Doping effect of precious metal on the activity of CuO-CeO$_2$ catalyst for selective oxidation of CO

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Abstract

Precious metals (Pt, Pd and Ru)-doped copper oxide-ceria (CuO-CeO$_2$) catalysts were prepared by a combination of conventional co-precipitation and impregnation methods and evaluated for the selective oxidation of carbon monoxide in a hydrogen-rich gas stream. It was found that the doping with the precious metal did not change the crystal structure of the catalyst. The binding energy of copper in the precious metal-doped CuO-CeO$_2$ catalyst shifted to a higher value. This indicates that a part of the copper in the CuO-CeO$_2$ catalyst is phase-separated and there is some possibility of the formation of copper chloride on the surface of the catalyst. The added precious metal inhibited the phase separation of copper. The degree of phase separation depended on the type of precious metal and the amount of precious metal loading. The catalytic activity for selective oxidation of carbon monoxide (CO) was the highest in the case of Pt-doped catalyst due to the strong interaction between doped Pt and CuO-CeO$_2$ catalyst. However, the activity of Pd- or Ru-doped catalyst for selective oxidation of CO was much less because doped Pd and Ru have good activity for hydrogen oxidation.
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1. Introduction

Fuel cells are being actively developed as alternative power generation systems, because they can produce electricity with substantially less impact on the environment. Thus, fuel cells are expected to replace conventional power generation systems in many of their current applications [1] such as transportation and stationary and portable devices. Among the various types of fuel cells, hydrogen-fueled proton exchange membrane fuel cells (H$_2$-PEMFC) are considered to be the most technically advanced for such applications [2]. Pure hydrogen is the preferred fuel with respect to simplicity in operation and getting highest power density in a proton exchange membrane fuel cell

(PEMFC), but it is very difficult to use hydrogen directly, considering the very low volumetric and gravimetric efficiency of hydrogen storage material and the non-existence of any cost-effective infrastructure for hydrogen distribution. It is more difficult to use hydrogen directly in the portable application. In that case, on-board hydrogen is one of the interesting ways for feeding fuel cells. One of the most promising way for on-board hydrogen production is the reforming process which converts hydrocarbons such as natural gas, gasoline, diesel, and so on, into a hydrogen-rich gas mixture [2]. This can be done by catalytic reactions like steam reforming and auto-thermal reaction. In these cases, the resulting gas mixture contains significant amounts of carbon monoxide and such carbon monoxide poisons the Pt anode catalyst in the H$_2$-PEMFC anode. Thus, carbon monoxide should be removed from the gas mixture before it is supplied to PEMFC. The tolerance limit for carbon monoxide differs depending on the anode material used. In the case of Pt anode which is more generally used, the CO-tolerance limit is less than 10 ppm [2–4]. On the other hand, if

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Pt-Ru alloy is used in the anode, the CO-tolerance limit can increase up to 100 ppm [5–7].

Some methods for cleaning the carbon monoxide in the reformate gas, such as hydrogen purification using metal membrane and adsorption, have been tested. Among the various methods available, the selective oxidation of carbon monoxide is undoubtedly the most straightforward, simplest and most cost effective one [2,8], because selective oxidation or preferential oxidation (PROX) of carbon monoxide is an exothermic reaction. The desired feature of such a catalyst for the selective oxidation of carbon monoxide is the high activity and selectivity at low operating temperature of below 200 °C. In the last few years, many research groups have developed catalysts which could selectively oxidize carbon monoxide in the presence of excess hydrogen, carbon dioxide and steam.

The catalysts proposed for the selective oxidation process are noble metal-based, such as alumina-supported platinum-group metal catalysts [8,9], zeolite-supported platinum catalysts [10], and transition metal oxide-supported gold catalysts [11–14]. In the case of oxide supported Pt or Pt-group catalysts, the reported selectivity was not so high [9,15–17]. For example, Al_2O_3-supported Pt catalyst has 50% selectivity, with a significant level of H_2 oxidation occurring simultaneously. The operating temperature for PROX with Pt based catalyst is also relatively high (~200 °C).

Recently, CuO-CeO_2 oxide catalyst has been proposed as a candidate for the selective oxidation of CO in the presence of excess hydrogen [18,19] because this catalyst is more active and selective at lower reaction temperatures than the Pt-based catalysts. Avgouropoulos et al. [18] reported that CuO-CeO_2 catalyst had the same activity as that of Pt/Al_2O_3 catalyst because of strong interactions between CuO and CeO_2. Other researchers reported [20,21] that superior activity in PROX was available with CuO-CeO_2 catalyst than with Pt-based catalyst because of strong interactions between highly dispersed CuO on the surface of CeO_2 support and the formation of Cu-Ce-O solid solution. The main disadvantages of CuO/CeO_2 catalyst are that it is highly temperature-sensitive and is active only in a very narrow temperature region.

In our previous study [22], the effect of calcination temperature on the activity of CuO-CeO_2 catalyst was investigated for the selective oxidation of carbon monoxide. It was concluded that the active sites for selective oxidation of carbon monoxide in CuO-CeO_2 catalyst were Cu-Ce-O solid solution and that CuO was formed on the surface of the CuO-CeO_2 catalyst with the increase of calcination temperature (above 800 °C) due to phase separation. More recent works on the catalyst for selective oxidation of CO are given in Table 1.

The main aim of the present study is the preparation of precious metal-doped CuO-CeO_2 catalyst in PROX reaction for operating over a wide range of temperature. Three different precious metals namely, Pt, Ru and Pd, were used. The catalytic properties with these combinations were investigated and compared. The interaction between the precious metal and the CuO-CeO_2 catalyst was investigated by different types of characterization tools such as XRD, X-ray photoelectron spectroscopy (XPS) and CO chemisorption analysis. The effect of chloride ion on the activity of the catalyst was studied by doping HCl in the CuO-CeO_2. The chloride ion may be present in the precious metal-doped CuO-CeO_2 catalyst coming from the precious metal precursor solution.

2. Experimental

2.1. Preparation of catalyst

The CuO-CeO_2 catalyst was prepared by co-precipitation. Aqueous solutions of $Cu(NO_3)_2 \cdot 3H_2O$ (Shinyo), $Ce(NO_3)_3 \cdot 6H_2O$ (Kanto) and NH_4OH (Acros) were gradually and simultaneously added into a continuously stirred flask filled with distilled water. The reaction mixture was kept at 80 °C. After a period of 1 h, the resulting precipitate was filtered, washed with hot water, and then dried in air atmosphere at 75 °C for 12 h. Finally, the precipitate was calcined at 700 °C for 4 h under air flow. The CuO content of the sample, as determined by atomic absorption spectroscopy (AAS), was 5.0 wt%.

Our previous study [22] found that the activity for selective CO oxidation was the highest for a CuO loading of 5.0 wt% at a calcination temperature of 700 °C and that the activity decreased for higher CuO loading and higher calcination temperature. Therefore, the CuO loading and calcination temperature were maintained at 5 wt% and 700 °C, respectively.

The precious metal-doped CuO-CeO_2 catalyst was prepared by impregnation method. Doping precious metals were platinum, palladium and ruthenium; the precious metal precursors were H_2PtCl_6, $PdCl_2$ and $RuCl_3$ (Aldrich), respectively. The doping amount of precious metal was 0.05 wt% with respect to the total weight of CuO-CeO_2 catalyst.

The ceria (CeO_2) supported precious metal catalyst (PM/CeO_2) was also prepared by impregnation method under the same conditions used as those for the preparation of precious metal-doped CuO-CeO_2 catalyst. The support material, CeO_2, was prepared by precipitation method using ammonium hydroxide as the precipitant and was calcined at 500 °C for 4 h under air flow. Then the precious metal solution was impregnated and finally the material was calcined at 500 °C for 2 h under air flow.

Finally, chloride-added CuO-CeO_2 catalyst was prepared using dilute hydrochloric acid (HCl) solution in order to observe the effect of chloride on the activity of the catalyst. This material was named CuO-CeO_2-HCl catalyst.

2.2. Apparatus and method used for activity measurement

The catalytic test was carried out in a conventional fixed-bed reactor at atmospheric pressure. A quantity of 250 mg of catalyst and a total flow rate of the reaction mixture of 156 cm^3 min^{-1} ($W/F = 0.09$ g cm^{-3}) were used for each run. The reaction mixture consisted of 0.8% CO, 23.5% CO_2, 3.8% air and the balance was H_2.