촉매산화를 통한 수소흐름내의 일산화탄소의 제거

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The removal of carbon monoxide in dihydrogen stream with catalytic oxidation

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Introduction

The polymer electrolyte fuel cell (PEMFC) is a promising candidate for utilizing hydrogen to produce electricity. Although a number of sources of hydrogen are known, most attractive one, at present, is hydrocarbons such as oil, natural gas, coal and biomass. To extract hydrogen from these, a couple of reactions should be carried out such as reforming and water-gas shift reactions. Until now, Pt has been utilized for anode of PEMFC and is prone to be poisoned with minute amounts of CO in dihydrogen stream. Therefore, carbon monoxide should be removed completely prior to fuel cell. Methanation and selective oxidation were proposed to accomplish this goal. CO removal through methanation does not require the introduction of any gases in the hydrogen-rich gas stream, while the selective oxidation of CO needs the introduction of air. However, methanation of CO consumes three molecules of dihydrogen per one molecule of CO, while dihydrogen is not consumed by the selective oxidation of CO assuming that dihydrogen is not oxidized with oxygen. Takenaka et al [1] investigated complete removal of carbon monoxide in hydrogen-rich gas stream through methanation over supported metal catalysts and found that Ni/ZrO_2 and Ru/TiO_2 were the most effective catalysts. Kim and Cha [2] studied $CuO-CeO_2$ mixed oxide catalysts for CO clean-up by selective oxidation in hydrogen-rich mixtures and reported that these catalysts had advantages over supported noble metal catalysts event though a slow, reversible deactivation was observed. Son et al [3] studied $Pt/\gamma-Al_2O_3$ for low-temperature preferential oxidation of CO in H_2 and found that a new pretreatment involving saturating the reduced catalyst with water and allowing it to vaporize during reduction enhanced the selective catalytic oxidation. Bethke and Kung [4] conducted selective CO oxidation in a hydrogen-rich stream over $Au/\gamma-Al_2O_3$ catalysts and obtained 50% selectivity at 373 K. Until now, comparison studies among catalysts active for preferential oxidation of CO in hydrogen-rich gas mixtures have not been conducted enough. In this study, the removal of carbon monoxide with catalytic oxidation over various catalysts is disclosed. Supported gold catalysts, mixed metal oxides, and supported noble metal catalysts are tested.

Experimental

Preparation of catalysts

For the preparation of $Au/\gamma-Al_2O_3$ catalysts, γ-alumina (Alfa, BET surface area = 170 m^2/g) powders were suspended in deionized water and the pH of the suspension was preadjusted to 8 with 1M NaOH. An aqueous solution of 0.01M $AuCl_3$ was subsequently added drop by drop into the slurry. After 1 h stirring at 343 K, gold-deposited alumina powders were filtered, washed several times to remove residual chloride ion, dried at 353 K, and stored as fresh samples. 20% $CuO-CeO_2$ and CuO

catalysts were prepared by a conventional precipitation method with an aqueous solution of 1 M NaOH. The Cu content in CuO-CeO$_2$ catalyst was designated as Cu/(Cu+Ce) atom ratio x 100 (at%). The gold contents were determined by an ICP. Commercial Au/Fe$_2$O$_3$/γ-Al$_2$O$_3$ catalysts were purchased and utilized without any further treatment. Commercial 1 wt% Pt/γ-Al$_2$O$_3$ and 5 wt% Pt/γ-Al$_2$O$_3$ catalysts were purchased and pre-reduced at 473 K with dihydrogen stream for 1 h before a reaction.

Selective Oxidation of CO in H$_2$-rich gas mixtures

Experiments were carried out in a small fixed bed reactor with catalysts that had been retained between 45 and 80 mesh sieves. A standard gas of 1.0 vol% CO, 1.0 vol% O$_2$, and 10 vol% H$_2$ balanced with helium was passed through the catalyst bed at atmospheric pressure. For activity tests under the wet condition, the reaction gases were directed through a water vapor saturator immersed in a constant temperature bath and fed to a reactor through a glass line warmed by a heating tape. The conversion of CO was determined through gas chromatographic analysis (HP5890A, molecular sieve 5A column) of the effluent from the reactor.

Results and Discussion

The preferential oxidation of CO in H$_2$-rich gas mixture was conducted over γ-alumina-supported Pt catalysts as shown in Fig.1. When reaction temperatures were less than a light-off temperature, 5 wt% Pt/γ-Al$_2$O$_3$ showed higher conversions of CO and O$_2$ than did 1 wt%Pt/γ-Al$_2$O$_3$. 100% CO conversion and 50% O$_2$ selectivity for CO oxidation could be maintained when the reaction temperatures was between 430 and 500 K. CO conversions decreased as the reaction temperature increased further because H$_2$ oxidation prevailed over CO oxidation at high temperatures.
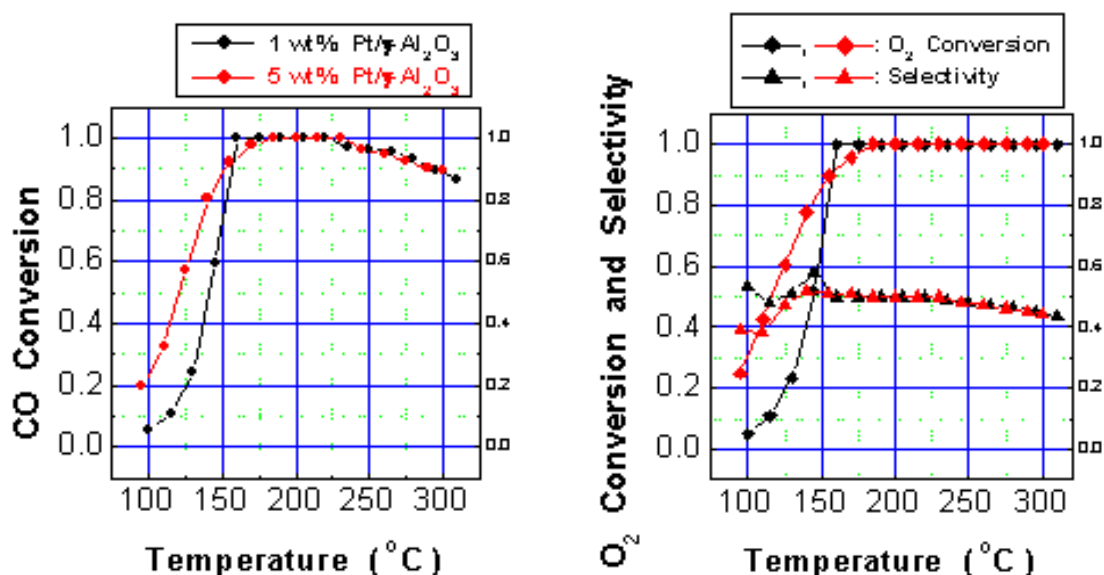

Figure 1. CO conversion, O$_2$ conversion, and O$_2$ selectivity for CO oxidation over Pt/γ-Al$_2$O$_3$ at different reaction temperatures. The reactants, 1 vol% CO, 1 vol% O$_2$ and 10 vol% H$_2$ in He, were directed through a water vapor saturator maintained at 288 K to obtain wet condition.

Commercial Au/Fe$_2$O$_3$/γ-Al$_2$O$_3$ catalysts containing 0.35 wt% Au and 10 wt% Fe were applied for selective CO oxidation. Gold catalysts showed better activity for CO oxidation in wet condition than in dry condition as shown in Fig.2. 100% CO conversion was achieved even at room temperature. However, O$_2$ selectivity for CO oxidation decreased rapidly.
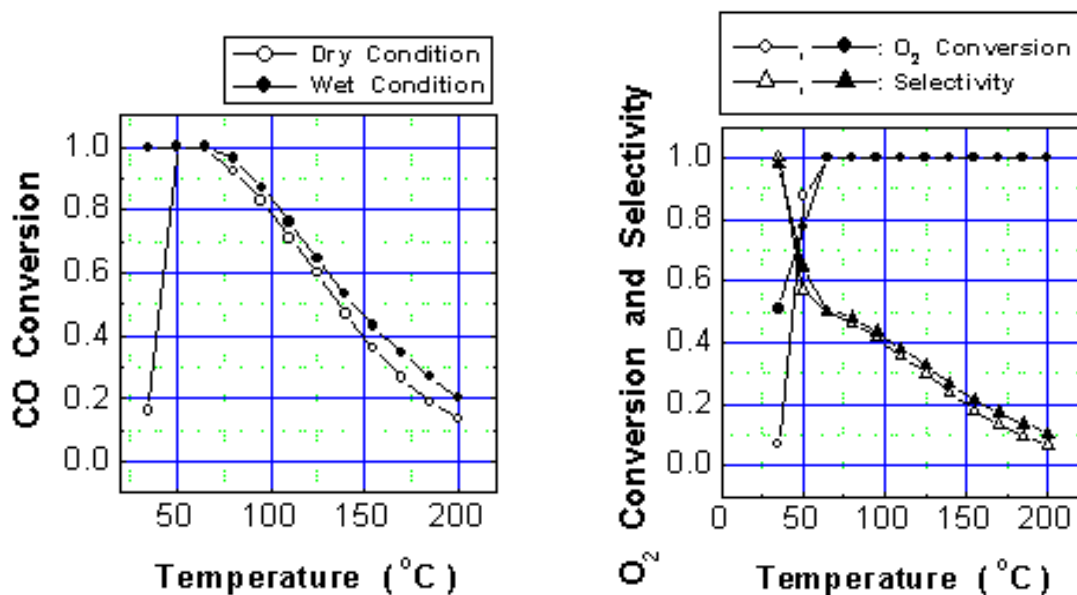

Figure 2. CO conversion, O$_2$ conversion, and O$_2$ selectivity for CO oxidation over Au/Fe$_2$O$_3$/γ-Al$_2$O$_3$ at different reaction temperatures. The reactants, 1 vol% CO, 1 vol% O$_2$ and 10 vol% H$_2$ in He, were fed directly to the catalyst in dry condition (open points) and the reactants were directed through a water vapor saturator maintained at 288 K to obtain wet condition (filled points).
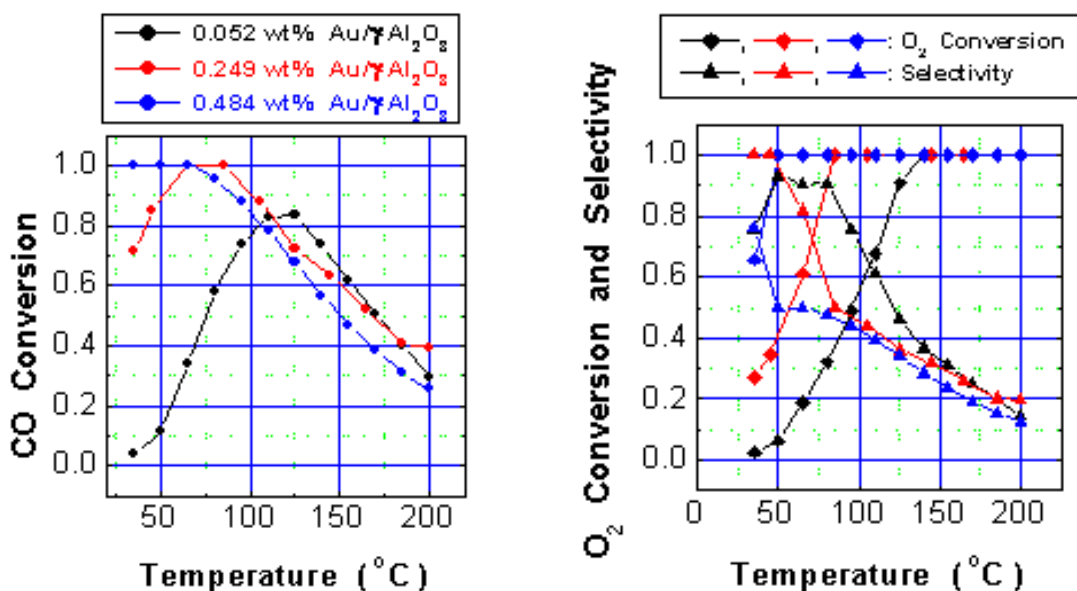

Figure 3. CO conversion, O$_2$ conversion, and O$_2$ selectivity for CO oxidation over Au/γ-Al$_2$O$_3$ at different reaction temperatures. The reactants, 1 vol% CO, 1 vol% O$_2$ and 10 vol% H$_2$ in He, were directed through a water vapor saturator maintained at 288 K to obtain wet condition.

Figure 4. CO conversion, O_2 conversion, and O_2 selectivity for CO oxidation over CuO-CeO_2 or CuO at different reaction temperatures. The reactants, 1 vol% CO, 1 vol% O_2 and 10 vol% H_2 in He, were directed through a water vapor saturator maintained at 288 K to obtain wet condition.
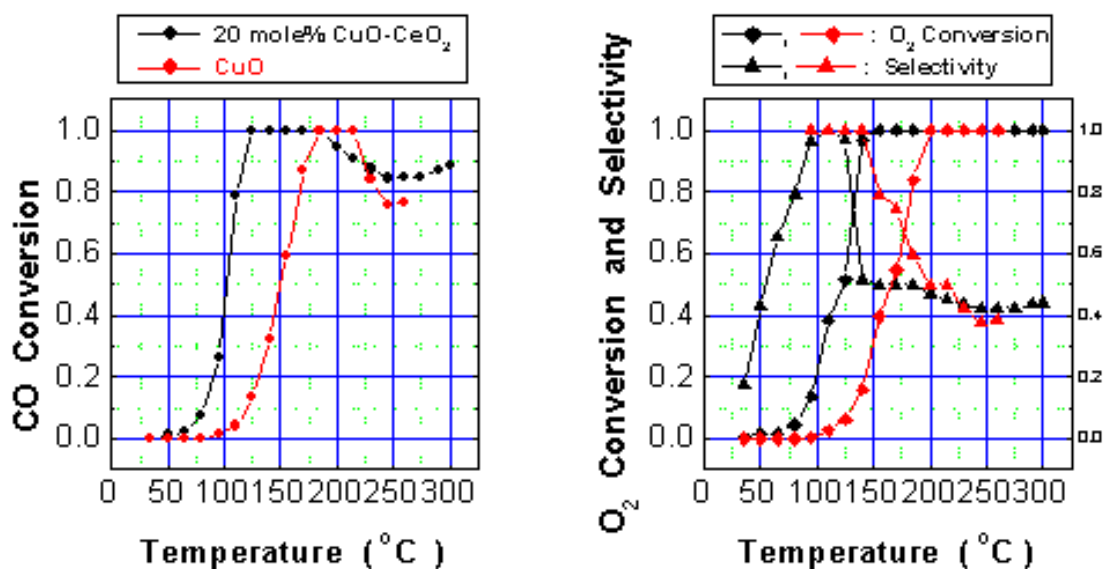
To change the catalytic activity for oxidation, Au/γ-Al_2O_3 catalysts with different Au loadings were prepared and tested for this reaction. As the Au loading decreased, CO conversion also decreased as shown in Fig.3. However, no improvement in O_2 selectivity for CO oxidation at the same CO conversion could be achieved.

20% CuO-CeO_2 catalyst was applied for this reaction. CuO catalyst was also tested for comparison. 100% CO conversion and 50% O_2 selectivity for CO oxidation could be maintained when the reaction temperature was between 400 and 450 K as shown in Fig.4. CO conversions decreased as the reaction temperature increased further because H_2 oxidation prevailed over CO oxidation at high temperatures.

Conclusion

Supported gold catalysts, CuO-CeO_2 mixed-oxide catalysts, and $Pt//\gamma$-Al_2O_3 catalysts were tested for selective oxidation of CO in hydrogen-rich stream. Each catalyst showed different reaction temperature regions to be effective in selective oxidation of carbon monoxide in dihydrogen stream.

References

[1] Takenaka S., Shimizu T., and Otsuka K., "Complete removal of carbon monoxide in hydrogen-rich gas stream through methanation over supported metal catalysts", *International Journal of Hydrogen Energy*, 29, 1065-1073 (2004).
[2] Kim D.H. and Cha J.E., "A CuO-CeO_2 mixed oxide catalyst for CO clean-up by selective oxidation in hydrogen-rich mixtures", *Catal. Lett*., 86(1~3), 107-112 (2003).
[3] Son I.H., Shamsuzzoha M., and Lane A.M., "Promotion of Pt/γ-Al_2O_3 by new pretreatment for low-temperature preferential oxidation of CO in H2 for PEM fuel cells", *J. Catal*., 210, 460-465 (2002).
[4] Bethke G.K. and Kung H.H., "Selective CO oxidation in a hydrogen-rich stream over $Au//\gamma$-Al_2O_3 catalysts", *Appl. Catal. A General* 194-195, 43-53 (2000).