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:부분산화 개질 및 수성가스 전환 반응용 촉매

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Development of Gasoline Fuel Reformer for Fuel Cell Powered Vehicles :Partial Oxidation (POX) Reforming and Water Gas Shift Catalysts

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Introduction

Fuel processor to produce hydrogen from conventional and alternatives fuels has been developed for fuel cell powered vehicles applications. The successful development of a fuel cell-powered vehicle is dependent on the development of a fuel processor. In order to develop of a gasoline fuel processor system for integration with a proton exchanged membrane fuel cell (PEMFC), we investigated the commercial reforming catalysts and various supported transition metal formulations for POX reforming (autothermal reforming, ATR) reaction of *iso*-octane in order to develop a high performance catalyst with high activity and stability. We also investigated high temperature water gas shift (HTS) reaction over Fe_3O_4-Cr_2O_3 catalysts and low temperature shift (LTS) reaction over $Cu/ZnO/Al_2O_3$ catalyst to remove CO from the hydrogen-rich stream produced by POX reforming of *iso*-octane. In our previous work [1,2], we pointed out the problems of commercial catalysts in the gasoline fuel processor system, and suggested the necessity of the development of high performance catalysts. As a part of the development of gasoline fuel processor for fuel cell-powered vehicles applications, the POX reforming reaction over supported transition metal catalysts and the LTS reaction over transition metal carbides and platinum supported cerium oxide catalysts were investigated.

Experimental

1. Catalysts

The commercial naphtha reforming catalyst (NRC) for gasoline reforming, HTS (Fe_3O_4-Cr_2O_3) and LTS ($Cu/ZnO/Al_2O_3$) catalysts for clean up of CO were obtained from ICI in the form of pellets. However, all the catalysts in this work were used in the form of powder with a mesh size of 120/230, after crushing.

Several compositions of the oxide-based formulations represented as $M/MgO/Al_2O_3$ and $M/M_1/MgO/Al_2O_3$(where M and M_1 = Ni, Co, Fe, Mo and/or Cr) have been prepared for the POX reforming of *iso*-octane. The various catalyst formulations were prepared by the method of incipient wetness of the γ-alumina with aqueous solutions of the corresponding metal nitrate [3]. Molybdenum carbide catalysts were synthesized by the carburization methods [4], and platinum supported cerium oxide catalysts were prepared by the impregnation method [5] for LTS reaction.

2. Gasoline fuel processor system

Gasoline fuel processor system consists of six sections: feed supply, evaporator, POX reforming reactor, HTS reactor, LTS reactor and GC. The gases were delivered by mass flow controllers, and H_2O and liquid fuels were fed by a liquid delivery pump (Young Lin Co., model M930). Evaporator and POX reforming reactor made up of an Inconel 600 tube (0.095m I.D. and 0.20 m length) were used. The HTS and LTS reactors made up of Inconel 600 tube (0.075m I.D. and 0.20m length) were employed 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℃ of the catalyst bed temperature. Unreacted H_2O was removed by an ice trap and then gas effluent was analyzed by on-line gas chromatograph (HP-5890 SeriesⅡ) equipped with TCD using a carbosphere column (10″×1/8″ SS, 80/100 meshes). The reaction products were identified by GC/MS(HP-5890/5971) with an HP-1 capillary column (0.0002m O.D. and 50m length).

Results and Discussion

1. Gasoline fuel processor system

In our previous works [1-3], we carried out POX reforming reaction of *iso*-octane and HTS/LTS reaction over commercial catalysts, and investigated the effect of the operating conditions such as reaction temperature, O/C molar ratio, H_2O/C molar ratio, space velocity and the effect of impurities contained in fuels. It was found that reaction temperature of 700 ℃, feed molar ratios of H_2O/C=3 and O/C=1 were desired for the POX reforming of *iso*-octane over commercial catalyst.

The WGS reaction is a critical step during the fuel processing since CO poisons the PEM electron catalyst. To reduce the CO concentration, the reformatted gas from POX reaction of gasoline undergoes a water gas shift (WGS) reaction, where steam is reacted with CO to form H_2 and CO_2. The exit gas from the HTS reactor in this system is cooled and passed into the LTS reactor.

From the preliminary experimental results [1, 3-5] and the recommendation from the catalyst manufacturer, the reaction temperatures used in HTS and LTS reactors were determined at 450℃ and 250℃, respectively. The product distribution data from three different reaction stages over the commercial catalysts such as ICI naphtha reforming catalyst, HTS catalyst and LTS catalyst are shown in Figure 1. The POX reforming reaction of *iso*-octane containing less than 5 ppm of sulfur was carried out at the reaction condition of space velocity 8776 h^{-1} and molar ratios of H_2O/C = 3 and O/C

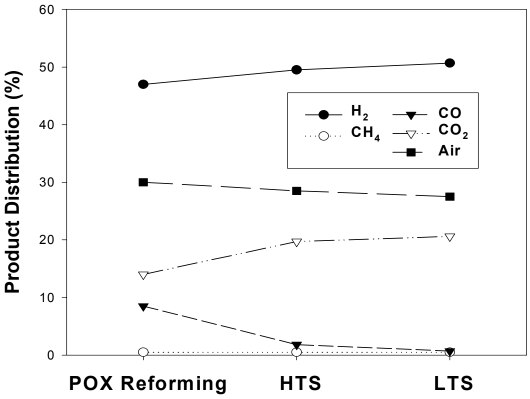

Fig. 1 The product distribution from three different reaction stages over commercial catalysts; NRC, HTS and LTS catalyst. The POX reforming over the NRC catalyst was carried out at the reaction condition of space velocity 8776h^{-1}, molar ratio H_2O/C=3 and O/C=1. Subsequently, HTS and LTS reaction were respectively, carried out at 450℃ and at 250℃.

= 1. Subsequently, HTS and LTS reactions were carried out at 450℃ and 250℃, respectively. The H_2 and CO_2 concentrations after the gases passed through HTS and LTS reactors increased, while those of CO and CH_4 decreased. We confirmed that the concentration of CO in hydrogen-rich stream is reduced to less than 3000 ppm as the reformated gas from POX reforming of gasoline over naphta reforming catalyst was passed through HTS and LTS reactors. If we find the optimum conditions for the fuel processor system using three different reaction stages, we will be able to reduce the concentration of CO to less than 2000 ppm. WGS reactors, charged with currently available commercial HTS/LTS catalysts, constitute about a third of the mass, volume and cost of the fuel processor system [4]. The Partnership for a New Generation of Vehicles (PNGV) has set up a goal to reduce the weight of the shift reactors to 75%. In conclusion, in order to reduce the concentration of CO in hydrogen-rich stream and to compact the size of fuel processor, a preferential partial oxidation (PROX) reactor and new high-performance catalysts with sulfur- and coke-resistance has to be developed.

2. POX Reforming Reaction

In our previous work [1,2], we identified the problems of catalyst deactivation by carbon deposition and sulfur poisoning in the POX reforming reaction of *iso*-octane over the commercial reforming catalysts. Therefore, we investigated various supported transition metal formulations for POX reforming reaction of *iso*-octane to develop a high performance catalyst with coke- and sulfur-resistance. Most of the catalyst formulations displayed reasonably good activity towards the POX reforming of *iso*-octane. The hydrogen selectivity of some systems was much higher than that of the commercial ICI and HT catalysts tested under the same conditions [1,2,3]. Figure 1 shows the effect of various minor components in Ni-based systems represented by the general formula $Ni_{(major)}M_{1(minor)}/\ MgO/Al_2O_3$. In the case of the systems possessing Ni as the major component, both Fe and Co are very effective components, which in very small amounts can considerably enhance the performance of the Ni-based systems. The considerable enhancement in the catalytic activities of the nickel based systems dopped with small amounts of other active components may be caused by a synergistic effect of the active components and of the supports, resulting in the proper dispersion of the active components and thereby, providing more active sites for the reaction. The screening test revealed that the formulations based on Ni as the major active component and Fe or Co as the minor component are promising systems with comparable activity or even superior to the commercial systems [1,2,3]. Also, some KIST catalysts displayed better activity and sulfur tolerance than the commercial catalysts in the POX reforming reaction of *iso*-octane containing sulfur [1,2].

3. Low Temperature Shift (LTS) Reaction

Molybdenum carbide catalysts were synthesized by the carburization of molybdnum oxide, and the carburization temperature was determined by thermal gravimetric analysis (TGA) using a Cahn Instruments TG-171 [4,5]. 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. It was found that the activity of carbide catalysts in WGS reaction is greatly dependent on the carburization temperature.

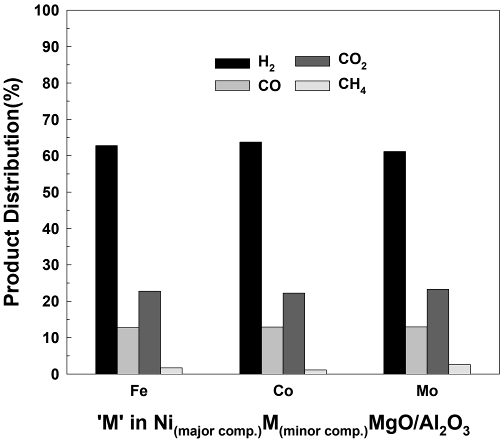

Fig. 2 The effect of minor components in Ni-based systems represented by the general formula $Ni_{(major)}M_{(minor)}MgO/Al_2O_3$ for the POX reforming of *iso*-octane. Reaction temperature = 700°C; space velocity = 8776h^{-1}; feed molar ratios of H_2O/C = 3 and O/C = 1.

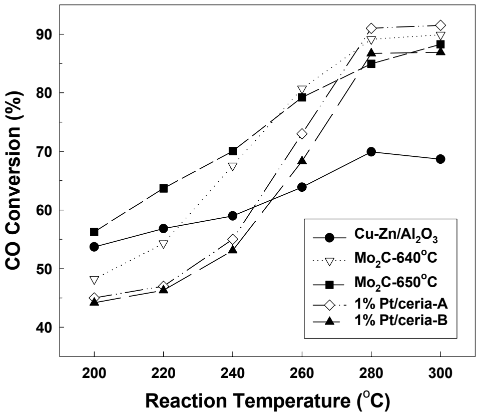

Fig. 3 Comparison of the catalytic activity of the various prepared catalyst with the commercial $Cu-Zn/Al_2O_3$ catalyst for the LTS reaction ; Space velocity =10,000h^{-1}, Feed molar ratio= H_2 (62.5%), H_2O (31.8%), CO (5.7%).

Comparison of the prepared catalysts with commercial $Cu-Zn/Al_2O_3$ catalyst is shown in Figure 2. It was found that transition metal carbide showed higher activity than the commercial LTS catalyst at a temperature range of 200℃ to 300℃ and the catalytic activity progressively increased with increasing reaction temperature. Maximum activity of Mo_2C and 1%Pt/ceria 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 a CO conversion of 70%. The results demonstrate that transition metal carbides are attractive candidates of LTS catalyst for automotive applications. The development of high performance metal carbides could lead to substantial reductions in the size, weight and cost of WGS reactors.

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