



Structure of bicomponent metal–oxide composites synthesized by electron beam irradiation method



Junichiro Kugai^{a,*}, Toshiharu Moriya^a, Satoshi Seino^a, Takashi Nakagawa^a, Yuji Ohkubo^a, Koji Ueno^b, Hiroaki Nitani^c, Takao A. Yamamoto^a

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

^b Japan Electron Beam Irradiation Service Co., 5-3 Odushima-cho Izumi-ohtsu, Osaka 595-0074, Japan

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

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ABSTRACT

In order to understand the formation process of metal–oxide composite in an electron beam irradiation method in aqueous phase, the structure and composition of obtained solid were correlated to the synthesis parameters. Transition metal did not precipitate alone by the electron beam irradiation, but they did in the presence of platinum or support. Due to the relatively high reduction potential, copper underwent reduction to metallic state and readily precipitated by forming Pt–Cu alloy and/or copper oxide on solid surface. In the Pt–Cu/CeO₂ system, the structure of Pt–Cu was ruled by two competing factors, growth of alloy nanoparticles promoted by sulfate ion and deposition of metal (alloy) on CeO₂ support with their concomitant partial oxidation. CeO₂ was suggested to immobilize the metals oxidatively before they coalesce. Iron barely formed alloy with Pt, but it directly precipitated on support as oxide without being reduced to metal due to its oxophilicity. Oxide was formed either via reduction to metallic state (for Pt and Cu) or through direct oxygenation or hydroxylation on solid (for Fe). Under the restriction of reduction potential, the size and composition of alloy nanoparticles and the content of oxide phase were drastically modified by support surface property and anion species in the solution.

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1. Introduction

The radiation-induced synthesis of nanocomposites has been increasingly obtaining researchers' interest since it is a one-pot quick method to synthesize structure-controlled materials used for catalysis and electrical purposes. Basic knowledge of this synthesis method has been established in 1990s [1,2]. Irradiating a solution containing metal precursors with γ -ray or electron beam or X-ray induces a radiolysis of solvent to produce radicals, such as hydrated electrons and hydrogen radicals, which in turn reduce metal ions to metallic nanoparticles. The synthesis of silver nanoparticles has been studied most, partly due to the antimicrobial activity and various optical properties [3]. The size, shape, and the rate of formation of Ag nanoparticles depended on the final dosage, the concentrations of Ag source, and the type of stabilizing polymer [3]. The ligand and nuclearity of Ag were shown to impact the redox potentials in these processes [4,5]. Using a pulse radiol-

ysis, extremely stable silver clusters were identified in the aqueous solution, which showed weeks of life time in the presence of polyacrylate [6,7]. Synthesis of other metals such as Au [8], Cu [9,10], Pt [11], and bimetallics [12–14] were also reported. With aqueous phase, formation of oxide is often accompanied. Silver acetate was converted to Ag₂O and Ag metal whose ratio was controlled by the electron fluence [15]. γ -Fe₂O₃ was formed from FeCl₃ by 300 kGy of 2 MeV electron beam in the presence of polyvinyl alcohol (PVA) [16].

We have been synthesized various supported Pt–M bimetallic composites (M = second metal) using an electron beam irradiation method in the aqueous phase [14,17]. Supported Pt–Au [14], Pt–Cu [14,18–20], and Pt–Fe [21] have been synthesized and applied as catalyst for CO oxidation or preferential CO oxidation (PROX) in a H₂-rich gas, Pt–Ru [17,22] for methanol electro-oxidation, Pt–Cu [23] for oxygen reduction reaction (ORR). Particularly in the PROX reaction, the copresence of Pt–Cu alloy and CuO_x on an oxide support was found to be effective for smooth adsorption and transport of oxygen to increase the CO oxidation rate by an order of magnitude [19]. The results have shown that the catalytic and electrochemical performances are strongly dependent on the structure of bimetallic phase, which is determined by the variables in the synthesis stage. It has been found that the extent of alloying

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

E-mail addresses: kugai@mit.eng.osaka-u.ac.jp (J. Kugai), t-moriya@mit.eng.osaka-u.ac.jp (T. Moriya), 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), Kji_Ueno@EBIS.shi.co.jp (K. Ueno), hiroaki.nitani@kek.jp (H. Nitani), takao@mit.eng.osaka-u.ac.jp (T.A. Yamamoto).

depends on the reduction potential of second metal and that oxide species are formed together with metallic nanoparticles in many cases. However, the conjunctive influences of second metal, support material, pH of solution on alloy and oxide formations have not been fully clarified yet. Understanding the effect of these synthesis parameters on the formation process and product structure in the radiation-induced reduction method would help tailoring the composite for the better catalytic function. In the present study, we synthesized bimetallic Pt–Cu, Pt–Co, Pt–Fe, and monometallic Cu, Co, Fe composites in the presence/absence of support powder using an electron beam irradiation method and their composition and structure were analyzed in a systematic way to draw the critical factors for alloy and oxide formations. The effect of anion species in the precursor solution was also investigated.

2. Material and methods

The aqueous precursor solution was prepared using metal salts (H_2PtCl_6 , CuSO_4 , CuCl_2 , CoCl_2 , FeCl_2 , $\text{Fe}(\text{NO}_3)_3$). 2-Propanol was added by 0.25 mol/L as a scavenger for oxidizing radicals formed in the electron beam irradiation. For the synthesis of supported nanoparticles, the commercial support powder from C. I. Kasei Co. (CeO_2 : $\sim 80 \text{ m}^2/\text{g}$ of surface area and 24 nm of particle size; Al_2O_3 : $\sim 60 \text{ m}^2/\text{g}$ and 31 nm; TiO_2 : $\sim 45 \text{ m}^2/\text{g}$ and 36 nm) was dispersed in the precursor solution. The amount of support powder was adjusted to achieve 2.5 wt.% of Pt loading. The solution was bubbled with argon gas to remove dissolved oxygen, sealed in a 750 mL polypropylene container, and then irradiated with 4.8 MeV of electron beam for 6–7 s (20 kGy) at a commercial facility for sterilization of medical supplies (Japan Electron Beam Irradiation Service Co. at Izumi-ohtsu, Japan). This induces water radiolysis to produce a high concentration of radicals such as hydrated electrons and hydrogen radicals at one time, which in turn reduce the metal precursor to metallic state. The reduced atoms then coalesce to become nanoparticles and/or deposit on support. The resulting solid was separated by filtration, dried at 80 °C overnight, and served for chemical and structural analyses. The composition of solid product was analyzed by an inductively-coupled plasma atomic emission spectroscopy (ICP-AES, ICPE-9000, Shimadzu). The crystal structure of nanoparticles was analyzed by X-ray diffraction (XRD, RINT2100-Ultima with $\text{Cu K}\alpha$ radiation, Rigaku). The lattice parameter of nanoparticle was estimated from the diffraction angle using the Bragg's equation:

$$d = A/2 \sin \theta \quad (1)$$

where d is the lattice spacing, A is the wavelength of incident X-ray (1.5418 Å for $\text{Cu K}\alpha$), and θ is the Bragg angle. The lattice parameter was further converted to the composition of alloy assuming the linear relationship of lattice constant to copper content in alloy known as Vegard's law [24]. Although the lattice of Pt–M alloy is dilated in nanoparticles compared to the bulk alloy, the effect of size is relatively small (3–4% deviation from Vegard's law at the maximum for the Pt–Cu case [25]). The particle size was estimated from the line broadening using the Scherrer's equation:

$$\tau = K\lambda/(\beta \cos \theta) \quad (2)$$

where τ is the crystallite size, K is the shape factor (0.9) which is an attribute of equipment, β is the line broadening at half the maximum intensity (FWHM). The oxidation state of metal species was analyzed by XANES spectra. Pt L_3 -edge and Cu K -edge XANES spectra were obtained by the fluorescence method using a synchrotron radiation at High Energy Accelerator Research Organization, Photon Factory (Tsukuba, Japan). Data acquisition was performed on the software Athena ver. 0.8.056.

3. Results and discussion

3.1. Pt–M system without support

Electron beam irradiation on aqueous precursor of single transition metal did not yield solid product. Therefore, transition metals are not reduced alone or even if reduced, they are unstable in aqueous solution and easily oxidized back to the ionic state [2,14,26]. However, the co-presence of hexachloroplatinic acid (H_2PtCl_6) in the precursor made transition metal precipitate together with it. Blackish precipitates were obtained upon the electron beam irradiation except for the case of $\text{H}_2\text{PtCl}_6\text{--Fe}(\text{NO}_3)_3$ precursor. The composition of solid products measured by ICP-AES was summarized in Table 1. The content of transition metal in the product ($\text{M}/\text{Pt}_{\text{solid}}$) reflected its reduction potential. Only Cu showed substantial precipitation with Pt. The result indicates that the precipitation occurs

Table 1

Composition of Pt–M solid product synthesized by electron beam irradiation on metal precursors in the absence of support.

Product ^a	M/Pt ratio in solid product ($\text{M}/\text{Pt}_{\text{solid}}$) ^b (mol/mol)
Pt10Cu10(CuSO_4)	0.59
Pt10Cu10(CuCl_2)	0.48
Pt10Cu10(CoCl_2)	ND
Pt10Fe60(FeCl_2)	0.03
Pt10Fe60($\text{Fe}(\text{NO}_3)_3$)	No precipitate

^a The notation of product reflects the recipe for catalyst synthesis, e.g. "Pt10Cu10(CuSO_4)" represents the catalyst prepared from 0.1 mM of H_2PtCl_6 and 0.1 mM of CuSO_4 . Inside the parenthesis denotes the transition metal salt used as the precursor. The precursor for Pt was H_2PtCl_6 for all the samples.

^b M = transition metal.

Table 2

Standard reduction potential of platinum and various transition metal ions.

Reaction equation	Standard reduction potential (V)
$\text{PtCl}_6^{2-} + 4 \text{e}^- = \text{Pt} + 6\text{Cl}^-$	+1.44
$\text{Fe}^{3+} + \text{e}^- = \text{Fe}^{2+}$	+0.77
$\text{PtCl}_4^{2-} + 2 \text{e}^- = \text{Pt} + 4\text{Cl}^-$	+0.73
$\text{PtCl}_6^{2-} + 2 \text{e}^- = \text{PtCl}_4^{2-} + 2\text{Cl}^-$	+0.72
$\text{Cu}^+ + \text{e}^- = \text{Cu}$	+0.52
$\text{Cu}^{2+} + 2 \text{e}^- = \text{Cu}$	+0.34
$\text{Cu}^{2+} + \text{e}^- = \text{Cu}^+$	+0.15
$\text{Fe}^{3+} + 3 \text{e}^- = \text{Fe}$	–0.04
$\text{Co}^{2+} + 2 \text{e}^- = \text{Co}$	–0.28
$\text{Fe}^{2+} + 2 \text{e}^- = \text{Fe}$	–0.44

only via reduction of transition metal to zero-valent state in the absence of support.

No solid product was obtained from the $\text{H}_2\text{PtCl}_6\text{--Fe}(\text{NO}_3)_3$ precursor. Since the $\text{H}_2\text{PtCl}_6\text{--FeCl}_2$ precursor yielded a solid product, Fe^{3+} is presumed to inhibit the reduction of platinum. Comparing the standard reduction potentials listed in Table 2, the reduction of Fe^{3+} to Fe^{2+} is more favored than that of PtCl_6^{2-} to PtCl_4^{2-} or PtCl_4^{2-} to Pt⁰. Although redox potential is lower in nanoscale [4], the remarkable difference in precipitation behaviors suggests the reduction of PtCl_6^{2-} to Pt⁰ undergoes two-electron reductions via PtCl_4^{2-} , which are inhibited by the presence of Fe^{3+} . The reduction potential of $\text{Fe}^{2+}/\text{Fe}^{3+}$ including the concentration variables is expressed by the following equation [27]:

$$E = E^0(0.77 \text{ V}) - 0.0591 \log(|\text{Fe}^{2+}|/|\text{Fe}^{3+}|) \quad (3)$$

where $|\text{Fe}^{2+}|$ and $|\text{Fe}^{3+}|$ are the concentration of Fe^{2+} and Fe^{3+} ions. The equation indicates that the initial 0.6 mM of Fe^{3+} needs to be lowered by about 90% for PtCl_6^{2-} reduction to occur preferentially.

The XRD patterns of unsupported Pt–M were presented in Fig. 1. The alloy composition was estimated from the lattice constant obtained using the Eq. (1) (Table 3). The precipitates from $\text{H}_2\text{PtCl}_6\text{--FeCl}_2$ and $\text{H}_2\text{PtCl}_6\text{--CoCl}_2$ precursors had Pt(111) diffraction peaks at slightly higher angle than that of pure Pt (39.8°), suggesting that Pt-rich alloys were formed. Meanwhile, those from $\text{H}_2\text{PtCl}_6\text{--CuCl}_2$ and $\text{H}_2\text{PtCl}_6\text{--CuSO}_4$ precursors had Pt(111) diffraction peaks at much higher angle, meaning a significant alloying occurred for Pt–Cu. Comparison of the M/Pt ratio in alloy ($\text{M}/\text{Pt}_{\text{alloy}}$ in Table 3) with the M/Pt ratio in entire solid product ($\text{M}/\text{Pt}_{\text{solid}}$ in Table 1) revealed that Co and Fe mainly exists as the Pt-rich alloys and Cu exists as both the Pt–Cu alloy and a non-crystalline part. The non-crystalline part would be amorphous CuO_x attached on Pt–Cu alloy nanoparticles since Cu would not be stable in metallic state in air [9,10].

The similar trends in transition metal content ($\text{M}/\text{Pt}_{\text{solid}}$) and alloying degree ($\text{M}/\text{Pt}_{\text{alloy}}$) corroborates that the precipitation

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