Short communication

Removal of carbon monoxide from hydrogen-rich fuels by selective low-temperature oxidation over base metal added platinum catalysts

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Abstract

Various catalysts containing different catalytic materials, supports, and additives were tested for the preferential oxidation (PROX) of carbon monoxide from a hydrogen-rich gas stream. The results were analyzed based on three reactions involved in the PROX: oxidation of carbon monoxide, H_2–O_2 reaction, and methanation. The PROX reactions were performed in two reaction systems, one for catalyst screening and kinetic study and the other for simulation of the catalytic performance under real reaction conditions. The performances of PROX on different catalysts, varying active components, supports, and additives, were ranked in terms of carbon monoxide conversion and hydrogen consumption. Base metal added platinum catalysts exhibited excellent ability for the carbon monoxide removal. TPR results indicated that a new active species was formed resulting in the enhancement of catalytic activity. $PtCo/Al_2O_3$ was tested with a simulated steam-reformed fuel for confirmation of its high activity. The effect of operating conditions was analyzed on the $PtCo/Al_2O_3$, and the optimum conditions for PROX were obtained.

1. Introduction

Due to the increasing concerns regarding proton exchange membrane (PEM) fuel cell technology, the selective removal of carbon monoxide in hydrogen-rich gas has attracted much attention recently. The partial oxidation and the steam reforming processes have been used to generate hydrogen from hydrocarbon fuels, such as gasoline, natural gas, or methanol. Since carbon monoxide is always present in the gas mixture produced from these hydrocarbon fuels, it must be reduced to a level less than 20 ppm in order to avoid rapid deactivation of the platinum electro-catalyst in the fuel cells [1]. The carbon monoxide level of the gases can be reduced by the shift reaction, but such reaction is generally incapable of reducing the carbon monoxide content of the gases much below about 0.2%. Therefore, the preferential oxidation (PROX) of

carbon monoxide may be the most suitable method to reduce the amount of carbon monoxide to a suitable level for use in electrochemical fuel cells.

Researchers attempted to find a new catalyst with high activity for carbon monoxide removal and with small hydrogen consumption. Pt/Al_2O_3 was first proposed by Los Alamos National Laboratory as an effective catalyst for selective oxidation of carbon monoxide in the presence of excess hydrogen [2]. Platinum supported on zeolite catalysts could oxidize carbon monoxide much more selectively in a large excess of hydrogen with the addition of a low concentration of oxygen than a conventional Pt/Al_2O_3 catalyst [3]. Several works showed that Ru/Al_2O_3 was a more efficient catalyst than a currently used Pt/Al_2O_3 [4–6]. Au/Fe_2O_3 offered superior activity and selectivity to Pt/Al_2O_3 at low temperature and high carbon monoxide concentration because steady-state coverage of carbon monoxide on the gold surface was below saturation [7,8]. Although such advances have been made to enhance the catalytic performance, their performances are not

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good enough to reduce the carbon monoxide content to below 20 ppm, therefore, multi-stage PROX is still a necessity [1].

In this study, we examined a variety of catalysts by changing the active material, support and additive to find efficient catalysts. We could develop a highly active catalyst, and then applied it to a simulated hydrogen-rich gas mixture of a steam-reformed fuel for investigating effects of reaction conditions.

2. Experimental

γ-Alumina support was purchased from Aldrich and aerogel supports were made by the sol–gel synthesis followed by supercritical drying [9]. The active components were deposited by the incipient wetness method. After the impregnation step, the catalysts were dried at $110\,°C$ for $12\,h$ and calcined at $500\,°C$ for $4\,h$. Base metal additives were impregnated on calcined platinum catalyst using nitrate precursors followed by drying and calcination at the above conditions [10]. The catalysts studied contained 1 wt.% noble metal and 1.8 wt.% base metal, respectively.

The PROX reactions on the catalysts were performed in two fixed-bed microreactor systems operating under atmospheric pressure. Prior to each reaction test, the catalysts were reduced with a pure hydrogen stream at $400\,°C$ for $2\,h$. For catalyst screening and kinetic study, the catalysts were tested in the reaction system 1 where a feed was diluted with nitrogen and did not contain carbon dioxide and water vapor. A feed stream (hydrogen 10,100 ppm, carbon monoxide 1100 ppm, oxygen 990 ppm, and nitrogen balance) was introduced to the reactor at a total flow rate of $100\,cm^3\,min^{-1}$. Since the amount of catalyst used was kept at $0.2\,g$, the space velocity varied in the range of $7500–36,000\,h^{-1}$ depending on the catalyst density. The outlet stream was analyzed for the gases by a Thermo Environmental Instruments 48C nondispersive infrared carbon monoxide analyzer and a Hewlett Packard 6890 gas chromatograph equipped with thermal conductivity detector and a column packed with Carbosphere.

The reaction system 2 was designed for the catalytic activity test using the simulated hydrogen-rich gas mixture for our steam-reformed fuel from methanol. Our steam reformer operating at $280\,°C$ produced a gas stream containing 8000–15,000 ppm of carbon monoxide. A feed stream (hydrogen 71.92%, carbon dioxide 23.46%, carbon monoxide 7700 ppm, and air 38,500 ppm) was introduced to the reactor containing $0.5\,g$ of catalyst. Water vapor equivalent to 12.1% of total dry gases was added to the feed stream. The total flow rates were $86.9–694.8\,cm^3\,min^{-1}$, therefore the space velocities were $7500–60,000\,h^{-1}$. The outlet stream was analyzed for the gases by a carbon monoxide analyzer.

The temperature programmed reduction (TPR) equipment consisted of a thermal conductivity detector (TCD) connected to a flow-control system and a programmed heating unit. Sample placed in a quartz reactor was reduced in a stream of 5% hydrogen/argon mixture (flow rate: $30\,cm^3\,min^{-1}$), with the temperature raised from 27 to $927\,°C$ at the rate of $5\,°C\,min^{-1}$.

3. Results and discussion

3.1. Noble metal catalysts

The concentrations of unreacted reactants and product gases obtained with Pt/Al_2O_3 in the reaction system 1 are presented in Fig. 1. The outlet concentration of carbon monoxide begins to decrease at $125\,°C$ and remains below 10 ppm in the temperature range of $175–200\,°C$. At higher temperatures, it gradually increases to a slight extent. About 1000 ppm of hydrogen is lost above $175\,°C$ as a result of the $H_2–O_2$ reaction, therefore, about 500 ppm of oxygen is available for the preferential oxidation of carbon monoxide in this temperature region. The gradual increase of carbon monoxide concentration is due to the scarcity of oxygen, although small decrease of hydrogen concentration in the temperature range of $200–300\,°C$ is not clearly observed in Fig. 1. The outlet concentration of carbon monoxide does not increase with temperature in an experiment with a hydrogen-free feedstream containing only carbon monoxide and oxygen [4]. Traces of methane produced above $275\,°C$ do not affect the outlet concentration of carbon monoxide significantly.

The above concentration profiles of products and remaining reactants are observed for all of platinum containing catalysts. The temperature regions, where concentrations of compounds change abruptly, shifts to higher or lower temperatures depending on the catalyst activity. With increasing temperature, carbon monoxide occupying active sites desorbs followed by oxygen adsorption and carbon monoxide oxidation. At slightly higher temperature, hydrogen can adsorb and react with oxygen. In the case of different active metal catalysts, methanation occurs at higher temperatures affecting the concentrations.
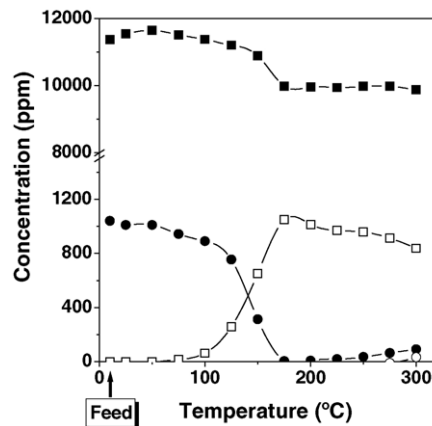

Fig. 1. Concentration profiles of reactants and products as a function of temperature over Pt/Al_2O_3 in the reaction system 1. Data are shown for hydrogen (■), carbon monoxide (●), carbon dioxide (□), and methane (○).
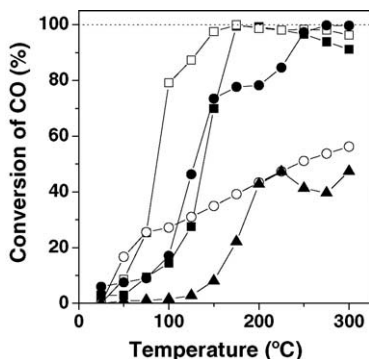
Fig. 2. Conversion of carbon monoxide over various noble metal catalysts during temperature run-up in the reaction system 1. Data are shown for Pt/Al$_2$O$_3$ (■), Ru/Al$_2$O$_3$ (□), Rh/Al$_2$O$_3$ (●), Pd/Al$_2$O$_3$ (○), and Au/Fe$_2$O$_3$ (▲).

Carbon monoxide conversion efficiencies measured in the reaction system 1 over five noble metal catalysts are presented in Fig. 2. The overall activity of carbon monoxide oxidation decreases in the order of Ru/Al$_2$O$_3$ > Pt/Al$_2$O$_3$ > Rh/Al$_2$O$_3$ > Pd/Al$_2$O$_3$ > Au/Fe$_2$O$_3$, although the order of activity with temperature is altered in several temperature regions. Ru/Al$_2$O$_3$ exhibits higher activity of carbon monoxide removal than Pt/Al$_2$O$_3$ in the temperature range of 25–175 °C and above 250 °C. Methane produced on Ru/Al$_2$O$_3$ above 150 °C suggests that the higher activity of Ru/Al$_2$O$_3$ at high temperatures is due to methanation. The conversion of carbon monoxide on Rh/Al$_2$O$_3$ does not approach 100% by selective oxidation alone up to 250 °C. At higher temperatures, it approaches 100% with the help of methanation. The conversion of carbon monoxide on Pd/Al$_2$O$_3$ shows a gradually increasing pattern without sharp increase, which is different from those observed on other catalysts. The catalytic activities of Pd/Al$_2$O$_3$ and Au/Fe$_2$O$_3$ are very poor compared with other three catalysts.

The hydrogen loss is in the order of Pt/Al$_2$O$_3$ ≒ Au/Fe$_2$O$_3$ < Ru/Al$_2$O$_3$ ≒ Rh/Al$_2$O$_3$ < Pd/Al$_2$O$_3$. Ru/Al$_2$O$_3$ and Rh/Al$_2$O$_3$ consume large amounts of hydrogen above 250 °C because methanation occurs in this temperature region. On Pd/Al$_2$O$_3$, the H$_2$–O$_2$ reaction occurs to a great extent at relatively low temperature (75 °C) resulting in large loss of hydrogen.

3.2. Platinum catalysts supported on different materials

The dependences of carbon monoxide conversion on support materials and temperature in the reaction system 1 are shown in Fig. 3. The activity of carbon monoxide oxidation decreases in the order of Pt/C > Pt/aerogel-SiO$_2$ > Pt/Al$_2$O$_3$. This order is not reversed in the whole temperature range, which is a different trend to one observed with different metal catalysts. The ranking of activity corresponds to the decreasing order of metal-support interaction, i.e., alumina > silica > carbon [11]. When gaseous carbon monoxide

adsorbs on platinum surface, the carbon−oxygen bond of carbon monoxide is weakened [12]. In this situation, carbon monoxide will more easily insert an oxygen atom and will quickly desorb as carbon dioxide [13]. Weak metal-support interaction promotes weakening of the carbon−oxygen bond of carbon monoxide by facilitating the electronic transfer from carbon to platinum.

Hydrogen is consumed on all catalysts on different supports to the extent of 1000 ppm at slightly higher temperature region than those of carbon monoxide oxidation. The overall trends of the outlet hydrogen concentration with different catalysts are similar to that of Pt/Al$_2$O$_3$ as shown in Fig. 1 except that the region of hydrogen consumption shifts to lower temperatures depending on the catalysts. Therefore, the order of hydrogen loss is the same as that of carbon monoxide removal, i.e., Pt/C > Pt/aerogel-SiO$_2$ > Pt/Al$_2$O$_3$. Weak metal-support interaction also promotes the H$_2$–O$_2$ reaction as well as oxidation of carbon monoxide.

3.3. Platinum catalysts with base metal additives

Cobalt, nickel, and manganese could improve the performance of Pt/Al$_2$O$_3$ greatly among additives tried. Fig. 4 shows the conversion of carbon monoxide on base metal
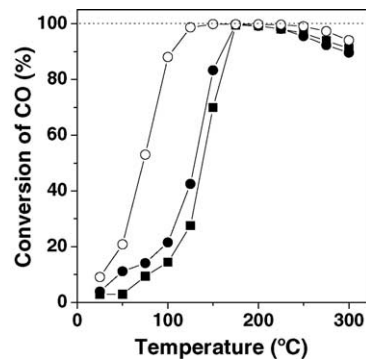

Fig. 3. Conversion of carbon monoxide over platinum catalysts supported on various materials during temperature run-up in the reaction system 1. Data are shown for Pt/Al$_2$O$_3$ (■), Pt/aerogel-SiO$_2$ (●), and Pt/C (○).
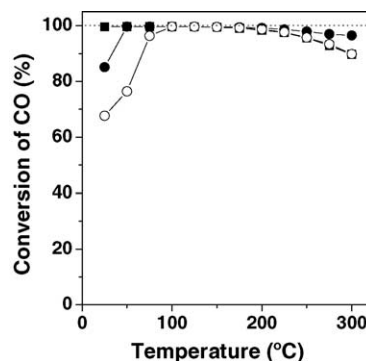

Fig. 4. Conversion of carbon monoxide over base metal added platinum catalysts during temperature run-up in the reaction system 1. Data are shown for PtCo/Al$_2$O$_3$ (■), PtNi/Al$_2$O$_3$ (●), and PtMn/Al$_2$O$_3$ (○).
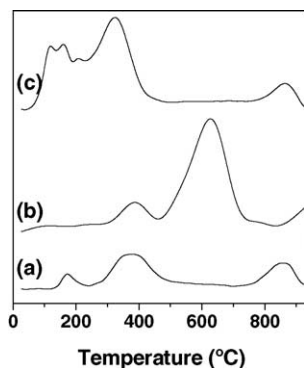
Fig. 5. TPR patterns of (a) Pt/Al_2O_3 (b) Co/Al_2O_3, and (c) $PtCo/Al_2O_3$.

added Pt/Al_2O_3 in the reaction system 1. All of them exhibit excellent performance for selective oxidation of carbon monoxide achieving more than 90% conversion in most of the temperature region tested. $PtCo/Al_2O_3$ reduces the outlet concentration of carbon monoxide to below 10 ppm in a wide temperature range of 25–175 °C. $PtNi/Al_2O_3$ shows lower conversion than that of $PtCo/Al_2O_3$ at room temperature, but the former removes carbon monoxide more efficiently than the latter at higher temperature regions of 200–300 °C by the help of methanation.

Pt/Al_2O_3 containing base metal offer another advantage of consuming substantially smaller amounts of hydrogen in oxidation of carbon monoxide under hydrogen-rich atmosphere than other catalysts. About 300 ppm of hydrogen is lost by the H_2–O_2 reaction up to 200 °C. Above this temperature hydrogen loss increases as a result of methanation, especially on $PtNi/Al_2O_3$. However, methane is not observed with $PtMn/Al_2O_3$ even at higher temperatures, which suggests that the hydrogen loss on $PtMn/Al_2O_3$ is very small.

In order to investigate the reason of activity increase, we have performed temperature-programmed reduction of $PtCo/Al_2O_3$ and their components as shown in Fig. 5. The TPR pattern of the base cobalt catalyst, curve (b), shows a major reduction peak around 600 °C. When cobalt is added to platinum catalysts, complicated peaks are observed below 500 °C, curve (c). Peaks corresponding to the reduction of the cobalt species alone are not observed distinctly with $PtCo/Al_2O_3$, suggesting that most of cobalt atoms are located around platinum species interacting strongly with platinum. This interaction also decreases the metal-support interaction between platinum and alumina. Platinum and the cobalt may form a new phase with lower reduction temperature resulting in a pronounced catalytic synergy effect. Accordingly, the excellent performance of the base metal containing catalyst is due to the formation of a new phase which may be more active for selective oxidation of carbon monoxide than Pt/Al_2O_3.

3.4. PROX on $PtCo/Al_2O_3$ in real conditions

The results obtained in the reaction system 1 show that $PtCo/Al_2O_3$ is the most active catalyst. $PtCo/Al_2O_3$ was
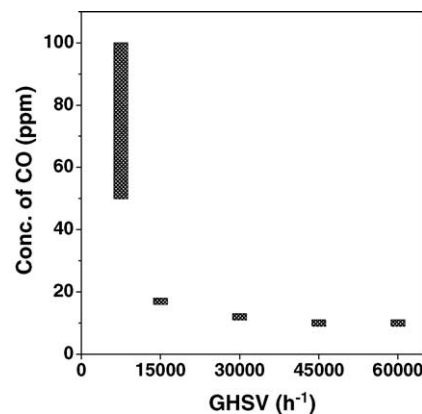

Fig. 6. Influence of GHSV on the outlet concentration of carbon monoxide with $PtCo/Al_2O_3$ in the reaction system 2. The inlet concentration of carbon monoxide = 8000 ppm, temperature = 80 °C, and $O_2/CO = 1$.

tested in the reaction system 2 with the reactant to simulate the hydrogen-rich gas stream from a steam reformer. The catalytic behavior of $PtCo/Al_2O_3$ was characterized from four viewpoints: presence of water and carbon dioxide, space velocity, temperature, and the concentration of oxygen.

As mentioned in Section 2, carbon dioxide and water vapor was introduced in the reaction system 2. The outlet concentration of carbon monoxide is scarcely affected by the presence of carbon dioxide in the reactant stream at 90 °C suggesting that carbon dioxide does not compete with carbon monoxide for adsorption sites nor the former converts to the latter by the reverse water-gas shift reaction. However, the presence of water vapor greatly influences the removal of carbon monoxide. The extent of inhibition by water vapor was found to be different with temperature and space velocity.

The effect of space velocity on the outlet concentration of carbon monoxide is small as shown in Fig. 6. With space velocity, the outlet concentration of carbon monoxide remains in 10–100 ppm, which corresponds to 98.8–99.9% of carbon monoxide conversion. This suggests that the catalytic activity of $PtCo/Al_2O_3$ is enough up to gas hourly space velocity
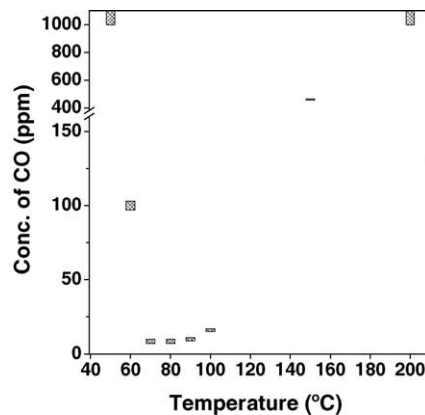

Fig. 7. Influence of operating temperature on the outlet concentration of carbon monoxide with $PtCo/Al_2O_3$ in the reaction system 2. The inlet concentration of carbon monoxide = 8000 ppm, GHSV = 15,000 h^{-1}, and $O_2/CO = 1$.
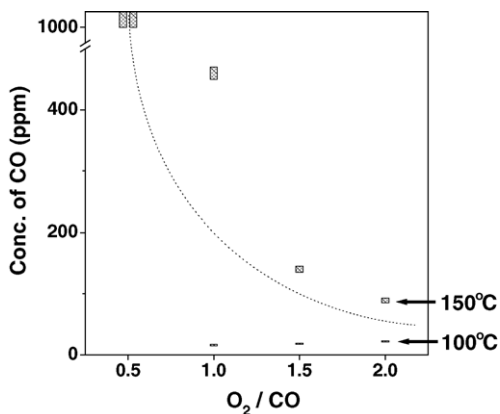
Fig. 8. Influence of O_2/CO molar ratio on the outlet concentration of carbon monoxide with $PtCo/Al_2O_3$ in the reaction system 2. The inlet concentration of carbon monoxide = 8000 ppm, GHSV = 15,000 h^{-1}, and temperature = 80 °C.

(GHSV) of 60,000 h^{-1}. However, the trend of the change in the outlet carbon monoxide concentration with space velocity is opposite to what one expects. With increasing space velocity, the conversion of carbon monoxide is enhanced. The lower conversion of carbon monoxide at 7500 h^{-1} may be related to the influence of water vapor. It is supposed that a portion of water vapor may be condensed on catalyst bed at relatively low temperature, 80 °C, and cannot be effectively removed at such low space velocity.

The effect of temperature on the PROX reaction in the reaction system 2 is shown in Fig. 7. With increasing reaction temperature, the outlet concentration of carbon monoxide decreases and it remains below 10 ppm in the temperature range of 70–90 °C. Further increase of temperature reduces the conversion of carbon monoxide as a result of oxygen consumption by the H_2–O_2 reaction and the shift thermodynamics. In the case of reaction system 1, reverse water-gas shift reaction does not occur even at higher temperatures. It is confirmed that the outlet concentration of carbon monoxide does not increase with temperature in an experiment with a hydrogen-free feedstream containing only carbon monoxide and oxygen [4]. However, the feed contains an excess of carbon dioxide in reaction system 2. Therefore, reverse water-gas shift reaction as well as deficiency of oxygen increases the outlet carbon monoxide concentration at higher temperatures. The influence of temperature in the reaction system 2 is roughly similar to the case in the reaction system 1, but its extent is much greater than that in the reaction system 1 because of the reverse water-gas shift reaction.

The effects of oxygen concentration on the PROX reaction at 100 and 150 °C are shown in Fig. 8. Since the H_2–O_2 reaction occurs to a small amount at 100 °C, 1.0 of O_2/CO is sufficient to reduce the outlet carbon monoxide concentration to below 10 ppm. However, the H_2–O_2 reaction occurs to greater extents at 150 °C, therefore, the outlet carbon monox-

ide concentration decreases with the ratio of oxygen to carbon monoxide.

4. Conclusions

Based on the above discussions and experimental observations, we may conclude the following about the reaction characteristics of the catalysts for selective oxidation of carbon monoxide:

1. Ru/Al_2O_3 is more active than Pt/Al_2O_3, but hydrogen consumption occurs greatly as a result of methanation. Other catalysts including Rh/Al_2O_3, Pd/Al_2O_3, and Au/Fe_2O_3 cannot oxidize carbon monoxide more efficiently than conventionally used Pt/Al_2O_3.
2. When platinum is supported on different supports, the activity for carbon monoxide removal slightly increases in the decreasing order of metal-support interaction, i.e., Pt–Al_2O_3 composite aerogel < Pt/Al_2O_3 < $Pt/aerogel$-SiO_2 < Pt/C.
3. Addition of base metal to Pt/Al_2O_3 enhances their performances for PROX to a great extent. The formation of a new active phase by the modification contributes to the enhancement of catalytic activity.
4. With the product stream from a steam reformer, $PtCo/Al_2O_3$ reduces CO concentration to below 10 ppm under following conditions: space velocity > 30,000, temperature = 70–90 °C, and O_2/CO = 1.

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