Effect of support for Pt—Cu bimetallic catalysts synthesized by electron beam irradiation method on preferential CO oxidation

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ABSTRACT

Supported bimetallic catalysts have been shown to improve properties and catalytic performance of monometallic catalysts in various fuel conversion reactions. To investigate the effect of support on bimetallic Pt—Cu system, Pt—Cu supported on γ-Fe$_2$O$_3$ and CeO$_2$ were synthesized using electron beam irradiation method and preferential CO oxidation (PROX) performance was investigated in relation to structural and chemical properties of the catalysts. The difference in performance among the catalysts existed in both oxygen transport ability and selectivity. While oxygen transport ability was influenced by support property such as crystallite size (within the comparison among catalysts supported on CeO$_2$ and γ-Fe$_2$O$_3$), selectivity was rather influenced by support material which led to clear differences in reducibility, reduction degree of catalyst, and alloying extent of Pt—Cu. CeO$_2$-supported catalysts are unique in the view point that they were able to convert CO selectively in high CO conversion region compared to Fe$_2$O$_3$-supported catalyst. Pt—Cu with small CeO$_2$ crystallite maintained high O$_2$ conversion (high capacity for oxygen transport) in O$_2$-rich atmosphere in addition to high selectivity. Compared to monometallic Cu which lost its activity in the O$_2$-rich wet condition, or compared to monometallic Pt which exhibited poor selectivity, Pt—Cu realized both high activity and selectivity on CeO$_2$ of small crystallite size, leading to more than 99% of CO conversion at 100 °C. By modifying the structure, it was demonstrated that Pt—Cu/CeO$_2$ system can be improved to have low-temperature activity comparable to monometallic Pt while keeping high selectivity of the original Pt—Cu catalyst in the practical PROX condition.

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1. Introduction

Preferential oxidation of carbon monoxide (PROX) is one of the critical reactions for hydrogen production for polymer electrolyte membrane fuel cell (PEMFC) since the anode catalyst is severely poisoned by ppm-order of CO in the H$_2$-rich fuel [1,2]. The poisoning is caused by CO strongly adsorbing on Pt surface through donating π-electron to d-orbital of platinum and backdonation of electron from platinum to anti-bonding orbital of CO. To avoid this, increasing reaction temperature is one of the solutions, but higher temperature causes low CO coverage, increasing the chance for H$_2$ adsorption and oxidation on the surface resulting in decrease of CO conversion [3]. Operating low temperature is another option which

has an advantage in obtaining high selectivity for CO oxidation, but highly active catalyst is indispensable. In this sense, catalyst that has both activity at low temperature and selectivity at high temperature is desired to supply CO-free H$_2$ to fuel cell on real-time output demand.

In seeking catalyst to achieve such PROX performance, researchers have modified electronic structure of Pt combined with transition metals. Kotobuki et al. added Fe to Pt/mordenite to see significant enhancement in PROX activity and selectivity [4]. Oxygen pulse reaction on CO-preadsorbed catalyst revealed that Fe provides O$_2$ chemisorption sites for dual-site reaction pathway, otherwise O$_2$ chemisorption is inhibited by high CO coverage on active Pt sites. Similar enhancement was reported for Pt—Fe/Al$_2$O$_3$ by Liu et al. and it was attributed to partial coverage of Pt surface by Fe oxide to provide electron-rich Pt and O$_2$ chemisorption sites. Au/TiO$_2$ was also modified by Fe successfully to increase low temperature performance [5]. Cobalt-modified Pt/Al$_2$O$_3$ or Pt/SiO$_2$ was reported to be promising formulation for PROX. Yan et al. impregnated Co on Pt/Al$_2$O$_3$ and observed a drastic shift in light-off temperature with little change in selectivity [6]. Choi et al. prepared Pt—Co/SiO$_2$ by sol–gel method in which Co cations

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selectively attached to Pt sites and stabilized Pt in a reduced state [7]. In intermetallic Pt—Co or Pt—Cu on SiO_2, the neighboring Co or Cu creates electron-deficient Pt to weaken CO adsorption and to accelerate O_2 adsorption [8]. Our group has studied copper-modification of Pt/Fe_2O_3 or Pt/CeO_2 using radiation-induced reduction method which is a unique one-pot aqueous-phase process to obtain supported bimetallic nanoparticles with uniform size and distribution in a matter of several seconds [9–11]. We found that Cu addition enhances oxygen transport and improves selectivity significantly.

While addition of transition metal can improve geometric, electronic structures, and catalytic performance, effect of support has not been much understood for these bimetallic catalysts. Each bimetallic formulation works only on specific support material. For instance, Pt—Fe has advantage over monometallic Pt on Al_2O_3, but not much on CeO_2 [11]. Similarly, Pt—Co can work on Al_2O_3 [6] or SiO_2 [7], but good performance on Pt—Co/CeO_2 has never been reported. Pt—Cu is also good on SiO_2 [8] or redox support such as CeO_2 [11], Fe_2O_3 [10], Nb_2O_5 [12], but Pt—Cu/Al_2O_3 performs worse than Pt/Al_2O_3 [12]. To help understanding of support effect in Pt—Cu system, in the present study, Pt—Cu on three redox supports, Fe_2O_3 and two CeO_2 from different sources, were synthesized by electron beam irradiation method and their PROX performances in various temperatures and O_2 partial pressures were compared in relation to their structural and chemical properties of catalyst. The advantages in bimetallic Pt—Cu over monometallic Pt or Cu supported on CeO_2 were also discussed.

2. Methods

The procedure for catalyst preparation is given elsewhere [9,13], so a brief description is given here. The aqueous precursor solution was prepared using $H_2PtCl_6 \cdot 6H_2O$ (99.9%, Wako), $CuSO_4 \cdot 5H_2O$ (99.9%, Wako). Powder of γ-Fe_2O_3 (NanoTek®, C. I. Kasei Co., $64\,m^2/g$ of specific surface area, 27 nm of average crystallite size) or CeO_2 (NanoTek®, C. I. Kasei Co., $78\,m^2/g$, 24 nm, denoted as CeO_2(NT), or HSA20®, Anan Kasei Co., $140\,m^2/g$, 10 nm, denoted as CeO_2(HSA)) were dispersed in the solution. The concentration of chloroplatinic ion in the solution was 0.1 mM, that of copper ion was 0.1 mM or 0.9 mM, and the amount of support powder was adjusted to achieve 2.54 wt.% of platinum loading and 0.83 wt.% or 7.5 wt.% of copper loading in total catalyst weight basis. The catalysts synthesized by these recipes are denoted as "Pt10Cu10" and "Pt10Cu90", respectively. 2-propanol (Wako) was added to scavenge hydroxyl radical which is formed in the radiation-induced reduction process. The concentration of 2-propanol was 0.25 mol/L. The solution was well mixed and sealed in a polypropylene flask after argon bubbling to remove dissolved oxygen. It was then irradiated with 4.8 MeV electron beam for several seconds at room temperature (20 kGy). The irradiation with electron beam induces water radiolysis to generate hydrated electrons and radicals, which in turn reduce the ionic precursors to form nanoparticles deposited on the support by electrostatic force [14,15]. Indeed, the greenish or bluish color of the solution immediately turned blackish upon irradiation of electron beam. The product was filtrated, washed, and dried at 80 °C to obtain catalyst samples.

The chemical composition of the catalysts was analyzed by an inductively coupled plasma atomic emission spectrometry (ICP-AES; SHIMADZU, ICPS-7500). Crystallographic information on support and Pt—Cu species was obtained by an X-ray diffractometer (XRD; RIGAKU, RINT2100-Ultima with Cu Kα radiation). Temperature-programmed reduction (TPR) was performed on AutoChem II 2920 (Micromeritics). About 50 mg of catalyst was heated in $10\%H_2/Ar$ flow from room temperature to 600 °C at 5 °C/min of ramp rate. Extended X-ray absorption fine structure

(EXAFS) spectra were measured at the beam line NW10A of photon factory advanced ring (High Energy Accelerator Research Organization, Tsukuba, Japan) using fluorescence method. Pt L_3 edge absorption (11–13 keV) of as-made catalyst was analyzed using software Athena ver. 0.8.056.

Performance for preferential CO oxidation was tested using a fixed-bed flow reactor. About 50 mg of catalyst powder was packed in a glass tube reactor with 4 mm of inner diameter. The reactant gas mixture was 1% CO, 0.5% O_2, 67.2% H_2, N_2 balance ($\lambda = 1$ dry), or 1% CO, 0.7% O_2, 66% H_2, N_2 balance plus 10% H_2O ($\lambda = 1.4$ wet), or 1% CO, 1% O_2, 64% H_2, N_2 balance plus 10% H_2O ($\lambda = 2$ wet) where "λ" is defined as degree of O_2 excess from stoichiometry, i.e. twice of O_2/CO ratio in the feed. Water vapor was introduced by bubbling dry reactant gas mixture in the water adjusted to 46.1 °C and all gas lines were heated at around 100 °C. The total gas flow rate was 25 ml/min (dry gas) for all above conditions. The temperature was measured inside the oven containing the reactor tube. The product gases (CO, CO_2, O_2) in the effluent were quantified by gas chromatograph Varian 490 Micro GC equipped with dual channels, one with MS-5 A column and the other with Plot Q, and TCD detector for each column. CO conversion, O_2 conversion, and CO_2 selectivity were calculated as follows:

$$CO\ conversion = \left(\frac{1 - |CO|_{out}}{|CO|_{in}} \right) \times 100$$

$$O_2\ conversion = \left(\frac{1 - |O_2|_{out}}{|O_2|_{in}} \right) \times 100$$

$$Selectivity = \left(\frac{(CO\ conversion/O_2\ conversion)}{\lambda} \right) \times 100$$

where $|CO|_{out}$, $|O_2|_{out}$, $|CO|_{in}$, $|O_2|_{in}$ are concentrations of CO, O_2 in outlet and those in inlet, respectively. The effluent was demoisturized at 0 °C before gas analysis.

3. Results and discussion

3.1. Characteristics of Pt—Cu/CeO₂ in preferential CO oxidation

Fig. 1 shows the results of PROX tests on Pt—M (M = second metal: Fe, Co, Cu) bimetallic catalysts supported on CeO_2 which were synthesized by radiolytic method. It has been shown in our previous study that Pt—Cu/CeO_2 is highly selective in PROX in wide temperature range [11] and the present results clarified difference of Pt—Cu from other Pt—M systems. Addition of Fe or Co did not change selectivity of monometallic Pt catalyst on CeO_2 and the light-off temperature was lowered by these metals instead. The enhanced light-off performance on Pt—M catalysts is consistent with literature. Pt—M supported on Al_2O_3 has been reported to be more active at low temperature compared to monometallic Pt, among which Pt—Co and Pt—Fe are distinguished, but the selectivity are similar to Pt at high temperature range [16]. Ko et al. have also shown that Pt—Co/YSZ (yttria-stabilized zirconia) shifted light-off temperature of Pt/YSZ by a matter of 50 °C though selectivity converged to certain value at high temperature [17]. Even Pt—Co core–shell structure obtained by calcination at 700 °C had 20–30 °C lower light-off temperature than Pt alone. The authors attributed it to oxygen vacancies on redox support in contact with Pt—Co nanoparticles. Regarding the enhanced light-off, Tanaka et al. have shown that Pt catalysts on carbon nanotube (CNT) containing Ni or Fe exhibit similar kinetic feature in PROX to FeO_x-added Pt/TiO_2 reported in their earlier study [18,19]. A reaction pathway via hydroxyl carbonyl or bicarbonate intermediates was proposed for improved activity at the low temperature region where the parent Pt/CNT or Pt/TiO_2 does not show activity. Regardless of