$Pt-Ni/CeO_2$ 촉매 상에서 WGS 반응 및 특성 분석

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Catalytic properties of $Pt-Ni/CeO_2$ catalyst for WGS reaction

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Introduction

The successful development of a fuel cell powered vehicle is dependent on the development of a fuel processor [1-3]. It was reported that WGS reactors, charged with currently available commercial catalysts (Fe_3O_4-Cr_2O_3 and Cu-Zn/Al_2O_3), constitute about a third of the mess, volume and cost of the fuel processor system [4-6]. The WGS reaction is one of the key catalytic stages in a fuel processor. Since the reaction is an exothermic, the equilibrium conversion of CO is highest at low temperatures. Consequently a two-stage process in often used [5-8]. In industrial reactors, Fe_3O_4-Cr_2O_3 catalyst was used for a high temperature shift (HTS) and Cu-Zn/Al_2O_3 catalyst was used for a low temperature shift (LTS) reaction. Existing commercial Cu-Zn/Al_2O_3 (LTS) catalyst, though highly active, was unsuitable for transportation applications because of their large size and weight, and the deactivation tendency of the copper-based catalysts under the severe conditions encountered in an automotive system. The Cu-Zn/Al_2O_3 catalyst also can not be used at temperatures above about 250℃, which further limits their utility. Therefore, the development of high performance WGS with thermal stability is very important.

In this works, we have studied the WGS reaction over Pt-Ni/CeO_2 catalyst. The catalytic properties of the prepared catalyst were compared with that over the commercial Cu-Zn/Al_2O_3 catalyst.

Experimental

The various metal supported cerium oxide catalysts were prepared by an impregnation method using raw materials such as cerium oxide (CeO_2, 99.9%, Sigma-Aldrich Chemicals), nickel nitrate ($Ni(NO_3)_36H_2O$, 99.9%, Sigma-Aldrich Chemicals) and chloroplatinic acid ($H_2PtCl_6 \cdot xH_2O$, 99%, High Purity Chemicals). The cerium oxide was used after calcining at 900℃ for 2-4 h in air. The catalyst was prepared by the impregnation of a solution of nickel nitrate and / or chloroplatinic acid on cerium oxide at room temperature, dried at 120℃ for 24 h, and then calcined at 550℃ for 2 h.

The used catalyst was characterized by N_2 physisorption, CO chemisorption [Quantachrome Co. Autosorb-1C], XRD [Shimazdu Co., XRD-6000] and temperature programmed reduction [TPR, Micromeritics Autochem Ⅱ].

The WGS reactor is consists of four sections: feed supply, preheater, WGS reactor and GC analysis sections. The gases were delivered by mass flow controllers, and H_2O was fed by a liquid delivery pump [Young Lin Co., model M930]. The LTS reactor made up of Inconel 600 tube (0.075 m I.D. and 0.20 m length) was used in this study. The reaction temperature was controlled by a PID temperature controller and was monitored by a separated thermocouple placed in the catalyst bed. This arrangement was capable of ensured an accuracy of 1℃ of the catalyst bed temperature. Unreacted H_2O was removed by an ice trap and then gas effluent was analyzed by an on-line gas chromatograph (Hewlett Packard Co., HP-6890 SeriesⅡ) equipped with a TCD and using a carbosphere column (0.0032 m O.D. and 3.048 m length, 80/100 meshes). The catalytic activity for WGS reaction was measured at the temperatures range of 200 to 300℃ and atmospheric pressure in the fixed bed reaction system. The $Cu-Zn/Al_2O_3$ catalyst was reduced at 200℃ in a mixture of 2% H_2 in N_2 balance for 4.5 h. The Pt-Ni/ceria catalysts were first reduced in 40 cc/min of 5% H_2 in Ar balance at 400℃ for 1 h, and then oxidized in 50 cc/min of 2% O_2 in Ar balance at 500℃ for 20 min. Before the reaction the Pt-Ni/ceria catalysts were reduced under flowing 40 cc/min of 5% H_2 in Ar balance at 200℃ for 30 min.

Results and Discussion

The WGS reaction is a critical step during fuel processing since CO severely and irreversibly poisons the PEM electrocatalyst. In our previous works [1-8], author reported that the commercial LTS catalyst deactivated by hydrothermal sintering during the thermal cycling test, and identified that the commercial LTS catalyst cannot be used at temperatures above about 250℃. It is considered that the development of the high performance alternate LTS catalyst with the high stability for thermal cycling is required for the commercialization of fuel cell powered vehicles.

The characteristics of the used catalysts are summarized in Table 1. It was found that the Pt-Ni/ceria catalyst displayed high surface area over the other catalysts.

Table 1. Characteristics of the prepared catalysts

Catalyst	BET surface area (m^2/g)	Total pore volume (cc/g)	Active metal surface area (m^2/g)
$Cu-Zn/Al_2O_3$	60	0.081	1.035×10^{-1}
Mo_2C (640℃)	61	0.036	1.285×10^{-1}
0.2wt.%Pt-40wt.%Ni/ceria	78	0.049	0.863×10^{-1}

TPR curves for NiO, CeO_2 and Pt-Ni/CeO_2 are presented in Fig.1. TPR profiles of the samples were obtained by heating the samples from room temperature to 1,100℃ at rate of 10℃/min, in a 5% H_2/Ar gas flow (50ml/min). It was identified that pure NiO shows a reduction peak at about 380℃ and at 580℃, and pure CeO shows a weak reduction peak at 810℃. It was found that three reduction peaks are registered in the spectra of Pt-Ni/CeO_2 catalysts. The low-temperature peaks at about 390℃ and 550℃ are assigned to the reduction of surface oxygen species, these reduction peaks is caused by NiO phase. The high temperature peak at about 800℃ corresponds to the reduction of bulk oxygen and the formation of lower oxides of cerium.

Figure 2 shows the effect of reaction temperature on the conversion of CO over the prepared and the commercial LTS catalysts. The WGS reaction of a feed containing 62.5% H_2, 31.8% H_2O and 5.7% CO was carried out at the reaction temperature of 200 to 300℃ and space velocity of 10,000 h^{-1}. It was found that cerium oxide supported catalysts showed higher activity than the Cu-Zn/Al_2O_3 at temperature range of above 260℃ and maximum activity was observed at 280~300℃ with CO conversion of more than 85%. However the activity of Cu-Zn/Al_2O_3 catalyst increased with increasing the reaction temperature up to 260℃, displayed the highest activity at 260℃ with CO conversion of 70%, and then decreased at high temperature over 260℃.

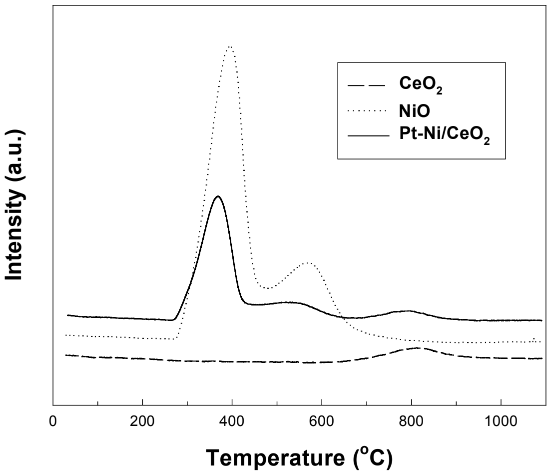

Figure 1. TPR profiles for NiO, CeO and Pt-Ni/CeO_2 samples.

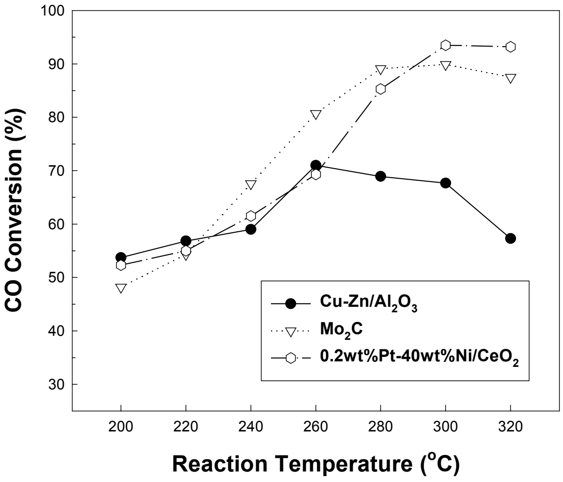

Figure 2. Catalytic activity of the catalysts for LTS reaction.

The thermal cycling runs were performed at the reaction temperature of 250℃ over a time period of 130 h. To change the reduction and the oxidation conditions of catalysts, the switch of electric furnace for heating WGS reactor was repeatedly operated on/off with some intervals. Figure 3 shows the result of thermal cycling runs for WGS reaction over the Cu-Zn/Al_2O_3 and the Pt-based catalysts. Even though both catalysts deactivated during the thermal cycling test, it was found that the Pt-based catalysts showed higher stability than the commercial Cu-Zn/Al_2O_3. It was found that the conversion of CO over 0.2 wt% Pt-Ni/CeO_2 catalyst after the thermal cycling reaction for 130 h decreased 3.5%, whereas that over the Cu-Zn/Al_2O_3 catalyst drastically decreased 17%. It was interpreted that the Cu-Zn/Al_2O_3 catalyst was deactivated by sintering of active metal during the thermal cycling test [2].

X-ray diffraction patterns of the Pt-Ni/CeO_2 catalysts before and after the reaction are presented in Fig. 4. The used catalyst was recovered after the thermal cycling reaction at 250℃ for 130 h. There was no major change in the XRD patterns of Pt-Ni/CeO_2 catalyst before and after the reaction.

The results suggest that the 0.2 wt% Pt-Ni/CeO_2 catalyst is an attractive candidate for development as the alternate commercial LTS catalyst for the fuel cell powered vehicles applications, because the cerium oxide supported catalysts showed higher activity and stability than the commercial LTS catalyst during thermal cycling test.

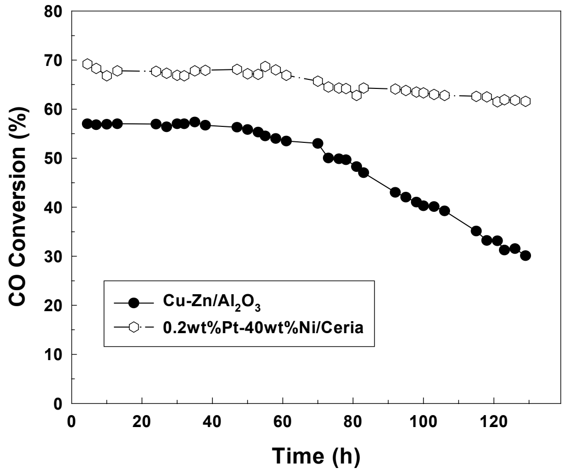

Figure 3. Thermal cycling runs for WGS reaction over Cu-Zn/Al_2O_3 and Pt-Ni based catalysts.

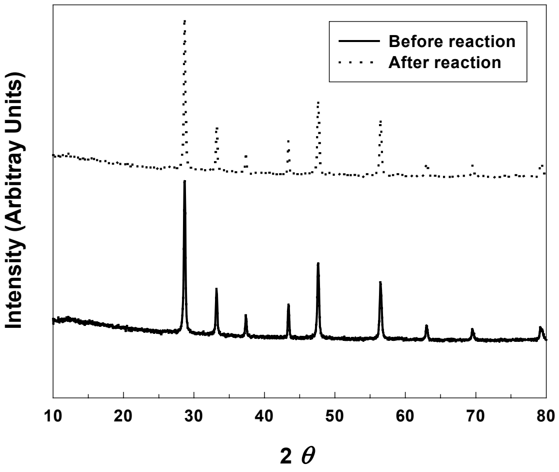

Figure 4. XRD patterns of 0.2 wt% Pt-Ni/CeO_2 catalysts before and after WGS reaction

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