

연료 개질기용 고성능 수성가스 전환반응 촉매 개발

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Development of High Performance WGS Catalyst for Fuel Processor Applications

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Key words : WGS(수성가스전환), Hydrogen Station(수소 스테이션), Fuel Processor(연료 개질기), Carbon mono-oxide(일산화탄소), Ceria(세리아), Catalyst(촉매)

Abstract : WGS reaction over Mo₂C and ceria based catalysts was investigated to develop an alternative commercial Cu-Zn/Al₂O₃ catalyst for fuel processor and hydrogen station. The Mo₂C catalysts were prepared by a temperature programmed method and the various metal supported cerium oxide catalysts were prepared by an impregnation method. The catalysts were characterized by the N₂ physisorption, CO chemisorption, XRD, TEM and TPR. It was found that Mo₂C and 0.2wt% Pt-40wt% Ni/CeO₂ catalysts had higher activity and stability than the Cu-Zn/Al₂O₃ above 260 °C. Moreover, CO conversion of more than 85% was observed at 280-300 °C. But all catalysts were deactivated during the thermal cycling runs. The results suggest that these catalysts are an attractive candidate for the alternative Cu-Zn/Al₂O₃ catalyst for fuel processor and hydrogen station applications.

1. Introduction

Hydrogen may be provided to the fuel cell in pure form or one may generate hydrogen from hydrocarbons in a fuel processor. A fuel processor is the most convenient method for supplying hydrogen in the absence of a suitable infrastructure such as hydrogen station⁽¹⁾. It was reported that water gas shift (WGS) reactors, charged with currently available commercial catalysts (Fe₃O₄-Cr₂O₃ and Cu-Zn/Al₂O₃), constitute about a third of the mass, volume and cost of a fuel processor system⁽²⁾. 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 higher at low temperature. In industrial reactors, Fe₃O₄-Cr₂O₃ catalyst was used for a high temperature shift (HTS) reaction, and Cu-Zn/Al₂O₃ catalyst was used for a low temperature shift (LTS) reaction. Existing commercial Cu-Zn/Al₂O₃ catalyst, though highly active,

was unsuitable for transportation applications because of their large size, weight, and the deactivation tendency of the copper-based catalyst under the severe conditions encountered in a fuel cell powered vehicles system. The Cu-Zn/Al₂O₃ catalyst also can not be used at temperatures above 250 °C, which further limits their utility⁽³⁾. Therefore, the development of high performance WGS catalyst with thermal stability is very important.

In this work, the WGS reaction over Mo₂C and various Pt-Ni based catalysts with different metal loading was investigated to develop a high performance LTS catalyst for fuel processor and hydrogen station applications. The catalytic performances for thermal cycling runs over the prepared catalysts were compared with those over the commercial Cu-Zn/Al₂O₃ catalyst.

2. Experimental

Molybdenum carbide catalysts were synthesized by

the carburization of molybdenum oxide⁽⁴⁾. A molybdenum oxide (99.99%) was obtained from Sigma-Aldrich Chemicals. Carburization of the oxide was done in a temperature programmed method using an equimolar mixture of CH₄ and H₂ in flowing 400 cc/min. Approximately 5g of the oxide was loaded into the quartz straight tube reactor. The temperature program for carburization consisted of linearly heating the oxide at a rate of 600 °C h⁻¹ to 300 °C, then at 60 °C h⁻¹ to the final carburization temperature. After 2 h soak period at the final temperature, the product was quenched to room temperature and kept for 4 h in a mixture of 1% O₂ in He balance with flow rate of 30 cc/min.

Various Pt-Ni/CeO₂ catalysts were prepared by the impregnation or co-precipitation method using raw materials such as cerium oxide (CeO₂, 99.9%, Sigma-Aldrich Chemicals), nickel nitrate (Ni(NO₃)₃·6H₂O, 99.9%, Sigma-Aldrich Chemicals) and chloroplatinic acid (H₂PtCl₆·xH₂O, 99%, High Purity Chemicals). The cerium oxide (CeO₂) was used after calcining at 900 °C for 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 °C for 24 h, and then calcined at 550 °C for 2 h. The commercial LTS catalyst for clean up of CO was obtained from ICI in the form of pellet. In this work, the catalyst was used in the form of powder with a mesh size of 120/130 after crushing.

BET surface area and pore size distributions of catalysts were measured by N₂ physisorption (Quantachrome Co., Autosorb-1C). The active metal surface area of the prepared catalysts was measured by CO chemisorption using a sorption analyzer (Micromeritics Co., Autochem II. Structure and morphology of the catalysts before and after the reaction were analyzed by the TEM [Philips Co., M30]. The WGS reactor consists of four sections: feed supply, preheater, WGS reactor and GC analysis sections. The gaseous reactants were delivered by mass flow controllers (BRONKHORST HI-TEC Co.), and H₂O was fed by a liquid delivery pump (Young Lin Co., M930). The LTS reactor made up of Inconel 600 tube (0.0075 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 ensuring accuracy of ±1 °C of the catalyst bed temperature. Unreacted H₂O was removed by an ice trap and then gas effluent was analyzed by an on-line gas chromatograph (HP-6890 Series) equipped with a thermal conductivity detector (TCD) and a carbosphere column (0.0032 m O.D. and 3.048 m length, and 80/100 meshes).

The catalytic activity for WGS reaction was measured at the temperatures range of 200 to 300 °C and under atmospheric pressure in a fixed bed reaction system. The Cu-Zn/Al₂O₃ catalyst was reduced at 200 °C in a mixture of 2% H₂ in N₂ balance for 4.5 h. The Mo₂C catalyst was reduced at 400 °C under the flow of H₂ for 4.5 h. The Pt-Ni/CeO₂ catalysts were reduced at 400 °C for 2 h in a mixture of 40 cc/min of 5% H₂ in Ar balance. The reactant gas consisted of 62.5% H₂ (99.999%), 31.8% deionized H₂O and 5.7% CO (99.999%).

3. Results and Discussion

The characteristics of the catalysts used are summarized in Table 1. It was found that the BET surface areas of Mo₂C catalysts were similar to that of Cu-Zn/Al₂O₃ catalyst within an experimental error while active metal surface area of Mo₂C was higher than that of Cu-Zn/Al₂O₃ catalyst. The surface area of Pt-Ni/CeO₂ catalyst showed high surface area over the commercial LTS catalyst.

Table 1 Characteristics of the Catalyst

Catalyst	Condition	BET surface area (m ² /g)	Active metal surface area (m ² /g)
Cu-Zn/ Al ₂ O ₃	Fresh	60	0.104
	Used	42	0.084
Mo ₂ C	Fresh	61	0.129
	Used	53	0.104
Pt-Ni/ CeO ₂	Fresh	78	0.086
	Used	65	0.079

Figure 1 shows the effect of reaction temperature on the conversion of CO over ceria based WGS and commercial LTS catalysts. The WGS reaction of a feed containing 62.5% H₂, 31.8% H₂O and 5.7% CO was carried out at the reaction temperature of 200 to 300 °C with space velocity of 10,000 h⁻¹. It was found that the Mo₂C and cerium oxide supported catalysts showed higher activity than the Cu-Zn/Al₂O₃ at temperature range of above 260 °C. The 0.2wt%Pt-Ni/CeO₂ catalyst exhibited the highest activity among the prepared catalysts and maximum activity was observed at 280~300 °C with CO conversion of more than 85%. However, the activity of Cu-Zn/Al₂O₃ catalyst increased with elevating the reaction temperature up to 260 °C showed the highest activity at 260 °C with CO conversion of 70%, and then decreased at the high temperature over 260 °C.

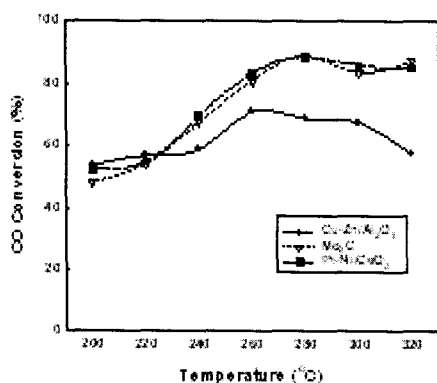


Fig. 1 The effect of reaction temperature on the conversion of CO over the prepared and the commercial LTS catalysts.

The thermal cycling runs were performed at the reaction temperature of 250 °C over a time period of 130 h. To change the reduction and the oxidation conditions of catalyst, the switch of electric furnace for heating WGS reactor was repeatedly turned on and off with some intervals. Figure 2 shows the results of thermal cycling runs for WGS reaction over the Cu-Zn/Al₂O₃ and the prepared catalysts. All catalysts were slowly deactivated during the thermal cycling runs. However, it was found that the Mo₂C and Pt-Ni/CeO₂ catalysts showed higher

stability than the commercial Cu-Zn/Al₂O₃ catalyst. In our previous works⁽⁵⁻⁶⁾, it was reported that the Cu-Zn/Al₂O₃ catalyst was deactivated by the sintering of active metal during the thermal cycling run. When the catalyst was repeatedly exposed on the stages of oxidation and reduction, it was easily deactivated by the sintering of the active metal. Therefore, the thermal cycling stability is very important for application in the on-board fuel cell vehicles, fuel processor and/or hydrogen station in which the system is repeatedly turned on and off. In this work, it was found that Pt-Ni/CeO₂ and Mo₂C catalysts showed higher catalytic stability for thermal cycling run than Cu-Zn/Al₂O₃ catalyst.

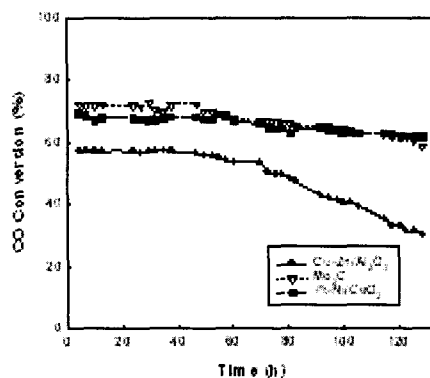


Fig. 2. Thermal cycling runs for WGS reaction over the prepared and the commercial LTS catalysts.

The characteristics of the catalysts before and after the thermal cycling run for 130 h are summarized in Table 1. BET surface areas of Pt-Ni/CeO₂, Mo₂C and Cu-Zn/Al₂O₃ catalysts after the thermal cycling reaction decreased as 12, 13 and 30%, respectively. Active metal surfaces areas of Pt-Ni/CeO₂, Mo₂C and Cu-Zn/Al₂O₃ catalysts after the reaction also decreased 4, 19 and 21%, respectively.

In our previous works⁽⁴⁻⁶⁾, it was suggested that the deactivation of Mo₂C catalyst can be caused by the transition of Mo⁶⁺ (MoO₃C₃), Mo^{IV} (MoO₂) and Mo₂C on the surface of Mo₂C catalyst to Mo^{VI}MoO₃ with the reaction of H₂O in the reactant.

Figure 3 presents the TEM micrographs of the Pt-Ni/CeO₂ catalysts before and after thermal cycling reaction. The dark spots less than 10 nm in the pictures

are Ni metal particle, while the lattice patterns of gray area are the CeO₂ support. It was found that the particle size of Ni after the reaction was increased compared to those of the fresh catalyst. It was concluded that the deactivation of Pt-Ni/CeO₂ catalyst during the thermal cycling run for WGS reaction was caused by the sintering of Ni particles. The results suggest that Pt-Ni/CeO₂ catalyst is an attractive candidate with high thermal stability for water gas shift reaction and more stable than commercial LTS catalyst even though all catalysts are slowly deactivated during the thermal cycling run.

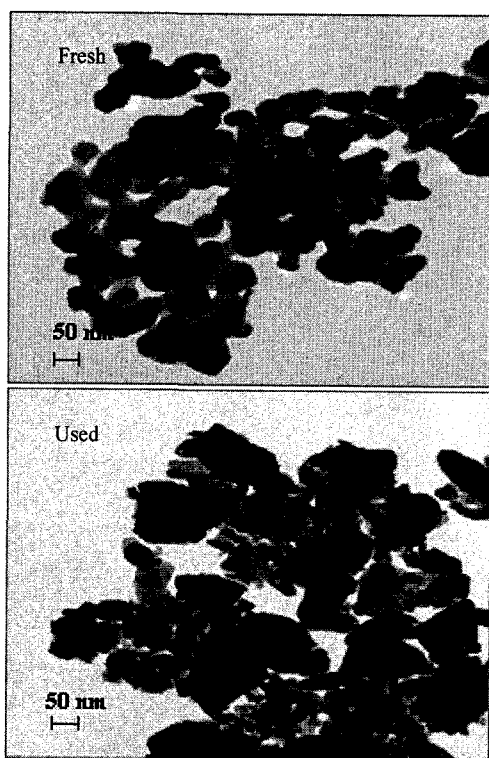


Fig. 3. TEM images of 0.2wt%Pt-Ni/CeO₂ catalysts before and after thermal cycling runs for WGS reaction.

4. Conclusion

It was found that Pt-Ni/CeO₂ catalysts showed higher thermal stability than the commercial LTS catalyst during the thermal cycling run performed at 250°C over a time period of 130 h. Even though this catalyst was slowly deactivated during the thermal cycling run, the results

suggest that the Pt-Ni/CeO₂ catalyst is an attractive candidate as the alternative commercial LTS catalyst for on-board fuel cell powered vehicles, fuel processor and/or hydrogen station applications.

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