DEVELOPMENT OF Cu-Mo BASED WGS CATALYST FOR HYDROGEN STATION AND FUEL PROCESSOR APPLICATIONS

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Introduction

The hydrogen may be provided to the fuel cell in pure form or one may generate hydrogen from hydrocarbons in a fuel processor. Fuel processor is the most convenient method for supplying hydrogen in the absence of a suitable infrastructure such as hydrogen station. Recently it was known that the development of hydrogen station and fuel processor is essential to opening the hydrogen economy society. The reforming of hydrocarbons generates gases, which contains 8-12% CO besides H_2, CO_2 and CH_4. This CO must be converted with the help of steam to CO_2 and hydrogen via the water gas shift (WGS) reaction

The WGS reaction is the reaction of CO with H_2O to form CO_2 and H_2, and one of the key catalytic stages in fuel processor and hydrogen station systems. The equilibrium conversion of CO for WGS reaction is highest at low temperatures. Therefore a two-stage process is often used [1-4], in industrial reactors. The reaction is usually carried out in two adiabatic shift reactors, the high temperature shift (HTS) reactor and the low temperature shift (LTS) reactor, separated with an intercooler in between. Fe_3O_4-Cr_2O_3 catalyst was used for the high temperature shift and Cu-Zn/Al_2O_3 catalyst was used for the low temperature shift reaction. The reaction is moderately exothermic with $\Delta H = -41.1$ kJ/mol [5,6]. Existing commercial LTS (Cu-Zn/Al_2O_3) catalyst, though highly active, was unsuitable for applications because of their large size and weight, and the deactivation tendency of an active metal under the severe conditions encountered in fuel processor and hydrogen station systems. Also, it can not be used at temperatures above about 250℃, which further limits their utility [7,8].

In our previous work [9,10], it was reported that commercial LTS catalyst was deactivated by the sintering of active metal during the thermal cycling runs. It was also reported that the deactivation of Mo_2C catalyst may be caused by the transition of $Mo^{\delta+}$ (MoO_xC_y), MoⅣ (MoO_2) and Mo_2C on the surface of Mo_2C catalyst to MoⅥ(MoO_3) with the reaction of H_2O in reactant, even though Mo_2C catalyst showed higher WGS activity than commercial LTS catalyst [11-14]. It was also reported that the Pt-Ni/CeO_2 catalysts showed higher catalytic activity even though this catalyst was slowly deactivated during the thermal cycling run [15].

In this work, the WGS reaction over Cu-Mo based $Ce_xZr_{1-x}O_2$ supported catalysts were investigated to develop a high performance LTS catalyst for fuel processor and hydrogen station applications. The catalytic performance of the prepared catalysts was compared with that of the commercial Cu-Zn/Al_2O_3 catalyst.

Experimental

1. Preparation of catalyst

Cerium nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$, Acros Organics) and Zirconyl oxynitrate hydrate ($ZrO(NO_3)_2 \cdot xH_2O$, Aldrich Chemicals) with the purity of about 99.5 ~ 99.9% were used fot the preparation of support without additional purification. The distilled and deionized water was used throughout whole the experiment. An aqueous solution of Zirconly oxynitrate was added the slowly with vigorous stirring into an aqueous solution of cerium nitrate at 60□. After saturating the solution, an 1M urea (CH_4N_2O) was slowly added to saturated solution and then continuously stirred at 60℃ for 4h. After filtration of pale brown powder this support was dried at 110℃ for 24h. Finally, calcination was carried out at 500℃ for 2h after heating 5℃/min.

The Cu-Mo based $Ce_xZr_{1-x}O_2$ supported catalyst was prepared by impregnation method using the ammonium molybdate tetrahydrate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, Dae Jung Chemicals, 99%] and Copper nitrate, $Cu(NO_3)_2\cdot 3H_2O$, Shinyo Pure Chemicals, 99%] and prepared $Ce_xZr_{1-x}O_2$. The catalyst was calcined at 550℃ for 4h after heating 5℃/min.

2. Characterization of catalysts

BET surface area and pore size distributions of catalysts were measured by N2 physisorption (Quantachrome Co., Autosorb-1C). The active metal surface areas of the prepared catalysts were 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 XRD and TEM [Philips Co., M30]. Characteristic of reduction over catalyst was measured by a temperature programmed reduction (TPR, Micromeritics Co., Autochem Ⅱ). TPR profiles were obtained by heating the catalysts from room temperature to 1,100℃ at rate of 10℃/min, in a 5% H_2/Ar gas flow (50 cc/min).

3. WGS reaction

The WGS reactor consists of four sections: feed supply, pre-heater, WGS reactor and GC analysis sections. The gases reactants were delivered by mass flow controllers (BRONKHORST HI-TEC Co.), and H_2O 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℃ 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 (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℃ and atmospheric pressure in the fixed bed reaction system. The $Cu\text{-}Zn/Al_2O_3$ catalyst was reduced at 200℃ in a mixture of 2% H_2 in N_2 balance for 4.5 h. The $Cu\text{-}Mo/Ce_xZr_{1-x}O_2$ catalyst was reduced at 400℃ under the flow of H_2 for 4.5 h. The WGS reaction for a feed containing 45.1% H_2, 37.1% H_2O, 11.3% CO and 6.4% CO_2 was carried out at the reaction temperature of 200 to 300℃ and space velocity of 10,000 h^{-1}[15].

Results and discussion

In our previous work [3], it was reported that the CO consumption rate for WGS reaction over $Cu\text{-}Zn/Al_2O_3$ catalysts decreased progressively with a time on stream during the thermal cycling run. The CO consumption rate of the catalyst after the thermal cycling reaction for 130 h decreased 17 %. BET surface area and active metal surface area of Cu-Zn/Al2O3 catalyst after the thermal cycling reaction decreased by 29% and 21%, respectively. It was found that commercial $Cu\text{-}Zn/Al_2O_3$ catalyst was deactivated by the sintering of active metal as showing in Fig. 1 [3].

The nomenclature and the characteristics of the catalysts used in this work are shown in Table 1. BET surface area of prepared catalyst using urea method was higher than those of the commercial LTS catalyst.

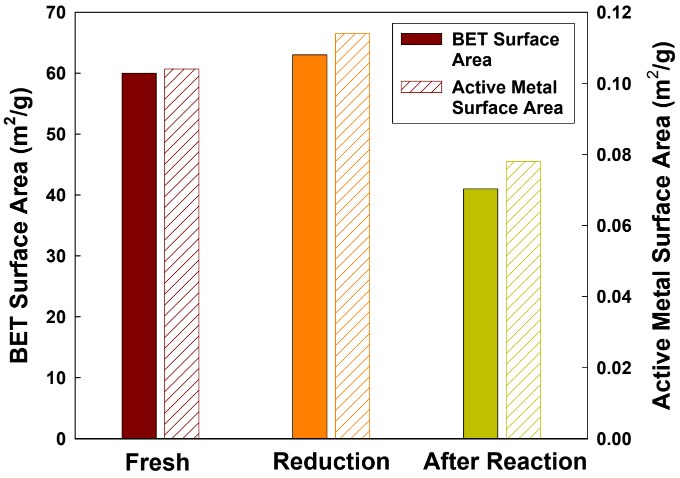

Fig. 1. The BET and active metal surface area of commercial Cu-Zn/Al_2O_3 catalysts before and after the WGS reaction with thermal cycling (temp. = 250℃, time = 130 h).

The TPR profiles of Cu based catalysts and $Ce_xZr_{1-x}O_2$ support were showed in Fig. 2 [16]. Generally, prepared Cu based catalyst was showed the reduction peak at 220℃ due to reduction of the surface oxygen species on CuO phase. 12 wt% Cu-2 wt% Mo/$Ce_{0.5}Zr_{0.5}O_2$ catalyst displayed the strong reduction peak of $CuMo_4$ and/or $Cu_3Mo_2O_9$ at 300-400℃. The Mo added Cu based catalysts obtained the reduction peak of MoO_2 phase at 440 and 840℃. All of catalysts reduced the CeO_2 and ZrO_2 phase at 600℃

Table 1. Characteristics of the prepared and Johnson Matthey catalysts used in this work

Catalyst	Metal content		BET (m^2/g)	Total Pore Volume (cc/g)	Average Pore Diameter (Å)
	Cu	Mo			
Cu-ZnO/Al_2O_3	30	-	62.3	0.0760	131
Cu/CeO_2	10	-	104.9	0.0806	149
Cu/$Ce_{0.5}Zr_{0.5}O_2$	10	-	117.1	0.1006	175
Cu-Mo/$Ce_{0.5}Zr_{0.5}O_2$	10	1	115.2	0.1020	176
Cu-Mo/$Ce_{0.5}Zr_{0.5}O_2$	10	2	109.4	0.0906	164
Cu-Mo/$Ce_{0.5}Zr_{0.5}O_2$	12	2	119.7	0.1042	176

Fig. 3 shows the effect of reaction temperature on the conversion of CO over the prepared and the commercial LTS catalysts. It was found that Cu/$Ce_{0.5}Zr_{0.5}O_2$ catalyst showed higher activity than the other catalysts at tested temperature and maximum activity was observed at 280~300℃ with CO conversion of more than 70%. Also, $Ce_{0.5}Zr_{0.5}O_2$ was the best composite of $Ce_xZr_{1-x}O_2$ support. 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℃.

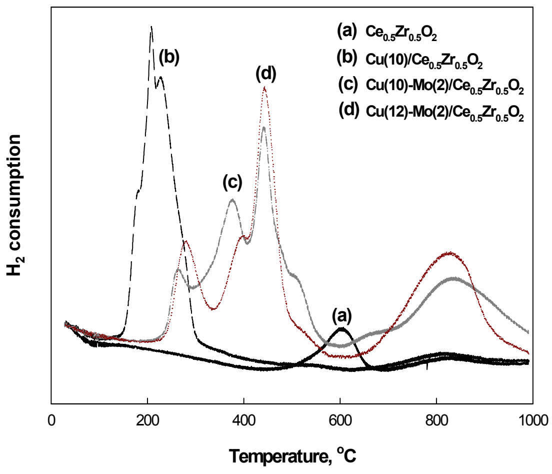

Fig. 2. The TPR profiles of prepared Cu-based catalysts (Heating rate : 5 ℃/min, Reducing gas : 5 vol% H_2/Ar balance).

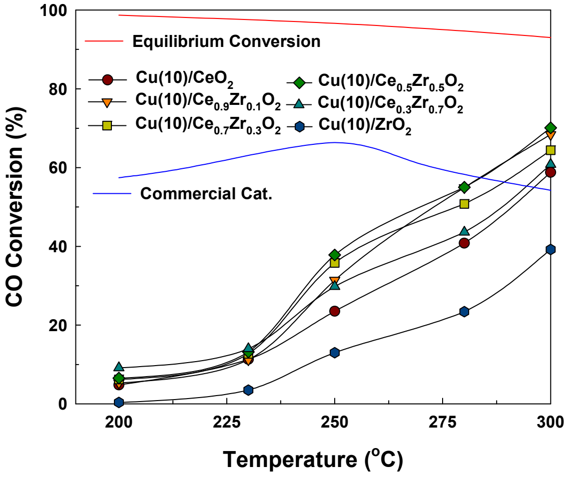

Fig. 3. CO conversion with WGS reaction over Cu-based catalyst in various temperature (GHSV = 10,000 h^{-1}, temp. = 200 ~ 300℃).

Fig. 4 shows the effect of reaction temperature on the conversion of CO over the Cu-Mo/$Ce_{0.5}Zr_{0.5}O_2$ and commercial LTS catalysts. The commercial catalyst showed higher activity than the prepared catalyst at 200~250℃ and maximum activity was observed at about 250℃. However, the activity of commercial catalyst decreased at high temperature over 250℃. It was found that 12 wt%Cu-2 wt%Mo/$Ce_{0.5}Zr_{0.5}O_2$ catalyst showed higher activity than the other catalysts at temperature range of above 260℃ with CO conversion of more than 70%. To investigate thermal stability of the commercial and prepared catalysts, the thermal cycling runs were performed at the reaction temperature of 250℃ over a time period of 130 h.

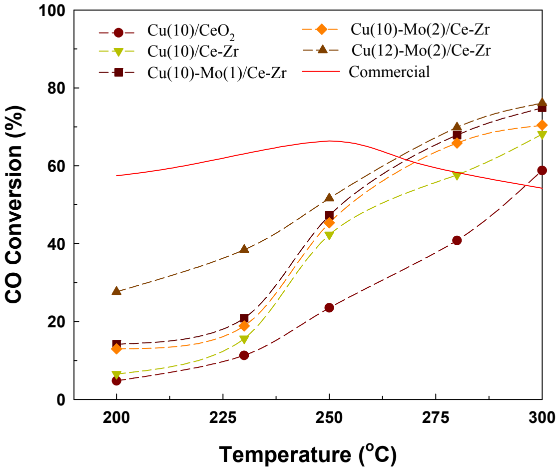

Fig. 4. CO conversion with WGS reaction over Cu-Mo based catalyst in various temperature (GHSV = 10,000 h^{-1}, temp. = 200 ~ 300℃).

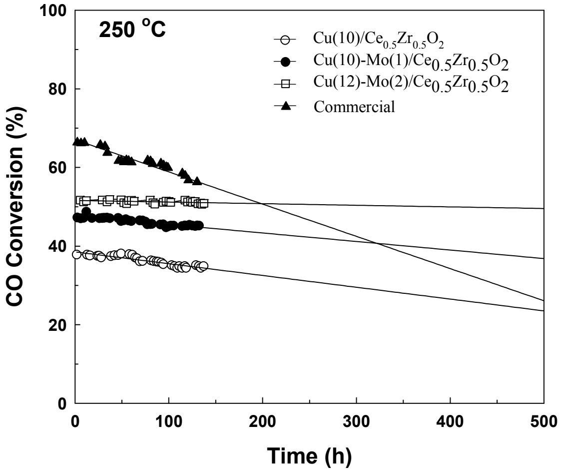

Fig 5. CO conversion with WGS reaction over Cu-Mo based catalyst with thermal cycling (GHSV = 10,000 h^{-1}, temp. = 250℃).

Fig. 5 and 6 shows the results of thermal cycling runs for WGS reaction over the commercial and $Ce_{0.5}Zr_{0.5}O_2$ mixed oxide supported catalysts. All catalysts slowly deactivated during the thermal cycling run. However, it was found that the 12wt%Cu-2wt%Mo/$Ce_{0.5}Zr_{0.5}O_2$ catalyst showed higher stability than the commercial catalyst.

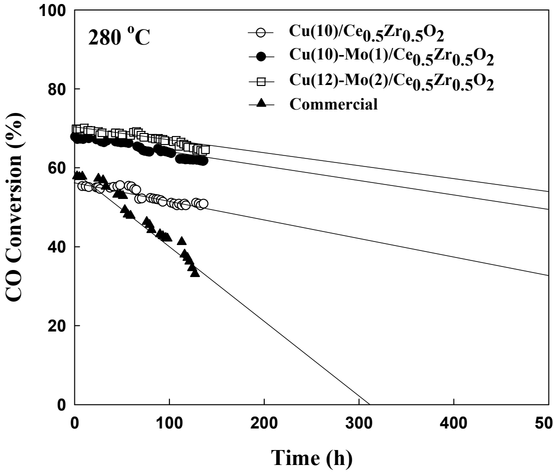

Fig. 6. CO conversion with WGS reaction over Cu-Mo based catalyst with thermal cycling (GHSV = 10,000 h^{-1}, temp. = 250℃).

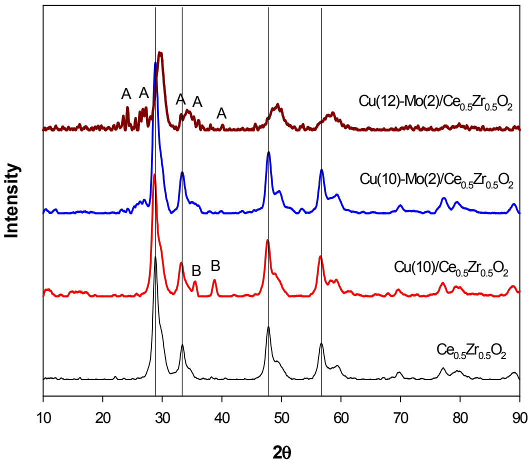

Fig. 7. XRD patterns of prepared Cu based catalysts (A: $CuMoO_4$ and/or $Cu_3Mo_2O_9$, B: CuO).

Fig. 7 shows the XRD patterns of prepared Cu-based catalysts. Notably, the XRD patterns of 12 wt% Cu-2 wt% Mo/$Ce_{0.5}Zr_{0.5}O_2$ catalyst show that peaks caused by $Ce_{0.5}Zr_{0.5}O_2$ shift toward a high 2Θ and peak's intensity decrease. This result suggests that the addition of Mo metal into Cu catalyst could make the Cu-Mo oxide composite due to improvement of interaction between Cu and Mo metal and finally increase the stability of catalyst as inhibiting the deactivation of Cu during the reaction.

Conclusions

It was found that Cu-Mo/$Ce_{0.5}Zr_{0.5}O_2$ catalysts showed higher activity and thermal stability than the commercial catalyst at temperature above 280℃. The results suggest that Cu-Mo/$Ce_{0.5}Zr_{0.5}O_2$ catalyst is a promising candidate as the alternative to commercial LTS catalyst for fuel processor and hydrogen station applications, even though the catalyst was slowly deactivated during the thermal cycling run.

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