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Hydrogen electrooxidation on PdAu supported nanoparticles: An experimental RDE and kinetic modeling study

A. Bonnefont[a,*], A.N. Simonov[b], S.N. Pronkin[c], E.Yu. Gerasimov[b], P.A. Pyrjaev[b], V.N. Parmon[b], E.R. Savinova[c]

[a] Institut de Chimie, UMR 7177, CNRS-Université de Strasbourg, 4 rue Blaise Pascal, 67000 Strasbourg, France
[b] Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, Prospekt Akademika Lavrentieva, 5, Novosibirsk 630090, Russia
[c] Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse, ECPM, Université de Strasbourg, UMR 7515 CNRS-UdS, 25 rue Becquerel, 67087 Strasbourg Cedex 2, France

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ABSTRACT

The influence of the apparent Pd coverage on Au nanoparticles on the kinetics of the hydrogen oxidation (HOR) reaction has been explored by combined experimental rotating disc and microkinetic modeling study. PdAu bimetallic electrodes with variable Pd coverage in the interval from 0.07 to 2 MLs were obtained by electrodeposition of Pd on carbon supported Au nanoparticles. The experimental rotating disc electrode curves have been analyzed with the help of a kinetic model, in order to shed light on the predominant HOR mechanism (Heyrovsky–Volmer vs. Tafel–Volmer), the nature of the rate determining step, and their dependence on the Pd coverage, and get an insight into the type of HOR intermediate. The kinetic modeling suggests that the Heyrovsky–Volmer mechanism can reproduce the experimental curves for the whole range of Pd coverages explored. However, the Tafel step cannot be fully discarded around the equilibrium potential, its eventual contribution increasing as the coverage of Pd is reduced. The results of this work support a weakly adsorbed H_{ad} intermediate in the HOR on Pd, its Gibbs energy of adsorption decreasing from positive to near-zero values with the decrease of the apparent Pd coverage, underlying the enhancement of the hydrogen oxidation activity of PdAu compared to pure Pd.

1. Introduction

The hydrogen evolution (HER) and the hydrogen oxidation (HOR) reactions are among the most important electrocatalytic processes both from the fundamental and from the practical point of view. HOR is the anode reaction in hydrogen-fed fuel cells [1], while HER occurs at cathodes of water electrolyzers [2]. Even if Pt remains the most commonly used catalyst of the hydrogen electrode reaction due to its excellent catalytic activity, there is a rising interest in the utilization of Pd-based catalysts due to the lower price of Pd, its higher natural abundance and higher tolerance to CO poisoning [3–7]. Numerous studies have demonstrated that the electrocatalytic activity of bimetallic PdAu electrodes toward the HOR/HER is significantly higher than that of pure Pd and is increasing as the Pd content decreases. Although to varying degrees, this effect has been observed for various types of PdAu bimetallic catalysts, viz. for PdAu alloys [5–8], for Pd submonolayers and overlayers on Au single crystals [9], for Pd deposited on carbon-supported Au nanoparticles [7], and for Pd nanoislands on Au single crystal substrates [10]. Considering that pure gold is inactive in the hydrogen oxidation/evolution, such a second metal enhancement effect attracted much attention of both experimentalists and theoreticians. There have been several attempts to explain the changes in the activity by changes in the Gibbs energy of adsorption of the hydrogen intermediate H_{ad} ($\Delta_{ad}G$). It has been predicted by the density functional theory (DFT) that in alloys and in Pd layers on Au [11–13],[1] the *d*-band of Pd becomes thinner and the *d*-band center shifts upwards closer to the Fermi level, resulting in a stronger hydrogen adsorption. Besides the electronic factor, stretching of Pd lattice in Pd/Au overlayers also results in an upshift of the *d*-band and then in a stronger hydrogen adsorption [12,14]. Although the band shape and its upshift strongly depend on the type of Pd nanostructure (embedded clusters, overlayers, etc.) the qualitative trend of increasing the strength of hydrogen adsorption on Pd atoms is similar (note however that at high coverage hydrogen may also occupy a weakly bonded state in the hollow site formed by two palladium and one gold atoms [15]). The relation between the overall reaction rate and the binding energy of the adsorbed

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* Corresponding author. Tel.: +33 03 68 85 14 18; fax: +33 03 68 85 14 31.
E-mail address: bonnefont@unistra.fr (A. Bonnefont).

[1] The approach of Schmickler and coworkers [12] goes beyond the DFT, and is based on combining the Marcus electron transfer theory with the Newns–Anderson adsorption model, and the DFT for the electronic structure calculation.

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hydrogen (H_{ad}) intermediate, in particular for the case of the hydrogen evolution, is often analyzed in the form of a volcano-plot [16–18]. This is an empirical illustration of the Sabatier's principle. Then, the optimum corresponds approximately to the zero Gibbs energy of H_{ad} adsorption, providing the highest activity towards HOR/HER, while both stronger or weaker adsorption result in lower activity. However, the utilization of such volcano plot requires a basic understanding of the mechanism of the reaction as well as a clear identification of the type of the HOR/HER intermediate: viz. strongly bonded H_{UPD}-type intermediate adsorbed at threefold hollow sites vs. weakly bonded atop hydrogen atom [13,19,20].

While much effort has been focused on correlating the enhanced activity of PdAu nanostructures with the changes in the $\Delta_{ad}G$, it is not clear yet whether the increase of the catalytic activity of Pd by "diluting" it with gold or by putting Pd atoms onto a gold substrate is associated with a change of the elementary steps of the HOR/HER, and the nature of the rate determining step (*rds*). The objective of this work is to fill up this gap. In order to do so we use carbon supported PdAu bimetallic electrodes with variable Pd coverage obtained by electrodeposition of Pd on Au nanoparticles. Utilization of carbon-supported nanoparticles offers an advantage of decoupling the coverage of Pd on Au, on the one hand, and the number of active sites per unit surface area of an electrode, on the other hand, and helps in studying the electrochemical reaction kinetics. Moreover, carbon-supported PdAu nanoparticles are of interest from the application point of view [5,6]. By varying the time of deposition we were able to obtain a set of PdAu/C samples with a systematic variation of Pd coverage. Then, the experimental HOR rotating disc electrode (RDE) curves were acquired and analyzed with the help of a kinetic model, in order to shed light on the predominant HOR mechanism (Heyrovsky–Volmer vs. Tafel–Volmer), the nature of the *rds*, and their dependence on the Pd coverage, and get an insight into the type of HOR intermediate. In order to simplify the model, the analysis of the influence of the Pd coverage on the experimental RDE curves is performed within a single variable parameter – the Gibbs energy of adsorption of the hydrogen intermediate.

2. Experimental part

2.1. Materials and methods

2.1.1. Electrochemical measurements

Electrochemical experiments were performed using an Autolab PGSTAT 30 potentiostat equipped with an analog Scangen module in a three-electrode cell comprised of individual compartments for each electrode. The counter electrode, a high surface area Pt foil and the Hg/Hg_2SO_4 reference electrode compartments were connected to the working electrode compartment via a glass frit and a Luggin capillary, respectively. In what follows, all potentials are given vs. the reversible hydrogen electrode (RHE). During the electrochemical experiments the cell was thermostated at 25 °C. The electrochemically active surface area of gold for the Au/C precursor and the total metal surface area for PdAu/C electrodes were measured using the copper underpotential deposition (Cu_{UPD}) method. The HOR current potential curves were measured using a rotating disc electrode in H_2-saturated 0.1 M H_2SO_4 electrolyte at 400, 900, 1600 and 2500 rpm. All solutions were prepared using Milli-Q water (MilliPore, 18.2 MΩ cm).

2.1.2. Preparation of PdAu/C

Gold nanoparticles (1.7 wt.% Au/C) supported on mesoporous carbon of Sibunit family [21] (BET surface area = 82 $m^2\,g^{-1}$ determined from N_2 adsorption at 77 K using an ASAP 2400 Micrometrics apparatus, total micropore volume <0.001 $cm^3\,g^{-1}$, average pore diameter 20 nm) were synthesized from $[Au(NH_3)_4](NO_3)_3$ complex as described elsewhere [22,23]. Electrodeposition of Pd on the Au/C substrate was performed as described in [22] following the method originally developed by Ruvinskiy et al. [7]. The working electrode was prepared by spreading a thin film of the Au/C powder (4.9 $\mu g_{Au}\,cm^{-2}_{geo}$) on the glassy carbon rod (0.2 cm^2 geometric surface area). After a blank electrodeposition transient in 0.2 mM HCl + 0.1 M H_2SO_4 electrolyte, the Au/C/GC electrode was immersed in a deaerated 0.1 mM H_2PdCl_4 + 0.1 M H_2SO_4 solution and kept at 1.135 V for 10 min. Then the electrode potential was linearly decreased down to 0.785 V at a scan rate of 10 mV s^{-1} and maintained at this potential for a certain period depending on the targeted Pd coverage. After correction of the charge of the transient to the blank measured under the same conditions in the 0.2 mM HCl + 0.1 M H_2SO_4 electrolyte, the charge of palladium deposition Q_{dep} can be recalculated into an *apparent* monolayer (ML) coverage θ_{Pd}, assuming that the formation of 1 ML of Pd on the surface of Au nanoparticles requires 422 μC cm^{-2}. Even though the growth mode of Pd on Au is not fully understood, such an apparent coverage is useful for discussing the trends. The desorption of chlorides from the surface of Pd particles was performed by applying 0.1 V during 5 min in 0.1 M H_2SO_4, further measurements being performed in a fresh chlorides-free electrolyte. The immersion of PdAu/C samples in the electrolyte was performed at a controlled potential in the double layer region of Pd in order to prevent palladium dissolution.

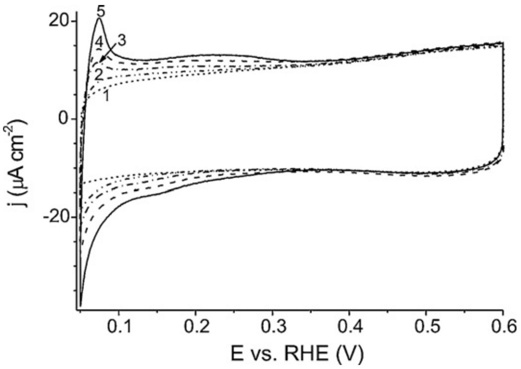

Fig. 1. (a) Cyclic voltammograms for the Au/C precursor (1) and for the PdAu/C samples with different apparent coverage of palladium on gold: 0.07 ML (2); 0.37 ML (3); 0.65 ML (4); 2.1 ML (5) in 0.1 M H_2SO_4 at 25 °C at the sweep rate of 10 mV s^{-1}. Currents are normalized to the metal surface area determined by Cu_{UPD}.

2.1.3. TEM and EDX characterization

The size and the structure of carbon-supported Au and PdAu particles were studied by transmission electron microscopy (TEM) using a JEM-2010 microscope (JEOL, Japan) with a lattice resolution of 0.14 nm at the accelerating voltage of 200 kV. The local elemental analysis was performed with EDX method using the Energy-dispersive X-ray Phoenix Spectrometer EDAX equipped with a Si (Li) detector with the energy resolution not worse than 130 eV. The particle composition was determined by focusing the probe on selected sample areas comprising particles of the same kind. Accumulation of numerous spectra at different probe locations was used in order to minimize an error.

2.2. Results of the experimental measurements

2.2.1. Characterization of PdAu/C catalysts

Fig. 1 features cyclic voltammetry (CV) curves registered for a bare Au/C and for selected PdAu/C catalysts with different apparent Pd coverages ranging from 0.07 to 2.1 ML. The low upper potential limit for CVs has been chosen in order to avoid the dissolution of Pd submonolayers. The charge of underpotentially deposited hydrogen, $Q(H_{UPD})$ shown in Table 1, was calculated by integrating the