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CeO₂-supported Pt–Cu alloy nanoparticles synthesized by radiolytic process for highly selective CO oxidation

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ABSTRACT

CeO₂-supported Pt–Cu bimetallic catalysts were synthesized by radiolytic process and their PROX activities were evaluated in relation to structural properties of the catalysts. Irradiating the aqueous precursor solution yielded Pt–Cu alloy nanoparticles and amorphous-like CuO on CeO₂ which are thermodynamically stable products formed from reduced Pt and Cu. Addition of Cu to Pt significantly improved CO selectivity in PROX reaction. The Pt–Cu catalysts had wide temperature window for 100% CO conversion in contrast to very narrow window for monometallic Pt and Cu catalysts. Much lower light-off temperature for Pt–Cu catalysts than Cu catalyst revealed that Pt–Cu alloy surface is the active center. Regardless of the amount of CuO phase, the bimetallic catalyst exhibited high catalytic performance, which further revealed that Cu in close contact with Pt is responsible for the improved selectivity. The CuO phase was suggested to promote oxygen supply to CO chemisorbed on Pt–Cu alloy surface.

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1. Introduction

Preferential CO oxidation (PROX) is one of the critical steps in hydrogen production for Polymer Electrolyte Fuel Cell (PEFC) since the anode catalyst in PEFC is strongly poisoned even by ppm-level of CO in the H₂-rich gas [1,2]. A lot of effort has recently been made for mitigating the cost for fuel processor by decreasing Pt loading in PROX catalyst and improving heat integration between the shift reactor and fuel cell [3]. Both minimizing Pt loading and expanding active temperature window towards low temperature keeping high selectivity are essential for development of the catalyst.

Al₂O₃-supported platinum is the conventional PROX catalyst, whose kinetics has been studied well [4,5]. Due to strong CO chemisorption, Pt surface tends to be highly covered by CO at low temperature, which inhibits O₂ adsorption to slow down CO oxidation [5]. When CO coverage is low at higher temperature, on the other hand, Pt surface chemisorbs and oxidizes H₂ to exhibit low selectivity [6]. For instance, with 0.375 of O₂/CO ratio at 90 °C, selectivity was only about 65% over 0.5 wt% Pt/Al₂O₃ catalyst [7]. Marino et al. demonstrated that no noble metal catalysts on various supports exceeded 60% of selectivity at 0.5 of O₂/CO ratio at 100–300 °C [8]. Platinum on CeO₂ or ZrO₂ was found to show low-temperature

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light-off but poor selectivity compared to platinum supported on SiO_2 or Al_2O_3 [9].

In attempt to modify such character of Pt in PROX, addition of second metal has been found to be very effective. Sirijaruphan et al. added 0.5 wt% of Fe to Pt/ Al_2O_3 and observed increase in CO conversion [10]. Their pulse kinetic study revealed that Fe addition increases intrinsic site activity rather than the number of sites by promoting oxygen chemisorption. Komatsu et al. synthesized various intermetallic compounds on SiO_2 support and found Pt_3Co and PtCu to be superior to Pt/ SiO_2 [11]. Their surface characterizations by XPS and infra-red absorption of chemisorbed CO revealed Co and Cu changes structure and electronic property of Pt. Similar claim was made by Kotobuki et al. who investigated promotional effect of Fe in Pt–Fe/mordenite catalyst [12]. Impregnation of Mn oxide to Pt/ Al_2O_3 was reported to have positive effect by Ayastuy et al. [13]. The promoting effect was attributed to new Pt– MnO_x interface, but the presence of H_2O caused detrimental effect on such sites. From these reports, addition of second component has large impact on the character of Pt sites or Pt-oxide interface.

The enhanced oxygen transport is also known to occur at interface of non-noble metal and reducible support. Nano-sized CuO particles or clusters interact with CeO_2 surface to exhibit synergistic effect in reducibility at the interfacial area [14,15]. Kinetic observations have suggested CO adsorbs on copper sites and oxygen is supplied from CeO_2 through the interface [16]. While CuO– CeO_2 shows high selectivity, it has drawback of slow kinetics at low CO concentration [17,18], which makes noble metal still necessary for deep CO removal from H_2 stream.

Our group has been developing supported Pt–Cu alloy nanoparticles synthesized by a unique radiation-induced synthesis process and we have recently reported $\gamma\text{-Fe}_2\text{O}_3$ -supported Pt–Cu alloy nanoparticles are more active in CO oxidation and preferential CO oxidation compared to monometallic Pt or Cu [19–21]. This radiolytic process is simple method to obtain nanoparticles with well-controlled structure and size through irradiating the aqueous ions of metal sources with no need for post-treatment by heat or other chemicals [22–25]. The radiation-induced radicals and hydrated electrons reduce these ions [22,26]. With high-energy electron beam, multiple components can be reduced fast enough to produce random alloy preferably depending on the metal composition and irradiation conditions [27]. The process is suitable for mass production since the process has been demonstrated in a commercial electron-beam irradiation facility for sterilization of medical supplies such as disposable syringes. In this context, we synthesized Pt–Cu catalysts supported on CeO_2 which has much higher oxygen transport ability than $\gamma\text{-Fe}_2\text{O}_3$ using the radiolytic method and investigated the origin of its high PROX performance in relation to structure and composition of the supported species.

2. Experimental

The procedure for catalyst preparation is described elsewhere [19,20], so that only a brief description is given here. The

aqueous precursor solution was prepared using $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (99.9%, Wako), $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (99.9%, Wako), and CeO_2 support (14 nm of average particle size, NanoTek™, C. I. Kasei Co.) dispersed in it. 2-Propanol (Wako) was added as a scavenger of hydroxyl radicals which can oxidize reduced ions or atoms back to a higher oxidation state. The solution was well mixed and sealed in a polypropylene flask after argon bubbling to remove dissolved oxygen. The concentration of platinum ion in the solution was 0.1 mM, the concentration of copper ion was varied from 0 to 1.8 mM, and the amount of the CeO_2 support was adjusted to keep platinum loading to 2.54 wt%. These concentrations of ions are reflected in notation of the catalysts, e.g. “Pt10Cu90” represents the catalyst prepared from 0.1 mM of Pt^{4+} and 0.9 mM of Cu^{2+} . The concentration of 2-propanol was 10 mL/L. The solution was then irradiated for several seconds with 4.8 MeV electron beam at room temperature (20 kGy). The irradiation with electron beam induces water radiolysis to generate hydrated electrons and radicals, which reduce the ionic precursors to form nanoparticles stabilized on the CeO_2 support. The product was filtered, 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) and X-ray fluorescence spectroscopy (XRF; SHIMADZU, EDX-720). For ICP-AES, the solid sample was dissolved in HCl– HNO_3 mixed solution and sprayed into a plasma torch through a nebulizer. Crystallographic structure of nanoparticles on the support was analyzed by an X-ray diffractometer (XRD; RIGAKU, RINT2100-Ultima with Cu $K\alpha$ radiation). The morphology of the samples was investigated using a transmission electron microscope (TEM; HITACHI, H-8100, 200 kV). Temperature-programmed reduction (TPR) was performed on BELCAT (BEL Japan Inc.). About 50 mg of catalyst was heated in 5% H_2 /Ar flow from –100 °C to 1000 °C at 5 °C/min of ramp rate. X-ray absorption spectra (XAS) were measured at the beamline BL01B1 of SPring-8 synchrotron radiation facility (Hyogo, Japan), NW10A of Photon Factory Advanced Ring and BL7C of Photon Factory (Tsukuba, Japan) using transparent method. The chemical states of metals were analyzed with the X-ray absorption near edge structure (XANES) spectra around Pt L_3 and Cu K edges. Information of local structure was obtained from the extended X-ray absorption fine structure (EXAFS) spectra around Pt L_3 edge. Experimental details of the XANES analysis were described in our previous paper [28].

Catalytic activity 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 or 1% CO, 2% O_2 , 60% H_2 , N_2 balance (25 ml/min in total) and the reactor temperature was controlled in the range from 60 to 200 °C. 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-5A column and the other with Plot Q, and TCD detector for each column. CO conversion, O_2 conversion, and CO oxidation selectivity were calculated as follows:

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