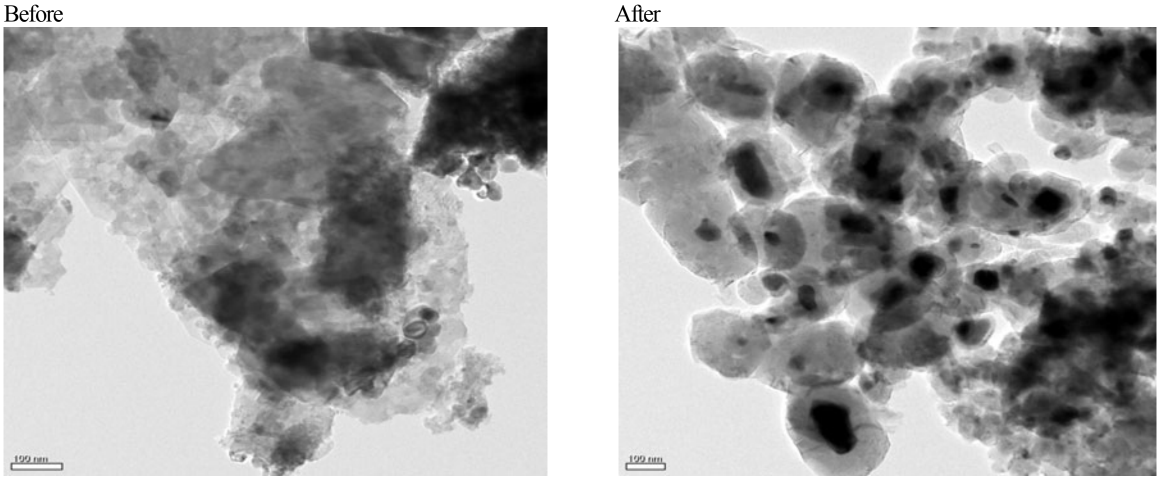

Fig. 3. TEM image of spc-Ni/MgAl catalyst before and after (186h) SR of LPG run at 800℃

Fig.3 presents the TEM images of spc-Ni/MgAl catalysts before and after the reaction. Ni particles of spc-Ni/MgAl increased in average size from 25 nm to 65 nm after SR of LPG at 800℃ for 186h due to sintering of Ni. The same result was also obtained for ICI catalyst [20, 21]. The XRD patterns of the catalysts before and after the reaction were investigated. No major changes were observed in the XRD phase pattern of spc-Ni/MgAl catalyst [20, 21].

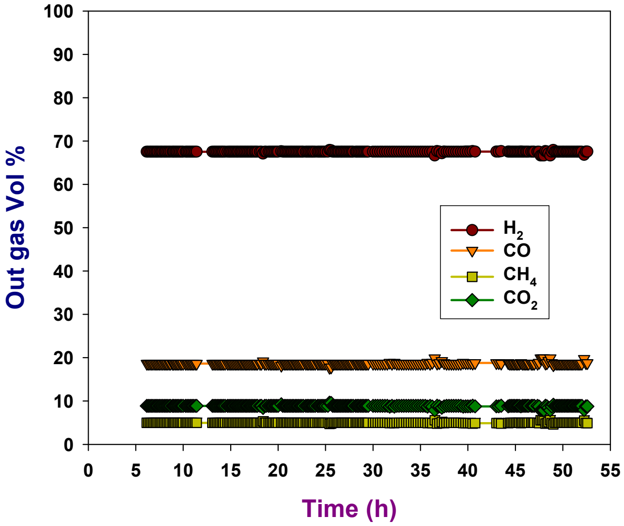

Fig. 4. Out gas distribution for SR of LPG over 0.3wt Rh-Ni/MgAl catalyst for 53h (S/C = 1.0, GHSV = 20,000 h^{-1}, temp. = 700°C).

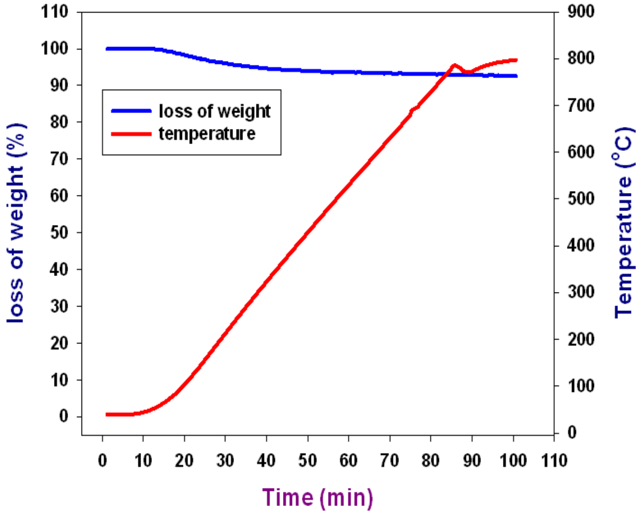

Fig. 5. The results of TGA for LPG SR reaction over 0.3wt% Rh-Ni/MgAl after the reaction 53h (S/C = 1.0, GHSV = 20,000 h^{-1}, temp. = 700°C).

However, as seen by FT-SEM, surface of the both catalysts was found to be coated with filamentous carbon after the reaction (not shown). For improving restraint capacity for carbon formation of the Ni/MgAl catalyst, noble metal modified spc-Ni/MgAl catalysts were prepared [22]. Their performance was tested for LPG SR at 700℃, feed molar ratio of $H_2O/C = 1.0$, and GHSV = 20,000h^{-1} for 53h.

Fig.4 depicts the results of LPG SR over 0.3wt% Rh-Ni/MgAl catalyst. It was found that 0.3wt% Rh-Ni/MgAl catalyst displayed higher stability than 0.3wt% Ru-Ni/MgAl catalyst (not shown) since the Rh metal exhibits faster oxidation and reduction mechanism than ruthenium and nickel, which in turn, inhibits the sintering on nickel during the reforming reaction. It was confirmed from thermal analysis that Rh metal improved the inhibition power of carbon formation in a reforming of hydrocarbon compared with Ru metal [24 ~ 25] as shown Fig. 5. It was also found that Rh-Ni/MgAl catalyst showed long term stability for 1024h in the SR of LPG under the tested conditions [22].

Conclusions

The spc-Ni/MgAl catalyst showed higher catalytic stability than ICI CH_4 SR catalyst under the tested conditions even though small amount of carbon was deposited on the surface of catalyst. However, 0.3wt% Rh-Ni/MgAl catalyst showed higher catalytic stability and durability for carbon formation under severe reaction conditions than the other catalysts. The results suggest that Rh modified Ni/MgAl catalyst can be applied in hydrogen station and fuel processor as LPG steam reforming catalyst.

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