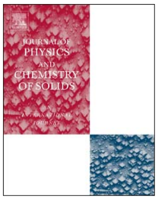
Journal of Physics and Chemistry of Solids 100 (2017) 49–56

Contents lists available at ScienceDirect

Journal of Physics and Chemistry of Solids

journal homepage: www.elsevier.com/locate/jpcs



Oxide composite prepared from intermetallic and amorphous $Zr_{67}Fe_{30}M_3$ (M=Au, Pt) alloys and their catalytic activity for CO oxidation

Yung-Han Huang [a], Sea-Fue Wang [a],*, Satoshi Kameoka [b], Kanji Miyamoto [b], An-Pang Tsai [b,c]

[a] Department of Materials and Mineral Resources Engineering, National Taipei University of Technology, 1, Sec. 3, Chung-Hsiao E. Road, Taipei 10608, Taiwan, ROC
[b] Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan
[c] National Institute for Materials Science, 1-2-1 Sengen, Tsukuba 305-0047, Japan

ARTICLE INFO

Article history:
Received 10 March 2016
Received in revised form
12 September 2016
Accepted 19 September 2016
Available online 20 September 2016

Keywords:
Gold
Platinum
Intermetallics
Amorphous alloy
Zirconium oxide

ABSTRACT

In this study, $Zr_{67}Fe_{30}M_3$ (M=Au, Pt) intermetallic compounds and amorphous alloys were prepared and used as precursors for the synthesis of oxides. Oxidation treatment of the intermetallic compounds at 500 °C followed by X-ray diffraction (XRD) analysis indicated that zirconium and iron were oxidized to ZrO_2 and Fe_2O_3, respectively. In the case of $Zr_{67}Fe_{30}M_3$ amorphous alloys, cubic Zr_6Fe_3O was observed on the surface of the ribbons after heat treatment at 500 °C in vacuum. Addition of 3% of gold or platinum to the alloy resulted in an increase in the lattice constants of the Zr_6Fe_3O phase. Grounding the treated ribbons into powders followed by an oxidation treatment at 500 °C in air produced Fe_2O_3 and ZrO_2 supports, where Au and Pt are dissolved in the oxides as confirmed by X-ray photoelectron spectroscopy (XPS). No matter precursors are intermetallics or amorphous phases, the resultant oxides are the same. Although Pt and Au dissolved in the oxides, catalytic activities for CO oxidation were significant improved.

1. Introduction

Catalysts are usually prepared using bottom-up processes such as the wet solution method or vapor deposition to form nano functional particles, which are then distributed on to the surfaces of supports using an impregnation or a deposition-precipitation process [1,2]. Top-down metallurgical methods such as selective etching of an alloy and pre-oxidation of an amorphous or an intermetallic compound have also drawn the attention of many researchers [3–5]. The atomic arrangement in an intermetallic compound follows a long-range ordered pattern. However, the atoms in amorphous materials are arranged arbitrarily, exhibiting only a short-range order. In these cases, the atoms have high coordination numbers and no grain boundary is observed. In the top-down metallurgical method, both the catalyst and the support are fabricated together and the active catalyst particles are homogeneously distributed on the support. Previous reports have shown that amorphous alloys are promising precursors for oxide-supported catalysts, primarily because of their easy preparation. These catalysts exhibit unique reactivity and selectivity in several important reactions [6].

Yamashita et al. [7,8] prepared catalysts for the hydrogenation of ethylene and butadiene from the precursors of amorphous Ni-P and Ni-B alloys. These alloys were pre-oxidized before being used as catalysts and their catalytic activities were strongly dependent on the conditions of oxidation treatment that determined the number of surface Ni particles. Yamasaki et al. [9,10] successfully prepared Ni catalysts from amorphous Ni-Zr alloy precursors. After oxidizing the precursors at 500 °C in air followed by reduction under hydrogen flow at 300 °C, tetragonal ZrO_2-supported Ni catalysts were formed. These catalysts reportedly showed good catalytic activities. Subsequently, the authors also found that addition of Sm to the Ni-Zr catalyst not only stabilized the tetragonal ZrO_2 but also increased the number and dispersity of active surface Ni sites [11]. Baiker et al. [12] prepared a catalyst consisting of Pd particles evenly dispersed in a ZrO_2 matrix from an amorphous $PdZr_2$ alloy using Chen's rapid quenching method [13]. The catalytic activity of this catalyst in the oxidation of CO was superior to those prepared using conventional chemical methods at low temperatures.

Takeshita et al. [14] discovered that intermetallic compounds, consisting of multiple rare earth elements such as Ce, Pr, and Er and transition elements such as Fe and Co, could promote the formation of ammonia (NH_3) after a hydrogen treatment. Soga

---

* Corresponding author.
E-mail address: sfwang@ntut.edu.tw (S.-F. Wang).

http://dx.doi.org/10.1016/j.jpcs.2016.09.010

et al. [15] and Endo et al. [4] prepared catalysts of metal hydrides through the reactions of lanthanum-nickel alloy ($LaNi_5$) and cerium-nickel alloy ($CeNi_2$), respectively, with hydrogen. These were found to possess excellent catalytic properties for the hydrogenation of ethylene. Luengo et al. [16] and Elattar et al. [17] have reported that $CeAl_2$ and $ThNi_5$ could be used as good catalysts for methanation.

In this study, oxide composites containing gold or platinum atoms were synthesized via a novel process. This involved heat treatment of the precursors of intermetallic compounds or amorphous alloys of a $Zr_{67}Fe_{30}M_3$ (M=Au, Pt) system in vacuum and in air. The oxide composites were characterized using X-ray diffraction (XRD), thermal gravimetric analysis (TGA), differential thermal analysis (DTA), and X-ray photoelectron spectroscopy (XPS). The catalytic activities of these catalysts for the CO oxidation reaction were also investigated.

2. Experimental procedure

Intermetallic compounds based on $Zr_{67}Fe_{30}M_3$ (M=Au, Pt) were arc-melted using pure zirconium (Rare Metallic Co. Ltd., 99.9%), iron (Rare Metallic Co. Ltd., 99.9%), gold (99.99%), and platinum (99.99%) under an Ar atmosphere. Melting was carried out four times to ensure the homogeneity of the samples. The intermetallic compounds were heated at 500 °C in air for 12 h to induce oxidation. The samples were crushed and ground into powders, and then analyzed. Subsequently, amorphous alloy ribbons were fabricated using the single-roller melt spinning technique in an Ar atmosphere with rapid quenching. Two routes were explored for preparing catalysts using these amorphous alloy ribbons. In the first method, the amorphous alloy ribbons were subjected to an oxidation treatment at 500 °C in air for 12 h, and then crushed and ground into powders. In the second case, the ribbons were heated at 500 °C in vacuum (10^{-5} Torr) for 6 h to trigger crystallization, and then crushed and ground into powders. These powders were finally oxidized at 500 °C prior to analysis.

Catalytic activity measurements for these catalysts were carried out using an apparatus comprising a standard fixed-bed flow reactor, a gaseous system, and an on-line gas chromatograph (Shimadzu GC-8A) equipped with Molecular Sieve 5 A (O_2, CO) and Porapak Q (CO_2). The reaction mixture consisted of CO (1 vol%) and O_2 (0.5 vol%) in a He flow. The reactor tube (with an inner diameter of 4 mm) was charged with 200 mg of catalyst at a total flow rate of 30 mL/min (total pressure: 1 atm; space velocity (SV): 30,000 h^{-1}). The data from the GC equipment were recorded when the reaction was maintained at a stable state after 30 min at each temperature.

Phase identification of precursors and oxidized powders was performed using X-ray diffraction (XRD, Rigaku RINT-2200). Thermogravimetric and differential thermal analyses (TG-DTA) were conducted in an Al_2O_3 crucible using a Rigaku Thermo plus TG8120 apparatus in an atmosphere of 20% O_2/Ar (400 mL/min) at temperatures ranging from room temperature to 1000 °C with a heating rate of 10 °C/min. The surface area of the particles was determined by Brunauer-Emmett-Teller (BET) analysis with a krypton adsorption analyzer (BELSORP Max, BEL Japan Inc.). The morphology and microstructure of the samples were observed with a field-emission scanning electron microscope (SEM, Hitachi S4700) and energy dispersive spectroscopy (EDS). High resolution X-ray photoelectron spectroscopy (HXPS) was carried out using high brilliance synchrotron radiation generated by NIMS undulator beam line BL15XU ($h\nu$=5.951 keV) at the SPring-8 facility in Japan.

3. Results and discussions

3.1. Oxides prepared from $Zr_{67}Fe_{30}M_3$ (M=Au, Pt) intermetallic compounds

Ingots of $Zr_{67}Fe_{30}M_3$ (M=Au, Pt) intermetallic compounds were prepared through repeated melting. XRD phase identification was performed on the powders produced by crushing and grinding the ingots of $Zr_{67}Fe_{33}$, $Zr_{67}Fe_{30}Au_3$, and $Zr_{67}Fe_{30}Pt_3$. The results of these experiments are shown in Fig. 1. The XRD pattern of the $Zr_{67}Fe_{33}$ powders was identified as an intermetallic compound with the tetragonal symmetric structure of I4/mcm(140) $CuAl_2$ (JCPDS#25-0420), and small amounts of second phases also being present including pure hexagonal *P*63/*mmc* (194) Zr (JCPDS#05-0665), pure cubic Fe (JCPDS#65-4899), and cubic Fd-3m(227) $ZrFe_2$ intermetallic compound (JCPDS#65-0595). These second phases could have been present in the host ingot after the smelting process and did not disappear even after repeated melting of the ingot. For the powders of $Zr_{67}Fe_{30}Au_3$ and $Zr_{67}Fe_{30}Pt_3$ intermetallic compounds, the XRD patterns were similar to that of $Zr_{67}Fe_{33}$ powders, while the intensities of their phases were slightly different.

To investigate the oxidation behavior of these intermetallic compounds at different temperatures, a DTA study of bulk $Zr_{67}Fe_{33}$, $Zr_{67}Fe_{30}Au_3$, and $Zr_{67}Fe_{30}Pt_3$ was undertaken at a heating rate of 10 °C/min. Results of these experiments are shown in Fig. 2. For the $Zr_{67}Fe_{33}$ intermetallic compound, a sharp exothermic peak at 368 °C and a broad exothermic peak centered at approximately

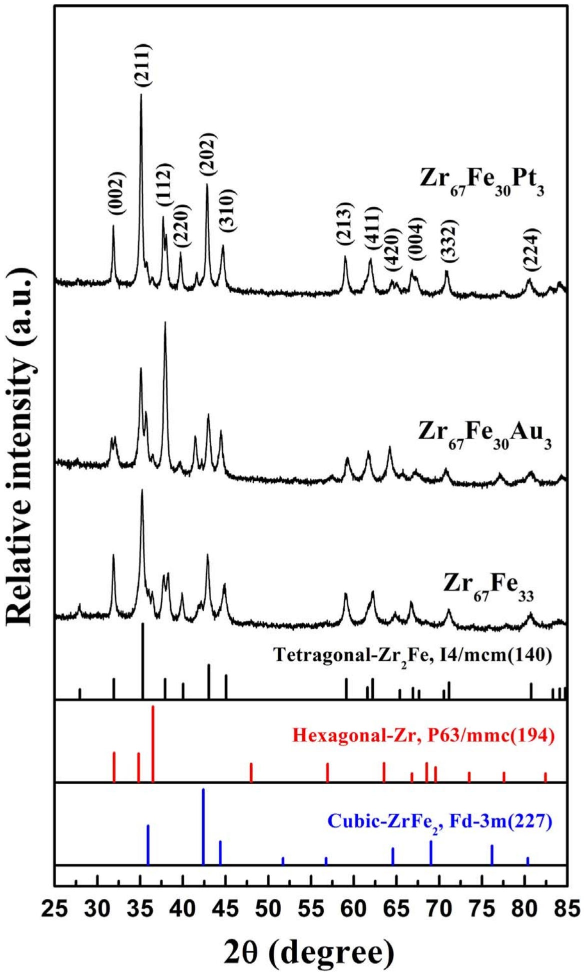


Fig. 1. X-ray diffraction patterns of as prepared Zr-Fe intermetallic compounds.