

## 저온 수성가스 전환 반응용 고성능 촉매 개발

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### Development of High Performance Catalyst for Low Temperature Water Gas Shift Reaction

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### Introduction

The successful development of a fuel cell powered vehicle is dependent on the development of a fuel processor [1-2]. It was reported that water gas shift (WGS) reactors, charged with currently available commercial catalysts ( $\text{Fe}_3\text{O}_4\text{-Cr}_2\text{O}_3$  and  $\text{Cu-Zn/Al}_2\text{O}_3$ ), constitute about a third of the mass, volume and cost of a fuel processor system [3-4]. The WGS reaction is one of the key catalytic stages in the fuel processor for a hydrogen station and a fuel cell powered vehicle application. Since the reaction is an exothermic, the equilibrium conversion of CO is the highest at low temperature [4-5]. In industrial reactors,  $\text{Fe}_3\text{O}_4\text{-Cr}_2\text{O}_3$  catalyst was used for a high temperature shift (HTS) reaction and  $\text{Cu-Zn/Al}_2\text{O}_3$  catalyst was used for a low temperature shift (LTS) reaction. The commercial LTS catalyst, though highly active at a low temperature, was unsuitable for commercialized applications because of large size, heavy weight and rapid deactivation tendency of the LTS catalyst under severe conditions. Moreover, the  $\text{Cu-Zn/Al}_2\text{O}_3$  catalyst is hardly used at temperatures above  $250^\circ\text{C}$ , that further limits their utilizations [6-7]. Therefore, the development of high performance WGS catalyst with thermal stability is very important.

In this work, the WGS reaction over Pt based catalysts was investigated to develop an alternate commercial  $\text{Cu-Zn/Al}_2\text{O}_3$  catalyst for an on-board fuel processor and hydrogen station application.

### Experimental

The various Pt-based catalysts were prepared by an impregnation method using raw materials such as cerium oxide ( $\text{CeO}_2$ , 99.9%, Sigma-Aldrich Chemicals), gamma alumina ( $\gamma$ -alumina, 2-3 microns, High Purity Chemicals.), titanium oxide ( $\text{TiO}_2$ , 99.99%, Degussa) and chloroplatinic acid ( $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ , 99%, High Purity Chemicals).

The used catalyst was characterized by  $\text{N}_2$  physisorption, CO chemisorption [Quantachrome Co. Autosorb-1C], XRD [Shimadzu Co., XRD-6000] and temperature programmed reduction [TPR, Micromeritics Autochem II].

The WGS reactor consists of four sections: feed supply, preheater, WGS reactor and GC analysis sections. The gases were delivered by mass flow controllers, and  $\text{H}_2\text{O}$  was fed by a liquid delivery pump [Young Lin Co., model M 930]. 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  $\pm 1^\circ\text{C}$  of the catalyst bed temperature. Unreacted  $\text{H}_2\text{O}$  was removed by an ice trap and then gas effluent was analyzed by an on-line gas chromatograph (Hewlett Packard Co., HP-6890 Series) 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  $300^\circ\text{C}$  and atmospheric pressure in a fixed bed reaction system. The Cu-Zn/ $\text{Al}_2\text{O}_3$  catalyst was reduced at  $200^\circ\text{C}$  in a mixture of 2%  $\text{H}_2$  in  $\text{N}_2$  balance for 4.5 h. The others catalysts were reduced under flowing 40 cc/min of 5%  $\text{H}_2$  in Ar balance at  $400^\circ\text{C}$  for 1 h.

### 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 [6-7], author reported that the commercial LTS catalyst was deactivated by sintering of active metal during the thermal cycling test, and identified that the commercial LTS catalyst was hardly used at temperature of above  $250^\circ\text{C}$ . 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 prepared and commercial catalysts are summarized in Table 1. It was found that the Pt based catalyst displayed high surface area over the commercial Cu-Zn/ $\text{Al}_2\text{O}_3$  catalyst.

Table 1. Characteristics of the prepared and commercial catalysts

Catalysts	BET surface area ( $\text{m}^2/\text{g}$ )	Total pore volume (cc/g)	Active metal surface area ( $\text{m}^2/\text{g}$ )
Cu-Zn/ $\text{Al}_2\text{O}_3$	60	0.081	$1.035 \times 10^{-1}$
1wt%Pt/ $\text{CeO}_2$	131	0.054	$1.065 \times 10^{-1}$
1wt%Pt/ $\text{Al}_2\text{O}_3$	142	0.048	$1.043 \times 10^{-1}$
1wt%Pt/ $\text{TiO}_2$	63.9	0.050	$0.897 \times 10^{-1}$

TPR curves for  $\text{CeO}_2$  and Pt/ $\text{CeO}_2$  and Pt/ $\text{TiO}_2$  samples are presented in Fig. 1. TPR profiles of the samples were obtained by heating the samples from room temperature to  $1,100^\circ\text{C}$  at a rate of  $10^\circ\text{C}/\text{min}$ , in a 5%  $\text{H}_2/\text{Ar}$  gas flow (50 ml/min). It was identified that pure Pt shows a reduction peak at about  $390^\circ\text{C}$  and pure CeO shows a weak reduction peak at  $810^\circ\text{C}$ . It was found that three reduction peaks are registered in the spectra of Pt/ $\text{CeO}_2$  catalyst. The low-temperature peaks at about  $390^\circ\text{C}$  and  $550^\circ\text{C}$  are assigned to the reduction of surface oxygen species, and these reduction peaks are caused by NiO phase and metal support interaction. The high temperature peak at about  $810^\circ\text{C}$  corresponds to the reduction of bulk oxygen and the formation of lower oxides of cerium. It was identified that Pt/ $\text{TiO}_2$  shows a reduction peak at about  $530^\circ\text{C}$ , this reduction peak was caused by the interaction Pt phase with  $\text{TiO}_2$ .

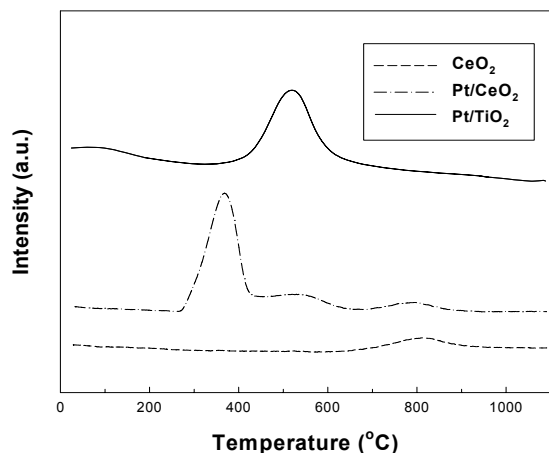


Figure 1. TPR profiles for CeO<sub>2</sub>, Pt/CeO<sub>2</sub> and Pt/TiO<sub>2</sub> samples.

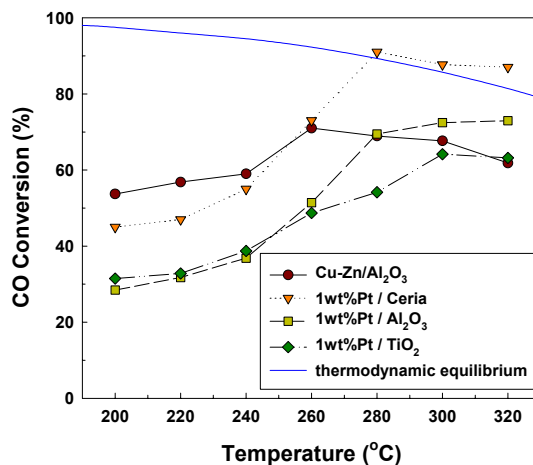


Figure 2. The effect of reaction temperature on the conversion of CO in WGS reaction.

Figure 2 shows the effect of reaction temperature on the conversion of CO over the prepared and the commercial LTS catalysts. The WGS reaction under a feed containing 62.5% H<sub>2</sub>, 31.8% H<sub>2</sub>O and 5.7% CO was carried out at the reaction temperature of 200 to 300°C and space velocity of 10,000 h<sup>-1</sup>. It was found that Pt/CeO<sub>2</sub> catalyst showed higher activity than the Cu-Zn/Al<sub>2</sub>O<sub>3</sub> at temperature range of above 260°C and maximum activity was observed at 280~300°C with CO conversion of more than 90%. However the activity of Cu-Zn/Al<sub>2</sub>O<sub>3</sub> catalyst increased with increasing the reaction temperature up to 260°C, displayed the highest activity at 260°C with CO conversion of 70%, and then decreased at high temperature over 260°C.

The thermal cycling runs were performed at the reaction temperature of 250°C over a time

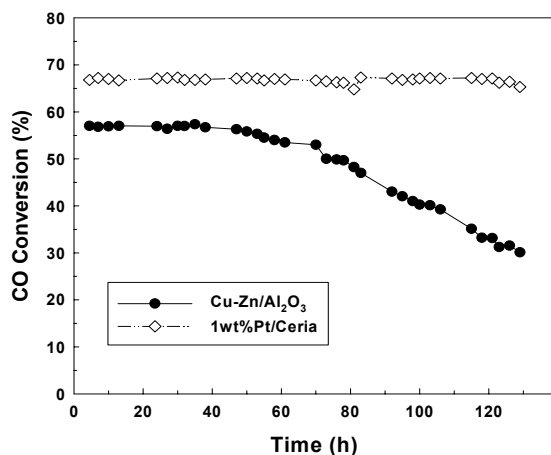


Figure 3. The results of thermal cycling runs for WGS reaction over commercial LTS and Pt/CeO<sub>2</sub> catalysts. The runs are performed at the reaction temperature of 250°C over a time intervals of 130 h.

period of 130h. In order to change the reduction and the oxidation conditions of catalysts, the 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<sub>2</sub>O<sub>3</sub> and the Pt/CeO<sub>2</sub> catalysts. Even though both catalysts deactivated during the thermal cycling test, it was found that the Pt/CeO<sub>2</sub> catalyst showed higher stability than the commercial Cu-Zn/Al<sub>2</sub>O<sub>3</sub> catalyst. Moreover, the conversion of CO over 1wt% Pt/CeO<sub>2</sub> catalyst after the thermal cycling reaction for 130 h decreased 1.3%, whereas that over the Cu-Zn/Al<sub>2</sub>O<sub>3</sub> catalyst drastically decreased 17%. It was interpreted that the Cu-Zn/Al<sub>2</sub>O<sub>3</sub> catalyst was deactivated by sintering of active metal during the thermal cycling test [2].

X-ray diffraction patterns of the Pt/CeO<sub>2</sub> and Pt/TiO<sub>2</sub> catalysts before and after the reaction are presented in Fig. 4. The used catalyst was recovered after the thermal cycling reaction at 250°C for 130 h. There was no major change in the XRD patterns of Pt/CeO<sub>2</sub> catalyst before and after the reaction. However, the XRD profiles of Pt/TiO<sub>2</sub> catalyst is convert the anatase phase to the rutile phase after the reaction.

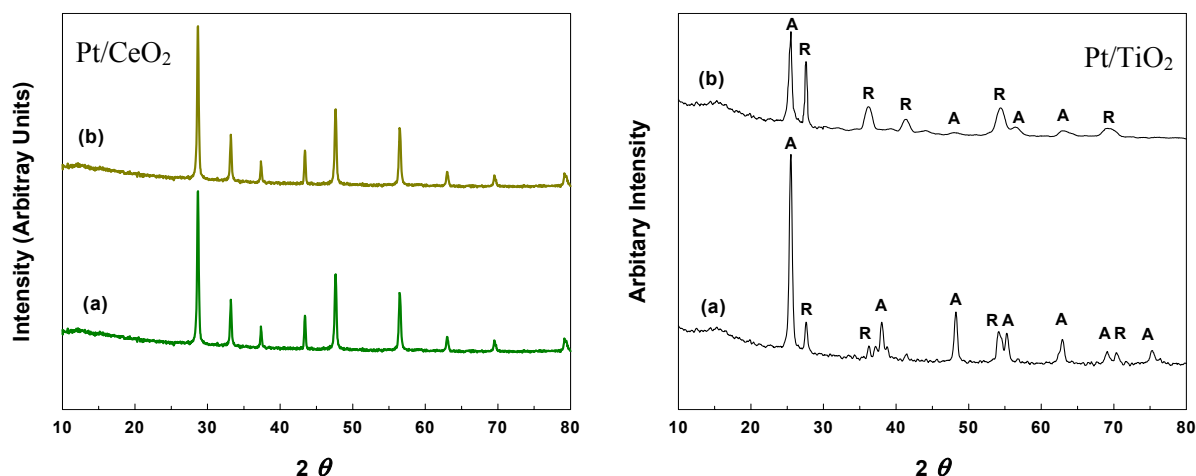


Figure 4. XRD patterns of Pt/CeO<sub>2</sub> and Pt/TiO<sub>2</sub> catalysts before and after WGS reaction.; (a) before reaction, (b) after reaction

The results suggest that the 1wt%Pt/CeO<sub>2</sub> catalyst is an attractive candidate as the alternate commercial LTS catalyst, because the cerium oxide supported catalyst showed higher activity and stability than the commercial LTS catalyst during thermal cycling test.

## Conclusions

The 1wt% Pt/Ceria catalyst was more active than a commercial Cu-Zn/Al<sub>2</sub>O<sub>3</sub> catalyst under the reaction conditions employed (220~300°C and atmospheric pressure). It was found that the cerium oxide supported catalysts showed higher activity and stability than the commercial LTS catalyst during the thermal cycling. These results suggest that the Pt/ceria catalyst is attractive candidates as the alternate commercial LTS catalyst for the hydrogen station and the fuel cell powered vehicle applications. However studies on the reduction of catalyst cost will be needed.

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