



γ -Fe₂O₃-supported Pt-Cu nanoparticles synthesized by radiolytic process for catalytic CO preferential oxidation

Junichiro Kugai^{a,*}, Ryota Kitagawa^{a,1}, Satoshi Seino^a, Takashi Nakagawa^a, Yuji Ohkubo^a, Hiroaki Nitani^b, Hideo Daimon^{c,2}, Takao A. Yamamoto^a

^a Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan

^b Institute of Materials Structure Science (IMSS), High Energy Accelerator Research Organization (KEK), 1-1 Oho, Tsukuba, Ibaraki 305-0801, Japan

^c Hitach Maxell, Ltd., 1-1-88 Ushitora, Ibaraki, Osaka 567-8567, Japan

ARTICLE INFO

Article history:

Received 17 March 2011

Received in revised form 25 July 2011

Accepted 5 August 2011

Available online 19 August 2011

Keywords:

Pt-Cu catalyst

Bimetallic Pt-Cu

Preferential oxidation

PROX

Radiolytic process

Radiation-induced synthesis

ABSTRACT

Pt-Cu bimetallic nanoparticles immobilized on γ -Fe₂O₃ support were synthesized by a unique radiolytic process and their physical properties and catalytic activity for CO preferential oxidation were investigated for various Pt/Cu atomic ratios. The chemical composition of the catalysts measured by inductively coupled plasma revealed most of the platinum and copper aqueous precursors were deposited on to the γ -Fe₂O₃ support after irradiation with electron beam. Crystallographic analysis of the catalysts by X-ray diffraction showed Pt-Cu alloy is formed for wide range of Pt/Cu ratio. From the lattice parameter of this Pt-Cu alloy, it was found that Cu can be incorporated into Pt lattice up to 30 at% with the present irradiation condition. The rest of Cu for high-Cu (low-Pt) samples was identified as divalent oxide with poor crystallinity by XANES spectrum. Detailed STEM-EDX analyses further confirmed that Pt-Cu alloy exists as nanoparticles with a few nanometers in diameter and CuO with low crystallinity distributes on entire surface of the γ -Fe₂O₃ support. The PROX activity showed different trends between high-Pt and high-Cu samples. The CO conversion decreased as the Pt loading was decreased to 50 at%, and it monotonically decreased with increasing temperature. However, as the Pt loading was further decreased, the activity increased with temperature by contraries, and reached the maximum conversion at 100 °C. Regardless of the low Pt loading, the sample with 10 at% Pt and 90 at% Cu exhibited the highest activity at 100 °C, which is preferable for low temperature fuel cell applications. This enhanced activity was attributed to oxygen supply via the copper of low crystallinity from the O₂-poor atmosphere to Pt-Cu alloy particles that chemisorbs CO molecules.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Hydrogen is one of the promising energy carriers for power generation, especially for polymer electrolyte fuel cells (PEFCs) [1,2]. This type of fuel cell operates around 80–100 °C and has high output density, which are suitable for compact stationary and mobile applications. However, hydrogen-rich gas supplied to PEFCs must be free from carbon monoxide (CO), since CO poisons the Pt

catalyst in the PEFC anode [3,4]. Thus, the hydrogen-rich gas typically obtained from a hydrocarbon reforming is purified by multiple processes, i.e. water gas shift (WGS) and preferential CO oxidation (PROX) to diminish CO concentration to ppm order [2,5]. For PROX, supported platinum catalysts are typically used due to its high catalytic activity, but platinum is the most expensive among the noble metals and lowering the cost for catalyst by decreasing Pt loading is one of the major issues. Meanwhile, it is desirable to carry out PROX at temperature close to the operating temperature of PEFC for simplifying heat integration of the fuel cell system and avoiding parasitic H₂ oxidation in the PROX stage, but the activity of the catalyst is not sufficient at such a low temperature at low O₂/CO ratio. This is because the surface of platinum is significantly covered by CO at low temperature and the site for O₂ chemisorption is thus blocked by CO to stall catalytic activity [6–8]. To solve these two issues, many efforts have been made for partially replacing Pt by other metals such as Fe [9–11] and Ru [12]. Fe-promoted Pt/Al₂O₃ catalyst has been developed for CO removal from NH₃ synthesis plant in early 1960s. The geometrical location and the mechanism

* Corresponding author. Tel.: +81 6 6879 4454; fax: +81 6 6879 7886.

E-mail addresses: kugai@mit.eng.osaka-u.ac.jp (J. Kugai), kitagawa.ryohta@fjri.co.jp (R. Kitagawa), seino@mit.eng.osaka-u.ac.jp (S. Seino), nakagawa@mit.eng.osaka-u.ac.jp (T. Nakagawa), okubo@mit.eng.osaka-u.ac.jp (Y. Ohkubo), hiroaki.nitani@kek.jp (H. Nitani), hdaimon@mail.doshisha.ac.jp (H. Daimon), takao@mit.eng.osaka-u.ac.jp (T.A. Yamamoto).

¹ Present address: Japan Research Institute Ltd., 1-16 Chiyodaku, Tokyo 102-0082, Japan.

² Present address: Graduate School of Engineering, Doshisha University, 1-3 Tatara-Miyakodani, Kyotanabe-shi, Kyoto 610-0321, Japan.

for promotional effect of Fe in the catalyst was later investigated and it was elucidated that Fe partially covers Pt surface to increase electron density on Pt and to provide active oxygen for selective oxidation of CO [10]. Sirijaruphan et al. pointed possible formation of intermetallic compound such as Pt₃Fe [13]. Ru was also found to be selective for CO oxidation [11]. The combination of Ru with Pt is well known to enhance catalytic activity for methanol electrooxidation. Ru in Pt–Ru creates hydroxyl next to a Pt site to remove CO poisoning the Pt site [14,15]. These reports show it is important to control the structure of alloy to obtain a promoting effect over a mere diluting effect. Addition of promoter such as Mn [16] or Fe [17] in oxide form and use of reducible supports such as CeO₂–ZrO₂ [18] are other strategies to improve Pt catalysts. These reducible supports have been reported to create Pt-oxide interface where oxygen is activated to invoke Mars–Van Krevelen type reaction pathway.

Recently, we have reported that Pt–Cu alloy nanoparticles supported on γ -Fe₂O₃ were successfully synthesized by the radiolytic process and that the catalytic activity for CO oxidation was enhanced by alloying Pt with Cu [19,20]. This new synthesis process is a simple and quick one-pot process in which the source materials are mixed in aqueous solution and irradiated for a few seconds of time scale without any treatment by heat or other chemicals [21–23]. During the irradiation, radiation-induced radicals reduce aqueous ions very quickly and uniformly in the solution [24] and produce random alloy nanoparticles, even when two or more ionic precursors with different redox potentials are reduced together. This process is also feasible for mass production because the process has been demonstrated in a commercial irradiation facility already industrialized for sterilization of medical supplies such as disposable syringes.

The purpose of this study is to make Pt–Cu alloy nanoparticles using the radiolytic process which realize low Pt loading and enhance PROX activity in large excess of H₂ at low temperature, and to identify the structure of nanoparticles to clarify how the structure relates to PROX activity. For these purposes, Pt–Cu alloy nanoparticles with different Pt/Cu atomic ratio were synthesized on γ -Fe₂O₃ support using irradiation. The γ -Fe₂O₃ was chosen as support since it is reducible and high CO oxidation activity was observed in our previous study [20]. The nanoparticles were characterized by ICP, XRD, TEM, and XAS to correlate to PROX activity.

2. Experimental

The procedure for catalyst preparation is described elsewhere [19,20], so that only a brief description is given here. H₂PtCl₆·6H₂O (99.9%, Wako) and CuSO₄·5H₂O (99.9%, Wako) were used as the metal precursors. Other source materials were ultrapure water (18 M Ω cm), 2-propanol (Wako), and γ -Fe₂O₃ support (Nanophase Tech. Corp.) with an average primary particle size of 21 nm. The source materials were charged together in a glass vial. The concentration of platinum and copper ions in the vial was 1 mM in total and the amount of the γ -Fe₂O₃ support was adjusted to achieve 10 wt% of metal loading. Seven samples were prepared with various Pt and Cu atomic ratios (Pt:Cu); 100:0, 90:10, 75:25, 50:50, 25:75, 10:90, and 0:100. As a reduction enhancer, 2-propanol was added at 10 mL/L. The vial was then irradiated for several seconds with 4.8 MeV electron beam at room temperature (20 kGy). The radiation energy induces water radiolysis to generate radicals, which reduce the ionic precursors to form nanoparticles stabilized on the γ -Fe₂O₃ support. The resultant powder was then washed and dried to obtain catalyst samples. This simple one-pot synthesis made it possible to obtain reduced metal species on γ -Fe₂O₃ support without any reduction pretreatment before catalytic activity tests.

The chemical composition of the catalysts was analyzed by an inductively coupled plasma atomic emission spectrometry

Table 1
Composition of Pt–Cu/ γ -Fe₂O₃ catalysts measured by ICP.

M/ γ -Fe ₂ O ₃	Total metal loading (wt%)		Pt:Cu atomic ratio	
	Target	Actual	Target	Actual
Pt100	10	10	100:0	100:0
Pt90Cu10	10	10.7	90:10	90:10
Pt75Cu25	10	10.5	75:25	78:22
Pt50Cu50	10	10.8	50:50	50:50
Pt25Cu75	10	9.3	25:75	21:79
Pt10Cu90	10	7.2	10:90	11:89
Cu100	10	–	0:100	–

(ICP–AES; SHIMADZU, ICPS–7500). The solid sample was dissolved in HCl–HNO₃ mixed solution and sprayed into a plasma torch through a nebulizer. The morphology of the samples was investigated using a transmission electron microscope (TEM; HITACHI, H–8100, 200 kV). For EDX mapping, a scanning transmission electron microscope (STEM; JEOL, JEM–2100F) equipped with an energy-dispersive X-ray spectrometer (JEOL, JED–2300T) was used. Crystallographic analysis was performed by an X-ray diffractometer (XRD; RIGAKU, RINT2100–Ultima with Cu–K α radiation). Average crystallite size was calculated from peak broadening using Scherrer equation:

$$\tau = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

where K is the shape factor (0.89 for the present instrument), λ is the wavelength of X-ray, typically 1.54 Å (Cu K α), β is the line broadening at half the maximum intensity (FWHM) in radians, and θ is the Bragg angle, τ is the crystallite size. The calculation was conducted on the software Jade+7 software (MDI). X-ray absorption spectra were measured at the beamline BL9C of the Photon Factory in the High Energy Accelerator Research Organization (Tsukuba, Japan) and at the BL14B2 of SPring–8 (Hyogo, Japan) using the conventional transparent method at room temperature. The chemical states of metals were analyzed with the XANES (X-ray absorption near edge structure) spectra around Cu K-edge. Experimental details of the XANES analysis were described in our previous paper [25].

Catalytic activity for CO preferential oxidation was tested using a fixed-bed glass tube 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% O₂, 67.2% H₂ and N₂ balance (25 mL/min in total) and the reactor temperature was controlled in the range from 60 to 200 °C. Both CO and CO₂ in the effluent from the reactor were quantified by a gas chromatograph. CO conversion was calculated from CO₂ production. CO conversion was also calculated from decrease in CO partial pressure at the reactor outlet from CO partial pressure in the feed to validate the data. For comparison, a commercial catalyst (TSSB–5, Tanaka Kikinzoku Kogyo K.K. [26]) was also examined.

3. Results

3.1. Catalyst composition

The actual metal composition in a series of Pt–Cu/ γ -Fe₂O₃ catalysts was analyzed by ICP. Fig. 1(a) shows the atomic percentage of Cu in the loaded Pt and Cu on γ -Fe₂O₃ after irradiation as a function of the molar percentage of Cu²⁺ in Pt⁴⁺ and Cu²⁺ in the precursor solution before irradiation, and Fig. 1(b) shows the total Pt and Cu loading after irradiation in weight percentage. The result is also summarized in Table 1. The total metal loading was close to the target value, 10 wt%. Thus, most of the Pt and Cu precursors

Download English Version:

<https://daneshyari.com/en/article/41220>

Download Persian Version:

<https://daneshyari.com/article/41220>

[Daneshyari.com](https://daneshyari.com)