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Ai Nozaki,* Ayane Yamashita, Ryosuke Fujiwara, Chiyako Ueda, Hiroaki Yamamoto, and Masao Morishita

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Nanoporous CeO₂ supports prepared from amorphous alloys: Enhanced catalytic performance for hydrogen generation from formic acid

Ai Nozaki,*1 Ayane Yamashita,1 Ryosuke Fujiwara,1 Chiyako Ueda,1 Hiroaki Yamamoto,1 and Masao Morishita1

¹ Department of Chemical Engineering and Materials Science Graduate School of Engineering, University of Hyogo, 2167 Shosha, Himeji,

Hyogo 671-2201

E-mail: nozaki@eng.u-hyogo.ac.jp



Masao Morishita received his Ph. D degree from Osaka University in 1986. He joined Kobe Steel, Ltd. as a research engineer. In 1992, he moved to University of Hyogo as a research associate and was promoted to Professor at the Department of Chemical Engineering and Materials Science in 2005. He has also served as a committeeman of the project of OECD for the nuclear fuel waste safety management since 2010. He was awarded the Spriggs Phase Equilibria Award (2005) from the American Ceramic Society. His research scope is chemical thermodynamics of materials related to energy conversion.



Ai Nozaki received her Ph. D degree in engineering from Osaka University in 2016. Then she was a postdoctoral researcher at Osaka University (2016). Currently, she is working at University of Hyogo as an assistant professor. Her present research focuses on catalytic performance of nanoporous material prepared from amorphous alloy.

Abstract

Nanoporous CeO₂ samples as supports were prepared by chemical dealloying of the Ce-Al amorphous alloy, followed by synthesis of the Au-Pd/CeO₂ catalysts. The synthesized Au-Pd/CeO₂ catalysts showed higher catalytic activity for hydrogen generation from formic acid than catalysts using supports prepared from a crystalline alloy precursor.

Keywords: nanoporous metal oxide, amorphous alloy, hydrogen generation.

1. Introduction

The properties and structures of the catalytic support greatly affect catalytic performance. CeO₂ is a simple basic oxide for promoting the dissociation of H^{+ 1-3}. Multiple methods exist for preparing CeO₂, such as calcination of cerium hydroxide or cerium oxalate. In the present study, we focused on nanoporous CeO₂ prepared by the dealloying method⁴⁻⁶. Nanoporous materials were prepared via selectively extracting a specific component from a mother alloy^{7, 87, 8}. The dealloying method possesses the following advantages: 1. The pore size can be controlled from nano to micro scales by controlling the extraction time and temperature; 2. Samples with high surface area and a co-continuous porous structure can be obtained; 3. Low coordination atoms tend to be exposed on the surface. We have already reported that using an amorphous alloy as the nanoporous material precursor results in a material with higher catalytic activity than can be obtained using a crystalline alloy9-12.

Amorphous alloys are disordered in the atomic arrangement, and many researchers across a wide range of fields have been attracted to study such materials because of their unique properties¹³⁻¹⁸. By using an amorphous alloy as the CeO₂ precursor, the resulting material was expected to exhibit much better catalytic performances than if a crystalline alloy precursor was employed. Al can form an amorphous structure with Ce (composition range of Ce: 7 to 10 atom%)¹⁹, and Al can be selectively extracted by NaOH treatment. Thus, a CeO₂ support was prepared from an amorphous Al-Ce alloy.

The hydrogen fuel cell, a next-generation energy candidate,

generates electric energy when hydrogen reacts with oxygen in the air; thus, it is a source of clean environmentally friendly energy. However, many problems must be addressed before the use of hydrogen fuel cells can be expanded, especially concerning the distribution of fuel remotely. From the viewpoint of energy and cost, it is difficult to store and transport hydrogen fuel. As a solution to this problem, a chemical hydrogen storage / generation system that can utilize a high hydrogen-containing compound for storing and transporting hydrogen in a stable state is attractive²⁰⁻²³.

We focused on hydrogen production from formic acid, which is an energy carrier that can effectively utilize carbon dioxide. Formic acid has a hydrogen content of 4.4 wt%, and CO₂, a by-product from the formic acid decomposition reaction, can be recycled back to formic acid by hydrogen reduction^{20, 23}. Development of a high-performance catalyst is the key to efficient hydrogen generation from formic acid. Pd is one of the most selective toward the hydrogen production as well as catalytically active for formic acid decomposition. However, monometallic Pd catalysts have low reusability due to the CO poisoning. Various bimetallic Pd-based catalysts are already reported in the literature (PdCu²³, PdCo, ²⁴ PdNi²⁵, PdAu²⁶⁻²⁹). Among them, Pd-Au bimetallic catalysts have received attention due to their higher resistance to CO poisoning and excellent catalytic performance in selective formic acid dehydrogenation.

In this study, we investigated the effect of the precursor's atomic arrangement on the resulting CeO₂ structure and the catalytic performance of the prepared catalysts for hydrogen generation from formic acid. We developed catalysts that demonstrated excellent performance for hydrogen generation from formic acid: Au-Pd particles supported on CeO₂.

2. Experimental

2.1 Catalyst preparation.

Scheme 1 presents the procedure for sample preparation. According to the literature, amorphous Ce-Al alloys can be prepared within a Ce range of 7%–10%. A master ingot of Ce₈Al₉₂ was prepared from a mixture of pure Ce and Al lumps using the arc-melt technique in a highly purified Ar atmosphere.



Scheme 1. Procedure for the preparation of Au-Pd/CeO₂.

Amorphous Ce₈Al₉₂ (a-CeAl) in the form of ribbons (1 mm wide, 10–20 μ m thick) were produced from master ingots through liquid quenching by a single roller melt-spinning method using a copper wheel. The Al moieties were selectively extracted from a-CeAl by immersion in 1 M aqueous NaOH at 343 K for 10 h followed by washing with distilled water and drying, to fabricate nanoporous CeO₂ (a-CeO₂). For the preparation of crystalline Ce-Al alloys (c-CeAl), a-CeAl was heated at 573 K under vacuum. The nanoporous CeO₂ samples prepared from NaOH treatment of c-CeAl was denoted c-CeO₂.

Au-Pd/a-CeO₂ and Au-Pd/c-CeO₂ (Au loading: 4 and 7 wt%, Pd loading: 3 wt%) were synthesized by depositing Au-Pd on the as-synthesized a-CeO₂ and c-CeO₂.The appropriate quantities of HAuCl₄ (11.8 mmol/L) and Pd(NH₃)Cl₂ (9.7 mmol/L) were dissolved in 20 mL water. After adding CeO₂ support to the solution, the mixture was stirred at room temperature for 18 h. The mixture was filtered and washed several times. Then, the solids were air-dried overnight and pre-reduced with NaBH₄. For comparison, Au-Pd particles (Au loading: 1, 2, 3, 4, and 5 wt%, Pd loading: 3 wt%) were deposited on JRC-CEO-2 (reference catalyst, The Catalysis Society of Japan) via the same method to yield Au-Pd/JRC-CEO-2 as a standard reference catalyst. Au/Pd/JRC-CEO-2 and Pd/Au/JRC-CEO-2 were prepared by depositing Au on Pd/JRC-CEO-2 and depositing Pd on Au/JRC-CEO-2, respectively.

2.2 Catalyst characterization.

X-ray diffraction (XRD; Rigaku, Ultima IV) was used to analyze the crystallinity of the samples. Field emission-scanning electron microscopy (FE-SEM; Jeol, JSM-7001) was used to observe the surface morphology of the samples. The sample surfaces were coated with carbon using an ion-sputtering instrument. The atomic ratio on the surface was analyzed by energy dispersive X-ray spectrometry (EDX, EDAX Ltd. DX-4). The surface areas of the samples were estimated by the Brunauer-Emmett-Teller (BET) method using nitrogen physisorption isotherms obtained at 77 K (MicrotracBEL Corp. BEL-SORP mini). X-ray photoelectron spectroscopy (XPS) was performed to evaluate the Au oxidation state on the sample surface.

2.3 Catalytic reactions.

The prepared Au-Pd/CeO₂ catalysts (100 mg) were placed into a rubber septum-sealed quartz reaction vessel. The reaction vessel was connected to a gas burette and purged with N₂. A mixture of formic acid (0.23 mL), triethanolamine (NEt₃: 0.286 mL) and distilled water (2.48 mL) was injected to initiate the reaction. During the reaction, the mixture was magnetically stirred at 333 K and no air was allowed into the system. After appropriate intervals, the generated gas was measured by reading the scale on the gas burette. To investigate catalyst reusability, the supernatant was removed after the reaction was completed and more reaction mixture was added using a syringe to start the next reaction cycle in the reusability test.

3. Results and Discussion 3.1 Characterization of the CeO₂ supports

To investigate the crystallinities of a-CeAl, c-CeAl, a-CeO₂, and c-CeO2, XRD measurements were carried out (Figure 1). Sharp peaks indicating the presence of crystalline phases were not observed in a-CeAl (Figure 1a), and broad peaks derived from the amorphous states were observed. It was confirmed that a-CeAl, prepared by the rapid quenching method, mainly existed in an amorphous state. The XRD pattern of c-CeAl showed sharp peaks, assigned to Al and Ce₃Al₁₁, indicating that c-CeAl mainly existed in a crystalline state (Figure 1c). The peaks assigned to the CeO₂ crystal were observed from a-CeO₂ and c-CeO₂, and Al could be selectively extracted from the Ce-Al alloy by the dealloying treatment (Figure 1b and d). After drying processes of a-CeO₂ and c-CeO₂, the color of the samples turned yellow in color which originates from CeO2 crystals. This result suggests that Ce species were easily oxidized during the drying process under air.

FE-SEM was used to observe the morphology of the sample before and after the dealloying treatment (Fig. 2). No pores and cracks were observed in a-CeAl and c-CeAl, while many pores and CeO₂ ligaments were observed in a-CeO₂ and c-CeO₂. The porous structure was expected to form from the selective



Figure 1. XRD patterns of (a) a-CeAl, (b) a-CeO₂, (c) c-CeAl, and (d) c-CeO₂.



Figure 2. FE-SEM images of (a) a-CeAl, (b) c-CeAl, (c) a-CeO₂, and (d) c-CeO₂.

Table 1. Atomic ratios, surface areas, pore volume and pore diameter of the prepared alloys and CeO₂ samples.

	Atomic ratio		Surface area	Pore	Pore
Sample	/ at%			volume	diameter
	Ce	Al	/ m-g -	$/cm^3 g^{-1}$	/ nm
a-CeAl	9	91	<1	-	-
c-CeAl	9	91	<1	-	-
a-CeO ₂	91	9	244	0.52	7.7
c-CeO ₂	95	5	117	0.31	12.4
JRC-CEO2	100	0	123	0.23	7.1

^a Atomic ratio determined by EDX

^b Surface area estimated by the BET method.

extraction of Al moieties from a-CeAl and c-CeAl by the dealloying treatment. However, some pores in c-CeO₂ collapsed, resulting in aggregated CeO₂ ligaments. The extraction of Al moieties from the crystalline alloys proceeded rapidly near the grain boundary, which tends to cause disaggregation of CeO₂. On the contrary, in the case of amorphous alloys, the Al moieties were extracted uniformly and slowly from the surface. Thus, the dissolution behavior of Al strongly affected the surface morphology of the resulting CeO₂ supports.

The composition ratios of Ce and Al in the samples before and after dealloying treatment were measured by EDX (Table 1). The composition ratios of the a-CeAl and c-CeAl were ca. 9 atom% Ce and 91 atom% Al. After the de-alloying treatment, the ratio of Al moieties decreased, indicating Al moieties were selectively extracted.

The BET surface areas of the samples were estimated using nitrogen physisorption isotherms (Table 1). The surface areas of a-CeAl and c-CeAl were quite low (<1 m² g⁻¹) due to their smooth surface morphologies (Figure 2a and b). a-CeO₂ had a high surface area compared to JRC-CEO₂. a-CeO₂ prepared from the Ce-Al amorphous alloy had a higher surface area (244 m² g⁻¹) than that prepared from the crystalline alloy (c-CeO₂, 117 m² g⁻¹). The collapse of pores and the aggregation of CeO₂ ligaments might have caused the low surface area for c-CeO₂.

3.2 Catalytic performance of Au-Pd/CeO₂

To investigate the loading method, metal species, and amounts of metal loaded, a decomposition reaction of formic acid was carried out by loading metals over JRC-CEO2 instead of a-CeO₂. The time course for the hydrogen production from formic acid decomposition reaction using various catalysts was monitored periodically, as shown in Figure S1. The reactions proceed over Pd/JRC-CEO2, while, in the reusability test, the catalytic activity decreased significantly. Pd surface poisoning from by-product CO generation was thought to be the source of this decreased activity. Pd is typically alloyed with Au to suppress this deactivation. Au-Pd/JRC-CEO2 showed excellent catalytic properties at 333 K and also performed well in the reusability test with excellent reuse activity. To improve the catalytic activity, the relationship between Au loading and gas production over the Au-Pd/JRC-CEO2 catalyst was investigated. As shown in Figure S2, Au(4wt%)-Pd/JRC-CEO2 showed high activity and reusability. The effects of loading order on the catalytic activity and reusability were examined (Figure S3). It was found that the Au-Pd/JRC-CEO2 catalyst supporting Au and Pd at the same time exhibited the highest activity and reusability.

According to the XPS measurement results (Table S1), the Au/Pd atomic ratio of Au-Pd/JRC-CEO2 (Au: 4 wt%, Pd: 3 wt%) was about 1. Yu et al. reported that Pd atoms which lack adjacent Au atoms favor dehydration of HCOOH, whereas Pd atoms that possess Au atoms as nearest neighbors favor dehydrogenation of HCOOH.²⁶ It is assumed that the Au atoms on Au-Pd/JRC-CEO2 (Au: 4 wt%, Pd: 3 wt%) contributes to the selective hydrogen production via formic acid decomposition..

To investigate the effect of catalyst support on the catalytic properties, the prepared porous CeO₂ (a-CeO₂ and c-CeO₂) substrates were used as catalyst supports. The activity of Au(4wt%)-Pd/JRC-CEO2 was higher than that of the prepared Au(4wt%)-Pd/a-CeO₂ catalyst (Figure 3 and S4). XPS results showed that the surface composition ratios of Au and Pd were different and much of the Pd was exposed on the Au(4wt%)-Pd/a-CeO₂ surface (Table 2). The surface atomic ratios were different depending on the support material. Despite the same amount of Au (4wt%) and Pd (3wt%) loaded, the surface of the CeO₂ support did not have the ideal 1:1 Au:Pd ratio; therefore, the differences in surface area and structure of CeO₂ as a support greatly influenced the structure of the supported metal. To make the surface composition ratio of Au and Pd approximately 1:1, the amount of Au supported was increased to 7 wt%. The catalytic activity of Au(7wt%)-Pd/a-CeO2 showed about 2 times as high as that of Au(4wt%)-Pd/a-CeO2. The catalytic performances of Au-Pd/a-CeO2 and Au-Pd/c-CeO2 prepared by liquid phase reduction were also investigated (Figure 3). Compared with Au-Pd/c-CeO₂, a higher catalytic activity was observed for Au-Pd/a-CeO2. In the reusability test, it was found that Au(7 wt%)-Pd/a-CeO₂ showed the highest activity among the prepared samples. (Figure S4).



Figure 3. Gas evolution from formic acid over Au-Pd/CeO $_2$ catalysts.

Table 2. Loading amounts of Au and atomic ratios of Au and Pd over Au-Pd/CeO₂ samples.

Sample	Au /wt%	Atomic ratio ^a / at%	
		Au	Pd
Au-Pd/JRC-CEO2	4	51.7	48.3
Au Pd/a CaOa	4	30.0	70.0
Au-Fu/a-CeO2	7	52.9	47.1
Au-Pd/c-CeO ₂	7	59.9	40.1

^a Atomic ratio determined by XPS.

In the Au 4f XPS spectra of the Au-Pd/CeO₂ samples (Fig.4), the binding energies of Au-Pd/CeO₂ samples were lower compared to that of Au/CeO₂. The Pd 3d XPS spectra of the Au-Pd/CeO₂ samples showed lower binding energies than Pd/CeO₂. The shifts in binding energy indicated the changes in the charge states of Au and Pd, verifying the formation of the alloy structures. ³⁰

Figure 5 shows the XRD patterns of the Au-Pd/CeO₂ samples (Au(7 wt%)-Pd/a-CeO2, Au(7 wt%)-Pd/c-CeO2 and Au(4 wt%)-Pd/JRC-CEO2). The peaks of Au-Pd/CeO2 samples were located between two dotted dash lines which are assigned to Au(111) (2θ =38.3°) and Pd(111) (2θ =40.1°) reflections. The peak position in the XRD patterns suggest that the prepared Au-Pd structures were alloy. The crystallite diameters of Au-Pd were estimated to be 4.7, 8.0, and 5.1 nm for Au-Pd/a-CeO₂, Au-Pd/c-CeO₂, and Au-Pd/JRC-CEO₂, respectively, which were calculated from the half height widths of the peaks. The crystallite size of Au-Pd particle on a-CeO2 is small, which suggests that Au-Pd/a-CeO2 may have small particle sizes. It is assumed that smaller Au-Pd alloy particles can be prepared by dispersing Au-Pd particles on a-CeO2 having the large surface area and leads to the high catalytic activity for hydrogen generation from formic acid. a-CeO2 showed excellent support performance and a fine porous structure; thus, it could be applied as a support for many reactions.



Figure 4. Au 4f and Pd 3d XPS spectra of the prepared samples ((a) Au(7 wt%)-Pd/a-CeO₂, (b) Au(7 wt%)-Pd/c-CeO₂, (c) Au(4 wt%)-Pd/JRC-CEO₂, (d) Au/JRC-CEO₂, (e) Pd/JRC-CEO₂).



Figure 5. XRD patterns of (a) Au(7 wt%)-Pd/a-CeO₂, (b) Au(7 wt%)-Pd/c-CeO₂, (c) Au(4 wt%)-Pd/JRC-CEO₂.

4. Conclusion

The sample supporting Au-Pd on nanoporous ceria prepared from an amorphous alloy exhibited high catalytic activities during the formic acid decomposition reaction. Although the appropriate amount of Au differed depending on the support, the catalyst activity was found to be improved by controlling the Au:Pd composition ratio to approximately 1:1. The CeO₂ supports prepared from the amorphous alloys had fine structures and appear to be effectively used for improving the catalytic activity compared with catalysts prepared from a crystalline alloy.

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