Applied Catalysis B: Environmental 221 (2018) 393–405

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

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

Research Paper

# Carbon-supported $Pd_{100-X}Au_X$ alloy nanoparticles for the electrocatalytic oxidation of formic acid: Influence of metal particles composition on activity enhancement

T. Szumełda, A. Drelinkiewicz*, E. Lalik, R. Kosydar, D. Duraczyńska, J. Gurgul

*Jerzy Haber Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Niezapominajek 8, 30-239 Krakow, Poland*

## ARTICLE INFO

*Keywords:*
Bimetallic nanoparticles
Palladium-gold
Electrocatalytic activity
Formic acid oxidation

## ABSTRACT

Two series of carbon-supported $Pd_{100-X}Au_X$ catalysts of different Au contents have been synthesized by the "water-in-oil" microemulsion method (Triton X 114, cyclohexane) using precursor solutions of low (series L) and high concentration (series H). The metal nanoparticles are characterized by XRD, electron microscopy (SEM, HRTEM) and XPS to determine their crystal structure, particles size, composition and morphology. The electrochemical measurements provide data concerning surface properties of the PdAu particles, including surface fraction of Pd and Au and the reactivity towards hydrogen sorption/desorption processes. The metal particles of low bulk Au-content (Au/Pd $<$ 1) are of high monodispersity and of smaller size than their monometallic Pd and Au counterparts, synthesized by the same method. At higher bulk Au-content (Au/Pd $>$ 1), the particle size increases approaching almost the size of Au particles. An enrichment of Pd toward the surface of all the $Pd_{100-X}Au_X$ particles occurs, much pronounced in the samples H series. The activity of catalysts (based on the current densities, and TOF values) in the electrooxidation of formic acid (FA) is correlated with the bulk and surface composition of the $Pd_{100-X}Au_X$ particles. The high monodispersity of the metal particle size in the studied catalysts made it possible to observe relation between FA electrooxidation activity and surface composition of the PdAu particles. The catalytically active sites formed at the Au surface fraction ca. 0.1–0.12 (Pd 0.9–0.88) display 1.6-times higher activity (TOF) as compared to pure Pd, while higher surface Au fraction strongly reduces activity. The occurrence of electronic modification of Pd by Au in the $Pd_{100-X}Au_X$ particles also results in a reduced hydrogen solubility, accompanied by weaker Pd—H bonds, which might influence the poisoning ability by CO formed through electroreduction of $CO_2$, the product of FA oxidation.

## 1. Introduction

Formic acid (FA) has great potential as an *in situ* source of hydrogen for fuel cells. It offers high energy density, is non-toxic and can be produced by renewable technologies, namely from lignocellulosic biomass. Currently, catalytic and electrocatalytic decomposition of formic acid in the presence of Pd-based catalysts is widely studied as a promising route of hydrogen generation under mild conditions.

The FA chemical decomposition carried out in vapor or liquid-phase and related electrochemical reaction can proceed via two alternative reaction pathways, dependent on the nature of metal sites; first, the desirable dehydrogenation to hydrogen and carbon dioxide, either $HCOOH \rightarrow CO_2 + H_2$ or $HCOOH \rightarrow CO_2 + 2H^+ + 2e$ Eq. (1), and second, the undesirable dehydration to carbon monoxide, $HCOOH \rightarrow CO + H_2O$ Eq. (2), a poison for Pd, Pt [1]. Current research has suggested that Pd is one of the most active catalyst for FA (electro)chemical decomposition as the direct pathway predominates on Pd-surface, consistent with the DFT calculations [2]. Unfortunately, deactivation of Pd catalysts is commonly observed, caused either by oxidation of Pd surfaces or its poisoning by adsorption of either CO or other unidentified organic species present in the FA fuel [1,3,4]. The spectroscopic studies revealed that CO(ads) accumulated on Pd electrode surface was formed via electrochemical reduction of $CO_2$ produced in the desired dehydrogenation pathway [5,6]. Such "self-poisoning" mechanism has been proved using electrocatalyst with thin Pd layers deposited on Au substrate [7].

However, Pd-based alloy catalysts offered better performance compared to pure Pd, related to higher resistance to poisoning species. Various bimetallic catalysts such as PdCu, PdPb, PdPt, PdSn, PdCo, PdIr, PdRu, PdNi have been already tested [1]. Among them, the PdAu catalyst has been shown to be one of the most promising catalyst for hydrogen generation via the FA electro(chemical) decomposition.

---

* corresponding author.
*E-mail address:* ncdrelin@cyf-kr.edu.pl (A. Drelinkiewicz).

http://dx.doi.org/10.1016/j.apcatb.2017.09.039
Received 13 July 2017; Received in revised form 14 September 2017; Accepted 16 September 2017

Recently published experimental and calculation studies demonstrated that activity of Pd-Au systems for FA decomposition through a desired dehydrogenation reaction is rationalized either by the "ensemble" effect or the "ligand" effect. The former manifests itself by the appropriate Pd/Au surface atomic arrangements, the latter by the electronic interaction between the Pd surface atoms and atoms (Pd, Au) in the subsurface layer [8]. The existence of electron-rich Pd species in the Pd@Au [9,10] and Pd@Ag [11] core-shell nanostructures enhanced activity as they can weaken the adsorptive strengths of reaction intermediates thus facilitating the O—H and C—H bond cleavage in the Pd – formate intermediates. Furthermore, enhanced tolerance toward CO adsorption observed in numerous FA electrooxidation reactions on the Pd-Au catalysts has been explained by much weaker CO adsorption on Au-surface than on Pd-surface.

An Au-promotion effect was observed using the Pd-Au (electro) catalyst of various configurations including core-shell structures, nanstructured systems, unsupported and carbon-supported PdAu particles. They were prepared by deposition of Pd shells of various thickness on hollow Au nanospheres [12,13], successive deposition of Pd onto Au particles [14] or by a subsequent deposition of Au on the Pd particles in PdAu/MWCNT catalysts [15]. The PdAu nanostructures obtained by typical preparation procedure e.g. co-reduction of Pd and Au precursors carried out at various conditions including different reducing agents and reaction medium (ethylene glycol and sodium citrate medium, THF-water instead of water medium) were also studied [16–21]. Alloying degree of Pd and Au components in these systems was observed to be decisive for the FA electrooxidation activity. The CNT-supported $Pd_{82}Au_{18}$ particles of alloy structure exhibited higher activity than non – alloy samples or pure Pd [17,18]. Zhang et al. [19] also observed that activity of $Pd_{88}Au_{12}$/C catalyst with metal particles of high alloying degree prepared in the THF-$H_2O$ mixture displayed higher activity than their counterparts of low alloying degree obtained in aqueous solution. Maiyalagan et al. [20] reported that electroactivity of functionalized graphene-supported $Pd_{100\text{-}X}Au_X$ particles increased with growing bulk Au content, but not linearly, the $Pd_3Au$ composition generated the highest electroactivity. For series of f-MWCNT-supported $Pd_{100\text{-}X}Au_X$ nanostructured catalysts, the activity dependence on bulk composition was bell-shaped, with maximum attained at the $Pd_{88}Au_{12}$ bulk composition [21].

In all these studies the activity has been related to bulk Au content in the PdAu structures in spite of the fact that surface properties like Pd/Au ratio and the arrangement of atoms (Pd, Au) are crucial for the electro(chemical) FA decomposition reaction. The identity of the metal atoms adjacent to the Pd atoms at Pd-Au surface was found to be decisive for the directing the FA decomposition via dehydrogenation or dehydration pathways [22]. Pd atoms that reside at Pd-Au interface sites favors FA decomposition through a desired dehydrogenation reaction pathway, whereas Pd atoms which lack neighboring Au atoms, favor dehydration of FA generating CO. It has been also showed by DFT that on the PdAu surface with the reduced amounts of Pd atomic ensembles consisting of three continuous Pd atoms the formation rate of CO can be suppressed because of very high activation energy barrier. [23]. According to Lee et al. [8] the Pd/Au atoms arrangements near the surface is crucial for the reactivity toward FA dehydrogenation path. Among four different PdAu model alloys of different surface and subsurface atomic Pd/Au arrangements, the $Pd_3Au_1$ was found to be the most preferred as it exhibited the lowest reaction energy barrier for FA dehydrogenation reaction.

However, the controllability over the size and composition of the catalyst particles in most of previous studies have been rather limited because of the choice of the synthesis method. Commonly applied the co-impregnation and subsequent deposition methods produce bimetallic particles of a broad size distribution and the high temperature treatment needed to obtain the alloy structures further facilitates particles aggregation. An alternative are the colloid-based procedures, allowing a better control of the nanoparticles size and composition, among them the reverse "water-in-oil" microemulsion (w/o) method. This method has attracted much attention for preparation of highly monodisperse particles of metal oxides, metal sulfides, polymers, supported monometallic (Pd, Pt) and bimetallic (PtRu, PtCo, PtAu, PtNi, PdAu, PdPt, AuAg) catalysts [24–27].

In the w/o method the formation of metal particles occurs inside the aqueous droplets acting as individual nano-reactors. As the result, it is possible to (i) control the metal particle size, (ii) obtain a narrow size distribution of metal particles (so-called "monodisperse particles") thereby allowing high uniformity of their structural and surface properties. The concentration of metal precursor and microemulsion composition are experimental variables playing decisive role in the size, morphology and metal components segregation in the bimetallic particles [27–29]. The formation of metal particles inside the reverse micelles proceeds via nucleation and growth processes. Metal particles are formed from nucleus, which can grow by building up new layers deposited over the previous one. The results of Monte Carlo simulations [28,30] showed that metal components distribution in final particle is defined by a sequence in metal components deposition and the key factor is the difference in their reduction rates mostly governed by a difference in the standard reduction potentials. The metal species having the higher redox potential will precipitate first forming core, followed by the co-precipitation of the second component, which prevails at the surface. The simulated metal components segregation profiles found well confirmation for various experimentally prepared bimetallic nanoparticles [27]. For example, a relatively large difference of the Pd and Au redox potential ($AuCl_4^-$/Au 1.00 V and $PdCl_4^{2-}$/Pd 0.68 V vs SHE) preferred segregation of metal components generating the PdAu nanclusters with Pd-rich surface [31]. It follows, that the segregation of metal components may be controlled by changing the concentration of metal precursors solution and/or by altering the water/surfactant ratio (parameter *W*). Such possibility has been not only predicted by calculations, but also confirmed by experimental data for the Pt-Au particles [27,29]. In diluted precursors solution almost homogeneous Pt-Au alloy structure was formed, while more concentrated solution promoted surface segregation of Pt [29].

In the present work, two series of carbon-supported catalysts with monodisperse $Pd_{100\text{-}X}Au_X$ alloy nanoparticles (from $Pd_{91}Au_9$ up to $Pd_{36}Au_{64}$) were prepared by the reverse "water-in-oil" microemulsion procedure, described in detail in our previous papers [32,33]. Keeping the microemulsions composition fixed (Pd/Au ratio) the precursor solutions of low and high concentrations were used to prepare series (L) and (H) catalysts, respectively. Several techniques have been used, namely: XRD, XPS and electron microscopy, to characterize physicochemical properties of nanoparticles, like their size, morphology, structure and composition. The electrochemical measurements provided data concerning surface properties of the PdAu particles, including surface fraction of Pd and Au components and the reactivity towards hydrogen sorption/desorption processes. The high monodispersity of the metal particle size in the studied catalysts made it possible to found the correlation between the bulk and surface composition of the PdAu/C catalysts and their activity for the FA electrooxidation. Due to a low Pd loading (2 wt%) in the studied catalysts, it was also possible to observe that the Au component reduces hydrogen solubility in the $Pd_{100\text{-}X}Au_X$ particles, compared to pure Pd, as well as that the Pd-H bonds formed in the PdAu alloys are weaker. This may possibly reduce the poisoning effect of CO formed in a side reaction of electroreduction of $CO_2$.

## 2. Experimental

Carbon (Vulcan XC72, supplied by CABOT) was used as the support. The catalysts are prepared by means of reverse "water-in-oil" microemulsion method as described in detail in our earlier paper [32]. All the PdAu/C catalysts are synthesized to have Pd loading equal to 2 wt% whereas the Au loading varies resulting in the molar ratio of Pd/Au