A comparative study of catalysts for the preferential CO oxidation in excess hydrogen

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Abstract

Selective CO oxidation in the presence of excess hydrogen was studied over metal oxides (CoO and CuO–CeO$_2$), supported gold catalysts (Au/γ-Al$_2$O$_3$, Au/CuO, Au/CeO$_2$/γ-Al$_2$O$_3$, Au/CuO–CeO$_2$ and Au/CeO$_2$), and supported Pt catalysts (Pt/γ-Al$_2$O$_3$, Pt–Ni/γ-Al$_2$O$_3$, and Pt–Co/γ-Al$_2$O$_3$). The methanation was dominant over CoO in the presence of excess H$_2$. CuO–CeO$_2$ was quite selective for CO oxidation at low temperatures. However, the presence of CO$_2$ and H$_2$O retarded its catalytic activity. No beneficial effect to CO$_2$ selectivity was observed when Pt, Ru, Ni, and Co was added to CuO–CeO$_2$ as a modifier. Supported gold catalysts showed the high CO conversion at low temperatures. However, the CO$_2$ selectivity decreased noticeably with increasing H$_2$ concentration in a reactant. Pt–Ni/γ-Al$_2$O$_3$ showed the highest CO conversion with a high CO$_2$ selectivity over a wide reaction temperature among above catalysts examined at the same reaction condition. This catalyst also showed the best performance in the presence of 2 vol.% H$_2$O and 20 vol.% CO$_2$.
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1. Introduction

Reforming of hydrocarbons followed by water–gas shift reaction is commonly used to produce the hydrogen fuel for the polymer electrolyte membrane fuel cell (PEMFC), which has been attracting much attention in the application to electric vehicles or residential power-generations [1]. However, 0.5–1 vol.% of carbon monoxide is usually contained in the hydrogen fuel from the water–gas shift reactor. Because platinum, an anode of PEMFC, is prone to be poisoned in the presence of small amounts of CO in the hydrogen stream, carbon monoxide should be removed to a trace-level. The acceptable CO concentration is below 10 ppm at Pt anode and below 100 ppm at CO-tolerant alloy anodes [2]. Several different methods for the CO removal have been studied including purification with metal membrane [3], selective CO oxidation [2], and CO methanation [4]. Among them, the

selective oxidation has been accepted as the most effective way to achieve this goal. In this system, the following three reactions can occur.

$$CO + (1/2)O_2 \rightarrow CO_2 \tag{1}$$

$$H_2 + (1/2)O_2 \rightarrow H_2O \tag{2}$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O \tag{3}$$

The third reaction, which is called methanation, should be avoided except that CO concentration was quite low because it consumed relatively large amounts of hydrogen compared with the preferential CO oxidation (PROX). A number of catalysts more active for the first reaction than the second reaction have been reported [2,5–49]. They can be grouped into metal oxides [5–20], supported gold catalysts [21–29], supported Rh catalysts [30], supported Ru catalysts [31,32], and supported Pt catalysts [32–49]. CoO was reported to show the best performance among 3d transition metal oxides [5]. Among mixed metal oxides, CuO–CeO$_2$ has been claimed to be quite active and intensively studied by several groups [6–20]. The effect of preparation method [11–13], pretreatment condition

[14], promoters [15–18], and support [19,20] on the PROX has been reported. For supported gold catalysts, Au/Mn$_2$O$_3$ [21], Au/Fe$_2$O$_3$ [22,23], Au/MOx/Al$_2$O$_3$ [24,25], and Au/CeO$_2$ [26–29] have been reported to be active for the PROX. Supported platinum catalysts have been considered to be promising since the PROX in excess hydrogen stream attracted attention for its practical applications. However, they usually showed notice-able activities only above 423 K [33–35]. Because PEMFC is usually operated below 423 K, catalysts operating at low temperatures can be more plausible. To increase catalytic activities at low temperatures, different methods have been tried for supported platinum catalysts. The pretreatment of Pt catalyst with water vapor was reported to enhance low-temperature catalytic activities for the PROX [36]. Several groups have reported that the PROX at low temperatures could be enhanced by the addition of 2nd metals such as Fe [37–40], Ce [41], Co [42–46], Ni [42,44], Mn [44], and alkali metals [46–49].

Most PROX catalyst was proved its superiority by comparison with a reference catalyst selected by each research group under different reaction conditions. Until now, only limited comparisons among these PROX catalysts have been conducted at the same reaction condition [50]. Recently, we found that supported Pt–Ni and Pt–Co catalysts could be promising PROX catalysts [42,43]. These catalysts were prepared by a co-impregnation method from metal precursors containing no chlorine compounds. In this work, these catalysts were compared with other well-known PROX catalysts under the same reaction condition.

2. Experimental

The cobalt oxide (Co$_3$O$_4$) was prepared by a precipitation method. The pH of an aqueous solution of Co(NO$_3$)$_2$ was increased to 8 by an addition of 1 M NaOH solution. The slurry was aged for 1 h at 353 K, filtered, and washed with de-ionized water several times to remove sodium ion. The cake was then dried at 373 K overnight. Cobalt oxide was reduced with hydrogen at 473 K before a reaction.

The CuO–CeO$_2$ catalyst was prepared by the co-precipita-tion method. The precursor salts, Cu(NO$_3$)$_2$·3H$_2$O and Ce(NO$_3$)$_3$·6H$_2$O, were dissolved in de-ionized water. One molar of NaOH solution was added to the mixed salt solution under vigorous stirring to precipitate the metals as hydroxides. The pH of the solution was controlled at 8. After aging for 1 h at 353 K, the precipitate was filtered, washed with de-ionized water to remove sodium ion and dried at 373 K overnight. The catalysts were calcined at different temperatures before a reaction. The Cu content of the prepared CuO–CeO$_2$ was intended to be 20 at.%.

The HCl-added CuO–CeO$_2$ catalyst was prepared by a wet impregnation method. The amount of chloride ion was equal to that of copper ion in the CuO–CeO$_2$. This catalyst was calcined in air at 973 K before a reaction. The metal-modified CuO–CeO$_2$ catalysts were also prepared by a wet impregnation method. Pt(NH$_3$)$_4$(NO$_3$)$_2$, H$_2$PtCl$_6$, Ru(NO)(NO$_3$)$_3$, Ni(NO$_3$)$_2$, and Co(NO$_3$)$_2$ were utilized as metal precursors. The content of

Pt and Ru was designed to be 0.05 wt.%. The content of Ni and Co was intended to be 1 wt.%. These catalysts were calcined in air at 573 K and reduced with H$_2$ at 573 K before a reaction. The Pt-modified CuO–CeO$_2$ using a Pt precursor such as Pt(NH$_3$)$_4$(NO$_3$)$_2$ and H$_2$PtCl$_6$ was denoted as Pt(N)/CuO–CeO$_2$ and Pt(C)/CuO–CeO$_2$, respectively.

Au/γ-Al$_2$O$_3$, Au/CeO$_2$-DP, Au/CeO$_2$/γ-Al$_2$O$_3$, and Au/CuO–CeO$_2$ were prepared by a deposition–precipitation (DP) method. γ-Al$_2$O$_3$ was purchased from Alfa and utilized without any further treatment. CeO$_2$ was prepared by a precipitation method. CeO$_2$/γ-Al$_2$O$_3$ was prepared by a wet impregnation method. The content of Ce was intended to be 10 wt.%. This support was calcined in air at 573 K. CuO–CeO$_2$ was calcined in air at 773 K. For the preparation of gold catalysts, these supports were suspended in de-ionized water and the pH of the suspension was preadjusted to 8 with 1 M NaOH solution. An aqueous solution of 0.01 M AuCl$_3$ was subsequently added drop by drop into the slurry, along with a 1.0 M NaOH solution to maintain a pH of 8. After 1 h stirring at 343 K, gold-deposited powders were filtered, washed several times with de-ionized water at room temperature to remove residual chloride ion, dried at 373 K, and stored as a fresh sample. These catalysts were reduced with H$_2$ at 473 K before a reaction.

Au/CeO$_2$-CP was prepared by the co-precipitation (CP) method. The precursor salts, AuCl$_3$ and Ce(NO$_3$)$_3$·6H$_2$O, were dissolved in de-ionized water. One molar of NaOH solution was added to the mixed salt solution with vigorous stirring to precipitate the metals as hydroxides. The pH of the solution was controlled at 8. After aging for 1 h at 353 K, the precipitate was filtered, washed with de-ionized water to remove residual chloride and dried at 373 K overnight. The catalysts were calcined in air at 773 K before a reaction.

Au/CuO was prepared by the deposition–precipitation method from Cu(OH)$_2$. The detailed preparation procedure was same to that of other supported gold catalysts. This catalyst was calcined in air at 573 K before a reaction.

γ-Alumina-supported Pt, Pt–Co, and Pt–Ni catalysts were prepared by a wet impregnation method from an aqueous solution of Pt precursor, Pt(NH$_3$)$_4$(NO$_3$)$_2$, and transition metal precursors, metal nitrates. γ-Alumina (Alfa) was utilized as a support. The content of Pt was 1 wt.% and the molar ratio of Co/Pt and Ni/Pt was 10 and 5, respectively. All the catalysts were calcined in air at 573 K. Before a reaction, Pt/γ-Al$_2$O$_3$, Pt–Ni/γ-Al$_2$O$_3$ and Pt–Co/γ-Al$_2$O$_3$ was reduced with H$_2$ at 573, 423 and 773 K, respectively.

The gold content was determined by inductively coupled plasma spectrometer (Direct Reading Echelle ICP, LEEMAN ABS. INC., U.S.A.).

Temperature programmed reduction (TPR) was conducted over 0.2 g sample in a 10 vol.% H$_2$/Ar stream from 313 to 873 K at a heating rate 10 K/min monitoring TCD signals.

Bulk crystalline structures of catalysts were determined with an X-ray diffraction (XRD) technique. XRD patterns were obtained by using Cu Kα radiation using a Rigaku D/MAC-III instrument at room temperature.

The CO chemisorption was conducted over 0.2 g sample in a He stream at 300 K by a pulsed injection of 50 μl of CO after