



Effect of CeO₂ support properties on structure of Pt–Cu nanoparticles synthesized by electron beam irradiation method for preferential CO oxidation



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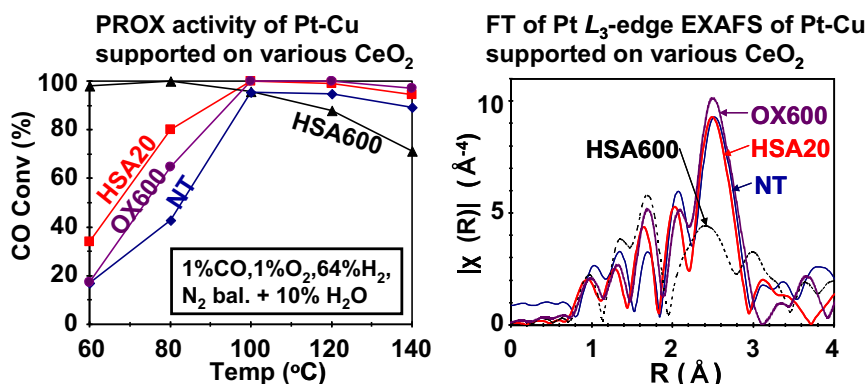
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HIGHLIGHTS

- Structure of Pt–Cu prepared by radiolytic method depends on surface property of CeO₂.
- Hydroxyls exposed on CeO₂ with low adsorbed water yield oxidic cluster-like Pt–Cu.
- This small Pt–Cu phase yields dispersed Pt contacting with CuO_x in CO atmosphere.
- The efficient contact of Pt and CuO_x realizes high oxygen transport in excess-O₂ PROX.
- Catalytic activity is related to CeO₂ surface property via structure of Pt–Cu species.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 29 August 2012

Received in revised form 18 February 2013

Accepted 26 February 2013

Available online 8 March 2013

Keywords:

Pt–Cu
Bimetallic catalyst
CeO₂ support
Electron beam irradiation method
Preferential oxidation
PROX

ABSTRACT

The influence of surface properties of CeO₂ support on the structure of Pt–Cu bimetallic system in an aqueous-phase synthesis process using electron beam irradiation and the resulting impact on PROX performance were investigated. The exposed hydroxyls on CeO₂ surface with low hydrogen-bonding water led to cluster-like Pt–Cu phase with low crystallinity and high oxidation state. It was attributed to a strong interaction of CeO₂ and Pt–Cu phase. In CO atmosphere, such oxidic or fine Pt–Cu phase was reduced to platinum and partially reduced CuO_x, and CeO₂ was concomitantly reduced to retain carbonate species on its surface. This in turn affected catalytic performance, i.e., a significant increase in O₂ conversion was observed in an oxygen-rich PROX condition compared to a stoichiometric condition while selectivity was retained in higher level than monometallic Pt. The higher oxidation state of Pt in the excess O₂ was suggested to be responsible for the drastic change in activity. The surface chemical property of CeO₂ was shown to affect PROX activity through the structure and oxidation state of Pt–Cu species which originates from metal–ceria interaction in the synthesis stage.

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1. Introduction

Preferential CO oxidation (PROX) is one of the critical steps in hydrogen production for polymer electrolyte fuel cells (PEFC) since the anode catalyst in PEFC is strongly poisoned even by

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ppm-level of CO in the H₂-rich gas [1,2]. Pt/Al₂O₃ has been studied as one of the most active formulations for this reaction, but the strong CO chemisorption on Pt surface inhibits O₂ chemisorption at low temperature leading to low light-off performance and the competing chemisorption/oxidation of H₂ interferes selective CO oxidation at high temperature [3,4]. To solve these problems, various bimetallic formulations such as Pt–Ru [5,6], Pt–Cu [7,8], Pt–Co [9,10], Pt–Ni [11,12], and Pt–Fe [13,14] have been proposed as alternatives. By adding these second metals to Pt, it was shown that the electronic structure and/or geometric structure of Pt (distance of neighbouring Pt atoms on the surface) are altered to weaken CO chemisorption and to provide O₂ chemisorption sites. Our group has developed Pt–Cu catalysts supported on redox oxides such as γ -Fe₂O₃ and CeO₂ using an electron beam irradiation method and has shown excellence of Pt–Cu in PROX [15–17]. While the effect of the reported second metal addition is related to light-off performance in many cases [10,13], we found that Pt–Cu/CeO₂ is unique in improving selectivity of monometallic Pt/CeO₂ rather than improving light-off performance [16]. Structural analyses revealed that Cu forms Pt–Cu alloy nanoparticles and amorphous CuO by the electron beam irradiation and these copper species in close contact with Pt modify the electronic/geometric structure of Pt to suppress H₂ chemisorption and H₂ oxidation. Our results showed the structure of Pt–Cu is critical for catalytic performance.

Meanwhile, the effect of support property is more complicated and has not been understood as much. Redox supports are generally more active for PROX due to their oxygen transport ability while they are not as selective as non-redox supports [18]. The mechanism for involvement of redox support to the reaction is still under argument, but a lot of evidences have been provided for high mobility of surface or bulk oxygen being related to the catalytic activity [19,20]. For instance, Cu–CeO₂ redox couple at the interface has been identified critical for CuO/CeO₂ catalyst [21] and Cu–V_o (V_o = oxygen vacancy) at the interface is proposed to be the active site for CO oxidation from in situ characterization techniques [22]. In the case of CeO₂-supported noble metal, Pt interacts more strongly with support to widen the metal–ceria interfacial active area to show high catalytic activity [23].

The impact of support on the structure and oxidation state of metal has also been pointed out. For example, copper dispersion and reducibility have been shown to depend on crystallite plane of CeO₂ support, which in turn have impact on the activity for water gas shift [24] and NO reduction by CO [25]. Higher electron density and significant weakening of CO chemisorption on Pt have been observed for Pt/TiO₂ reduced at 400 °C, which was presumably attributed to a decoration of Pt by the reduced TiO_x through a metal–support interaction [26]. Pt–Ti–O alloy was also detected upon annealing it in a ultrahigh vacuum above 550 K [27]. In the case of Au/TiO₂ prepared by a deposition–precipitation method, the surface and textural properties of TiO₂ influences the size of Au particle and the accumulation of carbonate in the course of CO oxidation [28]. O₃-pretreatment of Au/TiO₂ caused a partial oxidation of Au and stronger anchoring of Au particles on TiO₂ [29]. These reports show that the active structure is formed by the interaction of metal and support, which is strongly influenced by support material and its surface properties, yet the relation between structure of metal (or interfacial area) and support properties is not clarified enough and its contribution to catalytic performance is ambiguous. The present study focuses on understanding the effect of support property on metal particle structure, which in turn affects catalytic activity. Pt–Cu catalysts on four CeO₂ supports from different sources were prepared and the support property was correlated to the Pt–Cu structure and PROX performance. The electron beam irradiation method was employed for catalyst preparation, which is a simple one-pot aqueous phase process to

synthesize metal or alloy nanoparticles without any post-treatment such as hydrogen reduction, enabling to distinguish metal structure and oxidation state by support properties to probe metal–ceria interaction.

2. Materials and methods

2.1. Catalyst preparation

Pt–Cu bimetallic catalysts were prepared by the electron beam irradiation method in which aqueous precursor of H₂PtCl₆ and CuSO₄ containing dispersed CeO₂ powder was irradiated with 4.8 MeV electron beam for 6–7 s (20 kGy). This causes radiolysis of water to generate hydrated electrons and radicals, which in turn reduce the ionic precursors to form metallic nanoparticles immobilized on CeO₂ support [30]. We synthesized 2.5 wt.% Pt–0.83 wt.% Cu in the total catalyst weight basis or 2.2 mol% Pt–2.2 mol% Cu in the total molar basis supported on various CeO₂. Four different CeO₂ were used: HSA20 from Anan Kasei Co. (150 m²/g), HSA600 obtained by 600 °C calcination of HSA20 (137 m²/g), NT from C.I. Kasei Co. (84 m²/g), OX600 obtained by 600 °C calcinations of cerium oxalate (43 m²/g). The precursor solution consisted of 0.1 mM of H₂PtCl₆, 0.1 mM of CuSO₄, 0.25 mol/L of 2-propanol as a scavenger for oxidizing radicals, and CeO₂ powder dispersed in it. Before electron beam irradiation, the solution was bubbled with argon gas to remove dissolved oxygen and sealed in a 750 mL flask, in which one third of volume was filled with the solution. Irradiation of electron beam was conducted in a commercial facility for sterilization of medical supplies such as disposable syringes (Japan Electron Beam Irradiation Service, Izumi-ohtsu, Japan). The product was filtered, washed, and dried at 80 °C for characterization and reaction tests.

2.2. Characterization

Nitrogen physisorption isotherm was obtained for BET surface area, total pore volume, and average pore diameter of CeO₂ support using Autosorb-1 (Quantachrome). Temperature-programmed reduction was conducted to quantify the reducible surface of CeO₂ support using Autochem 2920 (Micromeritics). The sample was flushed in helium at 100 °C, cooled to room temperature, and heated up in 10% H₂/argon flow at the heating rate of 5 °C/min. Chemical composition was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES, ICPE-9000, Shimadzu). Crystallographic structure of nanoparticles was analyzed by X-ray diffraction (XRD, Rigaku RINT2100-Ultima with Cu K α radiation). The morphology of nanoparticles was investigated by transmission electron microscope (TEM, Hitachi H-800, 200 keV and JEOL JEM-3000F, 300 keV). The chemical state and local structure of metals were analyzed by X-ray absorption fine structure (XAFS) at synchrotron radiation facility (Photon Factory and Photon Factory Advanced Ring at High Energy Accelerator Research Organization, Tsukuba, Japan). Pt L₃-edge spectra were measured at the beamline NW-10A and Cu K-edge spectra were measured at the beamline BL-9C. Data acquisition was performed on software Athena ver. 0.8.056. The CO adsorbed on catalyst surface was characterized by infrared spectra (FT-IR, FT/IR-4100, JASCO) equipped with a diffuse reflectance cell. The spectra were obtained in 3% CO/N₂ flow at 80–100 °C after flushing with argon at 100 °C.

2.3. Catalytic tests

Catalytic tests were conducted using a fixed-bed flow reactor of 4 mm inner diameter, in which 50 mg of catalyst powder was packed. The reactant composition was 1% CO, 0.5% O₂, 67% H₂, N₂

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