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Exclusive formation of alloy phases via anchoring technique—From bimetallic catalysts to electrocatalysis

I. Borbáth[a,*], D. Gubán[a], I. Bakos[a], Z. Pászti[a], G. Gajdos[a], I.E. Sajó[b], Á. Vass[a], A. Tompos[a]

[a] Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, H-1117 Budapest, Magyar tudósok körútja 2, Hungary
[b] University of Pécs, Szentágothai Research Centre, H-7624 Pécs, Ifjúság útja 20, Hungary

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ABSTRACT

Alloy-type Sn-Pt/C electrocatalysts with desired Pt/Sn = 3.0 ratio have been prepared using commercial 20 wt.% Pt/C (20Pt/C (Q: Quintech)) and home-made 20Pt/C (H) catalysts by means of Controlled Surface Reactions. According to *in situ* XPS and *in situ* XRD studies the exclusive incorporation of Sn onto the Pt sites was achieved resulting in exclusive formation of Pt-Sn alloy phase. No evidence of the presence of SnO_2 phase was found by means of the XRD and EDS analysis. According to *in situ* XPS studies pretreatment of the air exposed catalyst in H_2 even at 170 °C resulted in complete reduction of the ionic tin to Sn^0, suggesting alloy formation. After contact of Sn-Pt/C catalysts with air Sn tends to segregate to the surface, where it oxidizes to a certain extent. Reversible interconversion of $PtSn \leftrightarrow Sn^{4+} + Pt$ in the presence of O_2 and H_2 was convincingly demonstrated by *in situ* XPS and *in situ* XRD studies.

The electrocatalytic performance of the alloy catalysts was tested in CO oxidation and oxygen reduction reaction (ORR). Only minor changes of the surface composition of the Sn-20Pt/C electrocatalysts were observed after 20 polarization cycles. Better performance in the CO electrooxidation for our Sn-Pt/C catalysts compared to the state-of-art CO tolerant PtRu/C benchmark was demonstrated. Optimal surface composition of the Sn-20Pt/C (H) catalysts results in increased activity in the ORR compared to the Sn-20Pt/C (Q) and both parent 20Pt/C catalysts.

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1. Introduction

1.1. *Sn-Pt/C electrocatalysts: requirements and preparation methods*

Polymer electrolyte membrane fuel cells (PEMFC) are expected to be one of the key devices to solve energy and environmental problems [1]. For the wide-range implementation of PEMFC, it is most essential to produce low-cost durable units. A significant part of the price belongs to the electrocatalysts, which contain high loadings of Pt. Key requirements for the implementation of fuel cells are: (i) reducing the amount of Pt; (ii) increasing of the metal dispersion; (iii) stability during long time application; (iv) high CO tolerance of the anode electrocatalysts, and (v) high activity and selectivity of the cathode electrocatalysts in the oxygen reduction reaction (ORR). One of the important approaches is to use co-catalysts in combination with platinum. A variety of transition metals have been used as co-catalysts such as Ru, Mo, Ni or Sn [2–4]. Amongst those, Sn-modified Pt/C supported electrocatalysts are recognized as the most active electrodes for the CO, methanol and ethanol oxidation reactions [5,6] and the ORR [7].

Most synthetic routes of Sn-Pt/C electrocatalysts lead to solids with a wide range of phases such as Pt, either reduced or as oxide, Sn oxides and Pt-Sn alloys or solid solutions with different stoichiometry [8]. The promoting effect of different forms of Sn on the activity of Pt-based catalysts has been comprehensively analyzed by Antolini and Gonzalez [9]. In analyzing various reports, it seems that production of Pt_3Sn as a pure and exclusive phase rarely occurs and its amount strongly depends on the synthetic procedure [9,10], even if this phase is associated with the best electrocatalytic properties [5]. Carbon-supported Pt-based alloy nanoparticles can be prepared by following methods: impregnation [11], water-in-oil microemulsion methods [12], the well-known “Bönnemann” method [13], the polyol synthesis [14], the borohydride [15] and formic acid [16] reduction methods, the polymeric precursor method [17]. Controlled formation of Pt-Sn alloy nanoparticles with cubic and hexagonal structure has been achieved by the “heating up” method [18].

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* Corresponding author: Irina Borbáth, P.O. Box 286, H-1519 Budapest, Hungary.
E-mail address: borbath.irina@ttk.mta.hu (I. Borbáth).

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1.2. Surface organometallic chemistry of tetraalkyl tin

Exclusive formation of supported Sn-Pt alloy phases with different Sn/Pt ratios can also be achieved by using Controlled Surface Reactions (CSRs) [19]. The surface chemistry of the tin anchoring reaction can be written as follows:

$$PtH_{ads} + Sn(C_2H_5)_4 \rightarrow Pt\text{-}Sn(C_2H_5)_{(4-x)} + xC_2H_6 \quad (1)$$

$$Pt\text{-}Sn(C_2H_5)_{(4-x)} + (4-x)/2H_2 \rightarrow Pt\text{-}Sn + (4-x)C_2H_6 \quad (2)$$

During the tin anchoring (step I) the organometallic precursors decompose only partly on the metal particle and surface organometallic species stabilized on the metal surface are formed (see Eq. (1)). Decomposition of these surface species (step II) can be done in hydrogen or oxygen atmosphere. Upon decomposition in hydrogen (see Eq. (2)) the net result is the exclusive formation of Pt-Sn alloy-type surface species as evidenced by Mössbauer spectroscopy [20]. Whereas decomposition in oxygen results in the formation of Lewis-acid type sites consisting of finely dispersed SnO_x surface species anchored onto the active metal creating the "metal ion–metal nano-cluster" ensemble sites [21]. The formation of the above species was evidenced by Mössbauer [20] and FTIR spectroscopy [22].

In our previous studies the modes and ways to increase the amount of tin introduced directly onto the parent metal has also been established. Based on CSRs a new method was developed for the preparation of different types of supported bimetallic (E_x-M_y, where E = Sn, Ge; M = Pt, Pd, Rh, Ru) catalysts with exclusive formation of metal–metal interaction even at high E/M ratios [23–26].

It has to be emphasized that the exclusive formation of tin-metal interaction requires special control to avoid the reactions with the involvement of surface OH groups [22,27,28]. Organometallic species anchored onto the support, formed upon using conditions favoring this side reaction, can be decomposed either in hydrogen or oxygen atmosphere with formation of SnO_x species grafted onto the support. It is necessary to mention that low-valent cations of an oxophilic metal grafted onto a support has an ability to stabilize small (1–2 nm) noble metal nanoparticles (e.g. gold [28]).

Catalysts prepared in this way showed unique properties in low temperature CO oxidation [29], selective hydrogenation of organic compounds (unsaturated aldehydes, citral, benzonitrile [23,24,30,31]), *n*-butane dehydrogenation [27], hydrogen-assisted 1,2-dichloroethane dechlorination [32] and naphtha reforming [33]. Our new results demonstrate [5,34,35] that upon using CSRs Sn-modified 40 wt.% Pt/C electrocatalysts highly active in both the electrooxidation of CO and C_1 or C_2 alcohols can be prepared.

In this contribution we report the peculiarities of commercial and home-made 20 wt.% Pt/C catalysts modification with Sn by CSRs with the aim to synthesize electrocatalysts with the desired nominal ratio Pt/Sn = 3 and homogeneous tin distribution over the Pt nanoparticles. The performance of these catalysts is also evaluated in both the CO electrooxidation reaction and the ORR.

2. Material and methods

2.1. Materials

The organometallic compound (tetraethyltin, $Sn(C_2H_5)_4$), platinum precursor ($H_2PtCl_6{\cdot}6H_2O$) and solvents (*n*-decane and *n*-hexane) were used as received (Sigma-Aldrich). Ethylene glycol (EG), $NaBH_4$, absolute ethanol, isopropanol, H_2SO_4 and HCl were purchased from Molar Chemicals. Abbreviations are listed in the Supplementary material.

2.2. Synthesis of home-made 20 wt.% Pt/C electrocatalyst

The home-made 20 wt.% Pt/C catalyst (20Pt/(H)) was prepared by $NaBH_4$-assisted EG reduction method using active carbon as a support (CABOT, Black Pearls 2000, 1475 $m^2\,g^{-1}$) and ethanol as a solvent. It should be noted that in Ref. [36] EG was used as a solvent.

H_2PtCl_6 (166 mg) was solved in 25 ml absolute ethanol and 200 mg of the support material was suspended in the solution. Hereupon a solution prepared by the reaction of $NaBH_4$ (590 mg) and EG (7.4 ml) was added dropwise to the suspension at 65 °C with stirring. After 3 h of stirring at 65 °C, 15 ml 0.5 M HCl was added to the suspension and stirred for an additional 2.5 h at room temperature (RT) to deposit the Pt particles onto the support material. The material was washed with water (18.2 MΩ) by centrifugation and dried at 80 °C overnight.

2.3. Synthesis of Sn modified Pt/C catalysts

Commercial 20 wt.% Pt (Quintech, C-20-Pt, Pt = 20 wt.% on Vulcan support; denoted hereafter as 20Pt/C (Q)) and 20Pt/(H) catalysts were modified with $Sn(C_2H_5)_4$ by CSRs. Tin anchoring (step I) was performed in a 40 ml stainless steel autoclave at 170 °C using P_{H2} = 5 bar and three or five consecutive tin anchoring periods. Detailed description of the synthesis procedure can be found in Ref. [34].

Pt/C catalyst was suspended in *n*-decane. The autoclave was purged with hydrogen for 10 min and then the hydrogen pressure was set up to 5 bar. The reactor was immersed in an oil bath and heated up to 170 °C, then the tin anchoring step I was started by an addition of the appropriate amount of $Sn(C_2H_5)_4$ solution in decane. For this purpose the calculated amount of tetraethyltin (needed for the preparation of Sn-Pt/C catalysts with desired Pt/Sn = 3 ratio) was divided into three or five equal portions and introduced into the reactor after equal periods of time. Preparation details are listed in Table 1. After the modification procedure, the catalyst was separated by centrifugation and carefully washed twice with decane and tree times with hexane. The catalyst was dried in air at 60 °C overnight.

Decomposition in hydrogen (step II) was accomplished by Temperature Programmed Reduction (TPR) technique (heating rate = 5 °C min^{-1}, hydrogen flow rate = 30 ml min^{-1}). The final temperature (T_{red}) applied was 250 or 350 °C. Catalysts were kept at final temperature for 2 h then the furnace was cooled down in flowing H_2 to RT. Finally, the atmosphere was changed to N_2.

2.4. Physical characterization

In situ X-Ray Diffraction (XRD) experiments were carried out by a Philips model PW 3710 based PW 1050 Bragg-Brentano parafocusing goniometer in a heated sample holder Anton Paar HTK 1200 using CuK_α radiation (λ = 0.15418 nm) operating at 40 kV and 35 mA, graphite monochromator and proportional counter. Silicon powder (NIST SRM 640) was used as an internal standard and the scans were evaluated with profile fitting methods. The cell parameters of the crystalline phases were determined from the fitted d-values.

About 50 mg catalyst sample was loaded into the cell and a powder XRD measurement was carried out in the 2 theta range of 10–90° at a scanning speed of 0.02° s^{-1}. Then after purging with N_2 for 15 min the sample was heated up to 200 °C with a rate of 5 °C min^{-1} in H_2 flow and kept at constant temperature for 2 h, then another XRD pattern was recorded as described earlier. The same procedure was repeated at 250, 300 and 350 °C, respectively. After the measurements the sample was cooled down to RT in H_2 and XRD pattern was recorded. Then after purging with N_2 15 min the

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