수소 Station과 연료 개질기를 위한 수성가스 전환 반응

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Water Gas Shift Reaction for Hydrogen Station and Fuel Processor

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Introduction

The WGS reaction is one of the key catalytic stages in a fuel processor and hydrogen station. Since the reaction is an exothermic, the equilibrium conversion of CO is highest at low temperatures [1-2]. Consequently a two-stage process in often used. 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 catalysts for integration with PEM fuel cells is very important [3-4].

In this works, we have studied the WGS reaction over Pt- and (or) Ni-containing cerium oxide catalysts. The thermal cycling performance over the prepared catalysts was compared with that over the commercial Cu-Zn/Al_2O_3 catalyst.

Experimental

1. Catalysts

The commercial LTS catalyst was obtained from ICI in the form of pellets. The catalyst in this work was used in the form of powder with a mesh size of 120/230, after crushing.

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 ($Ni(NO_3)_3 6H_2O$, 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.

BET surface area and pore size distributions of the used catalysts were measured by N_2 physisorption. The active metal surface area of the used catalysts was measured by CO chemisorption using a sorption analyzer [Quantachrome Co. Autosorb-1C]. Structure of the catalysts before and after the reaction was analyzed by the XRD [Shimazdu Co., XRD-6000].

2. Water Gas Shift Reaction

The schematic diagram of the WGS reactor is shown in Fig. 1. It 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℃ in 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 Series Ⅱ) equipped with a TCD and using a carbosphere column (0.0032 m O.D. and 3.048 m length, 80/100 meshes).

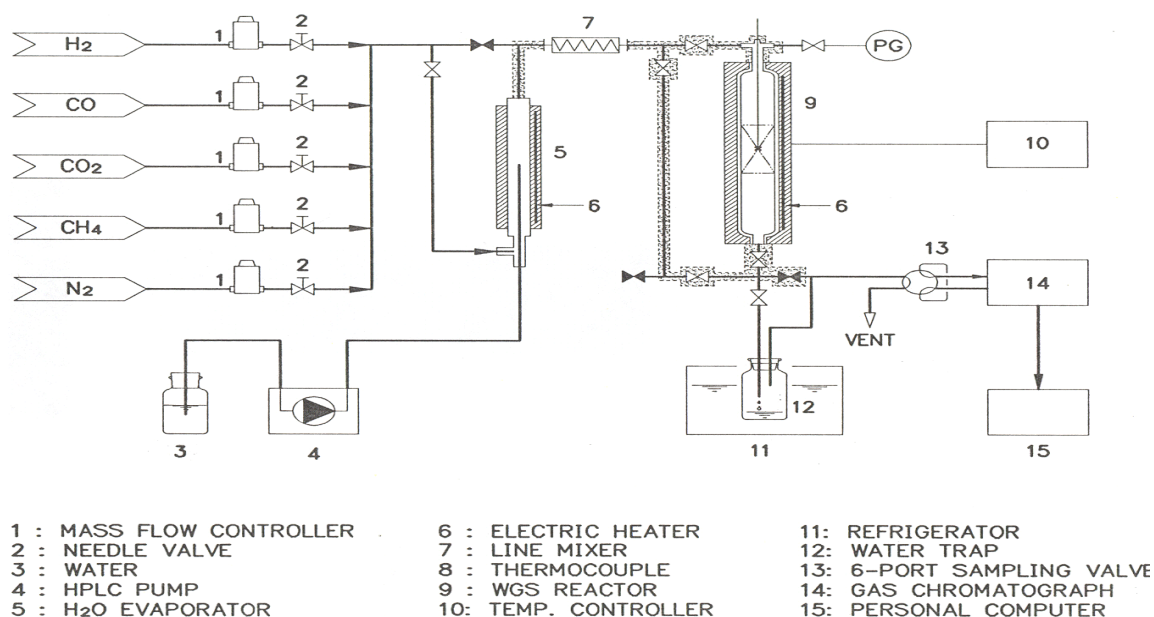| 1 : MASS FLOW CONTROLLER	6 : ELECTRIC HEATER	11: REFRIGERATOR
2 : NEEDLE VALVE	7 : LINE MIXER	12: WATER TRAP
3 : WATER	8 : THERMOCOUPLE	13: 6-PORT SAMPLING VALVE
4 : HPLC PUMP	9 : WGS REACTOR	14: GAS CHROMATOGRAPH
5 : H2O EVAPORATOR	10: TEMP. CONTROLLER	15: PERSONAL COMPUTER

Figure 1. A schematic diagram of WGS reaction system.

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 and (or) 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 and (or) Ni/ceria catalysts were reduced under flowing 40 cc/min of 5% H_2 in Ar balance at 200℃ for 30 min. The reactant gas contained 62.5% H_2 (99.999%), 31.8% H_2O and 5.7% CO (99.999%).

Results and Discussion

The WGS reaction is a critical step during fuel processing since CO severely and irreversibly poisons the PEM electrocatalyst. 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 [4-5]. In our previous works [6-9], 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.

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 57% 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℃. 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.
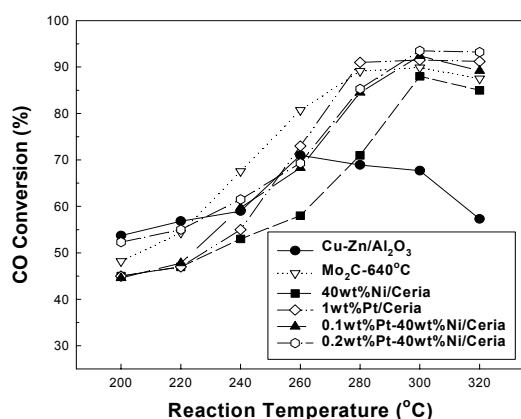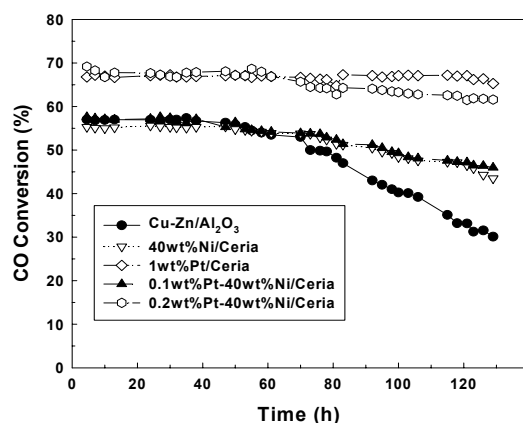

Figure 2. Comparison of the catalytic activity of the various prepared catalyst with the commercial Cu-Zn/Al_2O_3 catalyst for the LTS reaction; Space velocity = 10,000 h^{-1}, Feed ratio = H_2(62.5%), H_2O(31.8%) and CO(5.7%)

Figure 3. The results of thermal cycling runs for WGS reaction over commercial LTS and prepared catalysts. The runs are performed at the reaction temperature of 250℃ over a time intervals of 130 h.

Figure 3 shows the result of thermal cycling runs for WGS reaction over the $Cu-Zn/Al_2O_3$ and the prepared catalysts. Even though all catalysts deactivated during the thermal cycling test, the Pt-based catalysts showed higher stability than the commercial $Cu-Zn/Al_2O_3$. It was found that the conversion of CO over 1 wt% $Pt-Ni/CeO_2$ and 0.2 wt% $Pt-Ni/CeO_2$ catalysts after the thermal cycling reaction for 130 h decreased 1% and 3.5%, respectively, whereas that over the $Cu-Zn/Al_2O_3$ catalyst drastically decreased 17%. The results was interpreted that the $Cu-Zn/Al_2O_3$ catalyst was deactivated by sintering of active metal during the thermal cycling test [8-9].

Conclusions

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 processor and H_2 station applications, because the cerium oxide supported catalysts showed higher activity and stability than the commercial LTS catalyst during thermal cycling test.

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