Development of A new efficient hydrogen production system by using catalyst at low temperature and membrane reactor

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1. Introduction

It seems there has been a recent interest in environmental issues such as energy crises, global warming and so on. Therefore hydrogen is expected to play a major role in the future as a carbon free energy carrier. Its use in fuel cells is especially advantageous, due to their high efficiency and the complete absence of toxic emissions. The hydrogen is conventionally produced in large scale by the steam reforming of hydrocarbons such as methane. The onsite hydrogen station which produces hydrogen in small area should be more compact. Hydrogen production by steam reforming process consists of reformer, CO conversion, and a gas purification unit which reduces the CO content of the hydrogen rich gas. Especially it is important to reduce the volume of CO conversion, and purification processes. In this study, I attempt to reduce the volume of purification process by using membrane reactor for CO shift conversion reaction. The membrane reactor uses a polymer membrane as a CO_2 separation membrane, which has low heat resistant of less than 180°C, so it cannot use at a conventional reaction temperature of 250°C. The aim of this work is to develop high activity CO conversion catalysts at low temperature.

2. Experimental

Pt catalyst is prepared by impregnate method. Cu/Zn catalyst is prepared by glycine-nitrate process or co-precipitation method from metal nitrates.

3. Results and discussion

Figure 1 shows CO conversion at 200 °C, 180 °C, 160 °C, and 140 °C. Gas is fed by follow ratio ; H_2 : CO : CO_2 : H_2O = 59 : 4 : 14 : 23. In legend, CZA means Cu/Zn/Al, #1 means the catalysts prepared by the co-precipitation method, #2 means the catalysts prepared by the glycine nitrate process.CeO_2-supported Pt catalyst (Pt content 10 %) and 3.4 % Nb doped Cu/Zn/Al show a high CO conversion at low temperature. The activity of Nb-doped catalyst shows maximum value at 3 % of dope amount. Figure 2 shows the effect of CO_2 concentration on CO conversion. CO conversion decreased with increasing

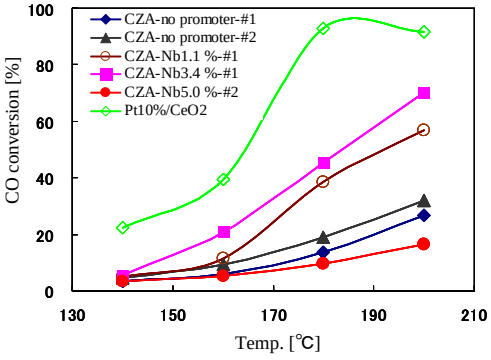

Figure.1 CO conversion of each catalyst

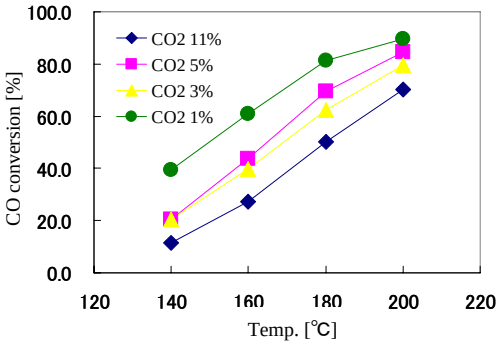

Figure.2 Influence of CO_2 concentration

CO_2 concentration. It is well known that CO_2 is an inhibitor for CO shift reaction using Cu-based catalyst so activity decreased with increasing CO_2 concentration. From these results, it was clarified that Nb acts as a CO_2 adsorbent and the activity for CO shift reaction was improved. By use of the membrane reactor CO conversion is expected to increase further because CO_2 is separated from reaction system.

Figure 3 shows the effect of doping other metals on CO conversion. Nb is most suitable as dope-metal but Mg also enhances the activity at low temperature.

After CO shift conversion process, CO_2 concentration can be less than 0.1 % by using the CZA-Nb catalyst prepared and the membrane reactor. As for study of total system of hydrogen station for 300 Nm^3/h of hydrogen production, it was confirmed that using membrane reactor and the catalyst having high activity at low temperature, volume of PSA (Pressure Swing Adsorption) and the area of the hydrogen station can be reduced by 1/4 and 1/2, respectively, and that H_2 recovery ratio also increased up to 92 % from 75 %. Making the hydrogen station compact and raising the energy efficiency in the hydrogen production, CO_2 emission can be decreased.

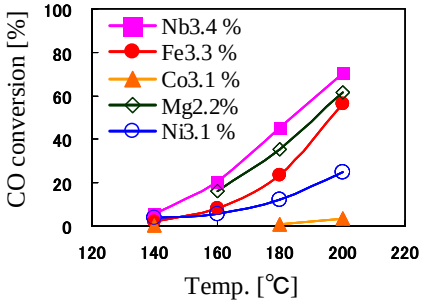

Figure.3 The effect of doping other metals on CO conversion

4. Conclusions

The precious metal-based catalyst and Cu-based catalysts are developed, which have high activity for the CO shift reaction at low temperature and are applicable to membrane reactors. It was clarified that the resistance against CO_2 is improved by adding Nb to standard Cu/Zn/Al catalyst.