Comparison of structure and catalytic performance of Pt–Co and Pt–Cu bimetallic catalysts supported on Al_2O_3 and CeO_2 synthesized by electron beam irradiation method for preferential CO oxidation

Junichiro Kugai [a,*], Toshiharu Moriya [a], Satoshi Seino [a], Takashi Nakagawa [a], Yuji Ohkubo [a], Hiroaki Nitani [b], 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

ARTICLE INFO

ABSTRACT

In order to investigate the effect of transition metal addition to platinum with different support materials on preferential CO oxidation, structure and chemical properties of supported bimetallic catalysts prepared by electron beam irradiation method were correlated to the catalytic performance. On Al_2O_3, decoration of Pt by small amount of Co (Co/Pt ∼ 0.03) drastically increased CO and O_2 conversions while addition of equimolar Cu to Pt increased them only above 100 °C, where the rate-controlling factor was suggested to change from oxygen transport to CO activation. On CeO_2, either addition of Co or Cu to Pt had minor or negative effect on high O_2 conversion inherent to high oxygen transport at Pt–CeO_2 interface. On Pt–Cu/CeO_2, however, metal-CuO_x interface dominates the reaction characteristics to give improved selectivity, which is suitable for deep CO removal in excess O_2/CO condition. The order of selectivity above 100 °C, Pt–CoO_x > Pt(alloy)–CuO_x > Pt–CeO_2 interfaces, was derived from structural analysis and catalytic tests.

1. Introduction

Selective oxidation of carbon monoxide (CO) in H_2-rich gas stream is critical for polymer electrolyte fuel cells (PEFCs) since the Pt-based anode catalyst of fuel cell is easily poisoned even by ppm order of CO contamination [1]. Recently, various structures of Pt–M bimetallic catalysts have been prepared and successful improvements in catalytic performance have been reported [2,3]. For instance, Pt–Co has been found to be more active than Pt in PROX on various supports [4–10]. These reports show both cobalt oxides (CoO_x) and Pt–Co bimetallic phase can promote catalytic activity. The CoO_x was identified in sequentially impregnated Co/Pt/TiO_2 catalyst which basically enhanced low temperature activity [4]. Similar enhancement was also reported for Co/Pt/Al_2O_3 system [5]. On the other hand, Co can also modify Pt structure by forming

* 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), hiroaki.nitani@kek.jp (H. Nitani), takao@mit.eng.osaka-u.ac.jp (T.A. Yamamoto).

Pt–Co bimetallic phase. Komatsu et al. reported formation of intermetallic PtCo which caused electron transfer from Pt to Co and the electron-deficient Pt adsorbed CO weakly to accelerate the oxygen adsorption on the intermetallic phase [8]. Uniform alloy phase was found to be more active than core–shell structure in the study of Pt–Co/YSZ (yttria stabilized zirconia) [10]. This is also supported by the better performance of those prepared by sol–gel method than those prepared by impregnation [9]. Pt–Cu has not much been reported for PROX partly because Cu addition is not as beneficial as Co addition. On some support materials, Cu addition have negative influence on activity [11]. Such complicated effects of copper on Pt is also seen in oxygen reduction reaction (ORR), where various structures such as dealloyed Pt–Cu [12], near-surface alloy [13], core–shell alloy [14] have been reported to show different enhanced activities.

We have been studying Pt–Cu system with redox supports such as Fe_2O_3 and CeO_2 prepared by electron beam irradiation method [15–17]. It was found that Pt–Cu on Fe_2O_3 shows higher activity than Pt on Fe_2O_3, when copper content is excess to Pt. The catalysts consisted of Pt–Cu alloy and amorphous CuO phases, but the contribution of copper in each phase to catalytic performance was left unclear. For CeO_2-supported Pt–Cu, investigated later on, we observed little enhancement in activity by Cu addition, rather we observed better selectivity. The reaction characteristics of Pt–Cu were different on Fe_2O_3 and CeO_2 supports. Therefore, the purpose of present work is to elucidate the roles of second metals on different supports in Pt–M systems. For this purpose, monometallic Pt, bimetallic Pt–Co and Pt–Cu catalysts supported on Al_2O_3 (non-redox support) and CeO_2 (redox support) were synthesized using electron beam irradiation method and their PROX performances and compositional, structural, and chemical properties were correlated to draw active interface for each catalyst.

2. Methods

Monometallic Pt, bimetallic Pt–Co and Pt–Cu catalysts supported on commercial Al_2O_3 (NanoTek® C.I. Kasei Co., ~60 m²/g of surface area, 31 nm of particle size) and CeO_2 (NanoTek® C.I. Kasei Co., ~80 m²/g of surface area, 24 nm of particle size) were synthesized by electron beam irradiation method. H_2PtCl_6, $CoCl_2$, and $CuSO_4$ were employed as metal precursors. These salts were dissolved in pure water to obtain 0.1 mM of aqueous precursor solution. Alumina or ceria support was added to the solution to adjust Pt loading to 2.54 wt% and 2-propanol (0.25 mol/L) was added to scavenge oxidizing radicals formed during electron beam irradiation. The solution was deaerated with argon bubbling and sealed in a 750 mL polypropylene container, which was then irradiated with 4.8 MeV of electron beam for 6–7 s (20 kGy). This induces water radiolysis to produce radicals such as hydrated electrons and hydrogen radicals at one time, which in turn reduce metal precursors to metallic state. The reduced metals then bind together to form nanoparticles deposited on support. The resulting solid was separated by filtration and dried at 80 °C overnight and served for characterization and catalytic tests.

The composition of catalyst was analyzed by inductively-coupled plasma atomic emission spectroscopy (ICP-AES, ICPE-9000, SHIMADZU). The structure of bulk crystalline phase of nanoparticles was analyzed by X-ray diffraction (XRD, RINT2100-Ultima with Cu $K\alpha$ radiation, RIGAKU). The morphology of nanoparticles was analyzed by transmission electron microscope (TEM, H-800, HITACHI). Infrared absorbance of carbon monoxide adsorbed on platinum and support surface was analyzed by infrared spectroscopy (FT-IR, FT/IR-4000, JASCO). The powder samples were placed in a temperature-controlled diffuse reflectance chamber with a ZnSe window in 50 ml/min of argon and 3%CO/N_2 gas flow. Local structure and oxidation state of platinum and copper were investigated by XAFS spectra obtained at Photon Factory, a synchrotron facility (KEK, Tsukuba, Japan).

The catalytic tests were conducted 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% H_2, N_2 balance without moisture and 1% CO, 1% O_2, 64% H_2, N_2 balance with 10% moisture. 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_2 selectivity were calculated as follows:

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

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

$$Selectivity = (CO\ conversion)/(O_2\ conversion)/\lambda \times 100$$

where $|CO|_{out}$, $|O_2|_{out}$, $|CO|_{in}$, $|O_2|_{in}$ are concentrations of CO and O_2 in outlet, and those in inlet, respectively. The "λ" is defined as degree of O_2 excess from stoichiometry, i.e. twice of O_2/CO ratio in the feed.

3. Results and discussion

3.1. Catalyst composition

Table 1 shows metal loadings of the as-synthesized catalysts. Pt and Cu loadings were close to the target values, 2.54 wt% and 0.83 wt% for both Al_2O_3 and CeO_2 supports. Cobalt loading

Table 1 – Actual metal loadings of catalyst measured by ICP-AES and metal phase detected in XRD.				
Catalyst	Pt (wt%)	Co or Cu (wt%)	M/Pt (mol/mol)	Metallic phase
Pt/Al_2O_3	2.64	–	–	monometallic Pt
Pt–Co/Al_2O_3	2.78	0.014	0.020	monometallic Pt
Pt–Cu/Al_2O_3	2.54	0.85	1.0	bimetallic Pt–Cu
Pt/CeO_2	2.47	–	–	monometallic Pt
Pt–Co/CeO_2	2.45	0.13	0.18	monometallic Pt
Pt–Cu/CeO_2	2.75	1.07	1.2	bimetallic Pt–Cu