연료전지 자동차용 가솔린 연료 개질기의 개발
: 수성가스 전환 반응용 촉매

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Development of Gasoline Fuel Reformer for Fuel-Cell Powered Vehicles
: Water Gas Shift (WGS) Catalyst

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Introduction

The WGS reaction is used industrially to produce H_2 for petroleum refining, chemicals production, and in processes that require synthesis gas with high H_2/CO ratios. Since the reaction is exothermic, the equilibrium CO conversion is highest at low temperatures. Consequently two-stage HTS and LTS process are often used for WGS reaction [1-3]. In industrial reactors, Fe_3O_4-Cr_2O_3 catalyst was used for the high temperature shift (HTS) reaction and Cu-Zn/Al_2O_3 catalyst was used for the low temperature shift (LTS) reaction. The existing commercial LTS catalyst 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. These copper-based catalysts were degraded by a thermal cycling mechanisms such as hydrothermal sintering during operation and oxidation when exposed to air. Copper-based catalysts also can not be used at temperatures above about 250℃, which further limits their utility. The goal of the research was to develop a high performance WGS catalysts for integration with PEM fuel cells. In this work, we have studied the WGS reaction over the transition metal carbides and the platinum supported cerium oxide catalysts, and the performance of the prepared catalysts were compared with the commercial LTS catalyst.

Experimental

1. Catalysts

The commercial LTS (Cu-Zn/Al_2O_3) catalysts for clean up of CO were also obtained from ICI in the form of pellets. The catalysts in this work are used in the form of powder with a mesh size of 120/230, after crushing.

Molybdenum carbide catalysts were synthesized by the carburization of molybdenum oxide [1-3]. A molybdenum oxide (99.99%) was obtained from Aldrich Chemicals. Carburization of the oxide was done in a temperature-programmed method using an equimolar mixture of CH_4 and H_2 flow of 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℃h^{-1} to 300℃, then at 60℃h^{-1} to the final carburization temperature. Following a 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%O_2 in He following at 30cc/min [1].

Two platinum supported cerium oxide catalysts were prepared by the impregnation method using ceria support (cerium oxide 99.9%, Aldrich Chemicals). Both the catalysts were calcined in air for 2～4 h at 600℃ or at 900℃. The ceria impregnated catalyst was prepared with a solution of chloroplatinic acid (H_2PtCl_6), dried for 24 h at 120℃ and then calcined for 2 h at 550℃ [2].

2. Characterization of catalysts

BET surface area and pore size distributions of catalysts were measured by N_2 physisorption. The active metal surface area of the prepared catalysts were measured by CO chemisorption using a sorption analyzer [Quantachrome Autosorb-1C]. The carburization temperature of molybdenum oxide was determined via thermal gravimetric analysis (TGA).

3. WGS reaction

The catalytic activity for WGS reaction was measured at atmospheric pressure and temperatures in the 200 to 300℃ in a 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 Mo_2C catalyst was reduced at 400℃ under the flow of H_2 for 4.5 h. The Pt/ceria catalyst was 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/ceria catalysts are 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% deionized H_2O and 5.7% CO (99.999%). The gas effluent was analyzed by on-line gas chromatograph (HP-5890 SeriesⅡ) equipped with TCD which use a carbosphere column (10″×1/8″ SS, 80/100 meshes).

Results and Discussion

Figure 1 shows the results of thermal cycling runs for WGS reaction over commercial LTS catalyst ($Cu\text{-}Zn/Al_2O_3$). 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 thermal cycling runs are performed at the reaction temperature of 250℃ over a time period of 130 h. We investigated the thermal cycling test for the catalyst of LTS reactor operating on/off repeatedly for the time (see figure 2). It was found that the catalyst was deactivated by carbon deposition and sintering during the thermal cycling test. Therefore, to develop of a new high performance LTS catalyst, we investigated the WGS reaction over the various catalyst formulations such as the transition metal carbides and the platinum supported cerium oxide catalysts.

The characteristics of the used catalysts are summarized in Table 1. The different calcination temperatures of ceria sample resulted in a high surface area at 600℃ and low surface area at 900℃. It was found that the Pt/ceria-A catalyst displayed better activity than the Pt/ceria-B catalyst in the LTS reaction.

It was observed that the activity of the carbide systems are greatly depending on the carburization temperature (see Fig. 3). As the temperature reaches 580℃, MoO_3 converts to Mo_2C. The formation of carbide phase begins at 615℃ and completes at 650℃. For temperatures in excess of 650℃, excess of carbon deposits on the carbide systems, thereby giving low activity. Comparison of the performances of prepared catalysts with that of commercial $Cu\text{-}Zn/Al_2O_3$ catalyst is shown in Figure 4. It was found that transition metal carbide showed higher activity than the commercial LTS catalyst at a temperature range of

200℃ to 300℃. The catalytic activity increased progressively with increasing reaction temperature. Maximum activity of Mo_2C and Pt/ceria-A were observed at 280~300℃ with a total CO conversion more than 85%. The $Cu-Zn/Al_2O_3$ catalyst displayed the highest activity in the temperature range of 270~280℃ with CO conversion of 70%.

The above results demonstrate that transition metal carbides are attractive candidates for development of high performance alternate LTS catalysts for automotive applications. The development of these materials could lead to substantial reductions in the size, weight and cost of WGS reactors.

Table 1. Characteristics of the prepared catalysts.

Catalyst	Pretreatment temperature (℃)		BET surface area	Total pore volume	Active metal surface area
	Support	Catalyst	(m^2/g)	(cc/g)	(m^2/g)
$Cu-Zn/Al_2O_3$	-	-	60	0.08025	1.035×10^{-1}
Mo_2C	-	640	61	0.03594	1.285×10^{-1}
1%Pt/ceria-A	600	550	131	0.05383	1.065×10^{-1}
1%Pt/ceria-B	900	550	58	0.05159	0.784×10^{-1}

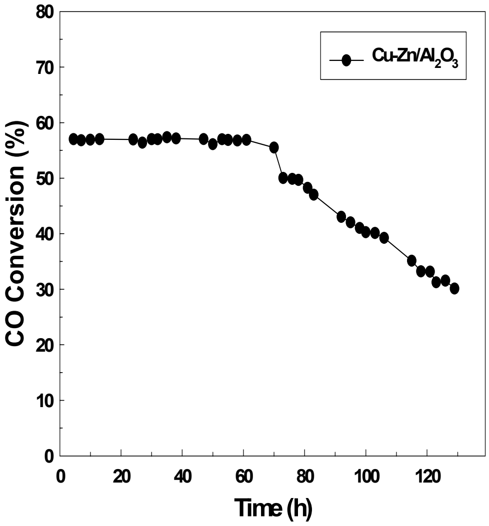

Fig. 1 The results of thermal cycling runs for WGS reaction over commercial LTS catalyst ($Cu-Zn/Al_2O_3$). The runs are performed at the reaction temperature of 250℃ over a time period of 130 h.

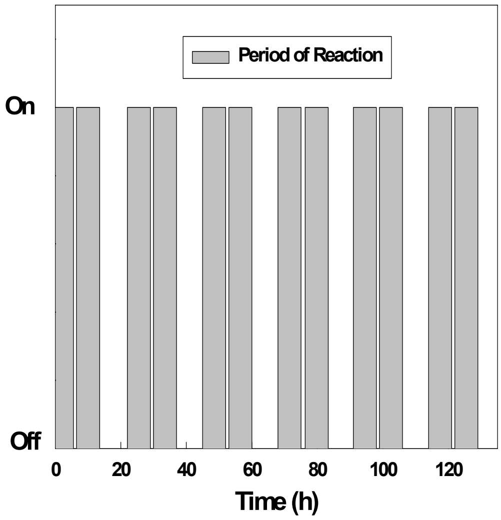

Fig. 2 The thermal cycling runs are performed at the reaction temperature of 250℃ over operating on/off repeatedly during the time period of 130h.

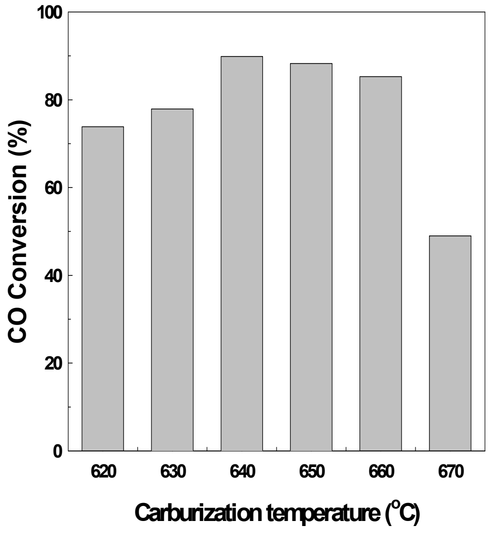

Fig. 3 Catalytic activity as a function of the carburization temperature of the molybdenum carbides prepared ; Reaction temp. 300℃, Space Velocity=10,000h^{-1}, Feed molar ratio = H_2(62.5%), H_2O (31.8%), CO(5.7%).

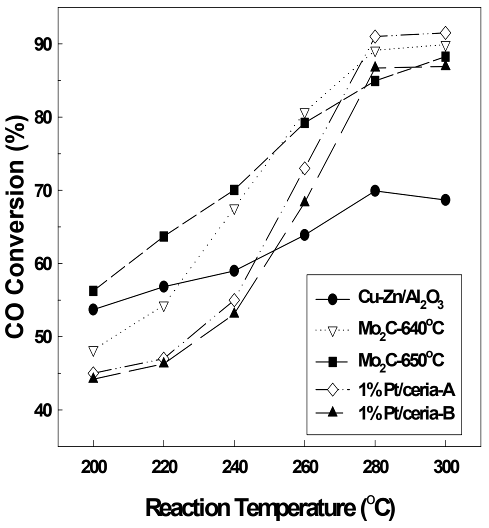

Fig. 4 Comparison of the catalytic activity of the various prepared catalyst with the commercial Cu-Zn/Al_2O_3 catalyst for the LTS reaction ; Space velocity =10,000h^{-1}, Feed molar ratio= H_2 (62.5%), H_2O (31.8%), CO (5.7%).

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