



Synthesis of PtSn nanostructured catalysts supported over TiO₂ and Ce-doped TiO₂ particles for the electro-oxidation of ethanol



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ABSTRACT

PtSn/TiO₂ and PtSn/Ce-doped TiO₂ catalysts were synthesized and evaluated for ethanol electro-oxidation in acid media. Titanium dioxide and Ce-doped TiO₂ nanoparticles were prepared by hydrothermal method followed by calcination at 923 K. Bimetallic PtSn catalysts supported on the oxide materials were synthesized by microwave assisted reduction in ethylene glycol (EG). The structural properties of the resulting materials were evaluated via TEM and XRD, and the compositions were assessed by EDX and ICP-AES analysis. PtSn nanoparticles of about 3–4 nm were deposited on TiO₂ and Ce–TiO₂ particles. It was found that the catalyst composition is scarcely influenced by the cerium content in the mixed oxides while the electrochemical surface area per unit mass decreases upon the incorporation of Ce in the anatase lattice.

The electrochemical tests pointed out that the electrocatalytic activity for ethanol oxidation decreases markedly as the Ce content increases. The results indicate that the presence of cerium in the titanium dioxide crystalline network induces local structural and electronic modifications, thereby leading to a reduction of the crystallinity, surface conductivity and the amount of OH species adsorbed on the surface of the oxide support.

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1. Introduction

Direct alcohol fuel cells (DAFCs) have emerged as one of the most versatile devices with high energy efficiency and low emissions for portable, mobile and stationary applications. However, the current bottlenecks for the widespread utilization of this technology are the elevated cost for market introduction, the low long-term stability of the stacks and the low energy efficiency [1,2]. Ethanol is a very suitable fuel for DAFC technology because it can be easily handled, stored and transported by using the existent fuel infrastructure and it provides a high energy density per unit volume. Furthermore, ethanol can be produced on an industrial scale from sunflower, corn and sugarcane plantations and it is the major renewable biofuel obtained from the fermentation of biomass, and hence the net carbon dioxide emissions can be reduced to near zero [3,4].

The low-temperature fuel cell technology available on the market today makes use of carbon powders as the catalyst support in both electrodes. The carbon supports have excellent electrical conductivity and high surface areas. However, they are susceptible to oxidation in the corrosive environment of the polymer electrolyte membrane fuel cell (PEMFC), inducing agglomeration, dissolution

and migration of platinum particles onto the membrane electrolyte and thus reducing the electrochemical surface area of the electrodes [5,6].

In the last decade, many research groups have been fully focused on the development of Pt-based nanoparticles supported over metal oxides, especially TiO₂, due to their high corrosion stability in acidic media [7–10]. Several authors have discussed the role of TiO₂ support on the performance of different Pt-based catalysts for methanol and ethanol oxidation in acid media [7,9,11–13] and on the photocatalytic degradation of organic compounds [14,15]. Some authors have indicated that the oxide support promotes the oxidation of the poisoning intermediaries, especially the removal of adsorbed CO, through the bifunctional mechanism [9,13], while others have explained the enhancement in catalytic activity in terms of metal reactivity variation through the change of the interaction energy between the adsorbate and the catalyst surface due to the electronic interactions between the noble metals and TiO₂ [7,12].

Apart from that, carbon supported Pt-based catalysts in combination with cerium [16,17] and cerium dioxide [18–20] nanoparticles have been proposed in the last years as electrode materials for DAFCs. In general a synergistic effect between Pt and CeO₂ nanoparticles was proposed. It was suggested that CeO₂ nanoparticles provide labile OH_{ads} species for the electro-oxidation of the adsorbed intermediary species on the Pt surface at a lower overpotential (bifunctional mechanism).

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Taking into account these favorable antecedents, an investigation was undertaken to study the effect of combining TiO₂ and Ce on the electrocatalytic activity of bimetallic PtSn nanoparticles supported on different cerium–titanium–oxide substrates for the ethanol oxidation reaction (EOR). TiO₂ and different Ce-doped TiO₂ materials were synthesized by a hydrothermal route followed by calcination and used as catalyst supports for PtSn nanoparticles synthesized via microwave-assisted reduction in EG. The physico-chemical characteristics of the samples were determined by TEM and XRD analysis, whereas the catalyst composition was obtained by EDX and ICP-AES. The electrocatalytic activity of the electrodes for the EOR was evaluated via cyclic voltammetry and potentiostatic experiments. Contrarily to the expected, it was found that doping of TiO₂ nanoparticles with Ce has a detrimental effect on the electrocatalytic behavior of PtSn/TiO₂-xCe catalysts toward ethanol oxidation reaction in acidic media. To the best of our knowledge, this is the first time that a study reports the effect of doping TiO₂ supports with Ce for ethanol oxidation on Pt-based nanoparticles.

2. Experimental

2.1. TiO₂ and Ce–TiO₂-synthesis

The catalyst support was obtained through experiments performed on water/CTAB-ButOH/n-heptane microemulsion systems by a single microemulsion method [21,22]. Briefly, a microemulsion “A” (containing CTAB, ButOH, oil and aqueous phases) was mixed with a solution “B” formed by titanium (IV) isopropoxide (Ti[OCH(CH₃)₂]₄) in n-heptane without stirring and left to equilibrate for 20 minutes (sample CT1). For the synthesis of different Ce-doped TiO₂ materials different amounts of ceria valerate (Ce(Val)₃) were added respectively to microemulsion “A” before mixing with solution “B”. The as-synthesized gels were left for 24 h in an autoclave at 373 K. The obtained materials were filtered, washed with bi-distilled water, dried at room temperature and then calcined for 6 h at 923 K in air flux to completely remove the surfactant impurities. Table 1 lists the specification of all Ce-doped TiO₂ materials, with varying ceria loadings (samples CT2–CT4). The complete EDX analysis of the support materials was reported in a previous work [22].

2.2. Catalysts synthesis

The bimetallic PtSn nanoparticles supported on different Ce-doped TiO₂ materials were synthesized via a microwave assisted reduction method in ethylene glycol. In this method ethylene glycol is used as the reaction medium due to its high boiling point and high dielectric loss in addition to its excellent reducing capacity for noble metal salts at high temperatures. Besides, the microwave heating is preferred with respect to conventional heating methods because of the rapid heating of the reaction mixture. The 100.00 mg of Ce–TiO₂ was mixed with 50 mL of ethylene glycol (EG, Anedra) and stirred for 15 min. Then, the pH value of the mixture was adjusted to 10 by the drop-wise addition of 0.1 M KOH (>85%, Sigma-Aldrich)/EG and a well-dispersed slurry was obtained by sonication for 45 min. After that, 1.4 mL of 20 mM SnCl₂ (Merck) solution in ethanol and 2.19 mL of an aqueous solution of 38.6 mM H₂PtCl₆·6H₂O (Aldrich) were added and sonicated for an hour. That time was

sufficient to ensure that the substrate contained the appropriate amount of precursor. Next, the suspension was introduced in the middle of a microwave oven (2450 MHz, 700 W), heated for 90 s, and then cooled naturally at room temperature. Finally, the black dispersion was filtered, washed with ethanol and dried in an oven at 333 K overnight. The nominal atomic ratio of Pt:Sn used in the synthesis was 75:25. The catalyst inks were prepared by the procedure described in our previous paper [23]. The as-prepared catalysts were named in the following way: Pt–Sn/TiO₂ (PS-CT1), Pt–Sn/TiO₂-Ce 0.71 wt.% (PS-CT2), Pt–Sn/TiO₂-Ce 2.09 wt.% (PS-CT3) and), Pt–Sn/TiO₂-Ce 11.1 wt.% (PS-CT4).

2.3. Characterization of materials

The characterization of TiO₂ and Ce-doped TiO₂ samples was performed by field emission scanning electron microscopy (FE-SEM), high resolution transmission microscopy (HR-TEM), X-ray energy-dispersive (EDX) analysis and X-ray diffraction experiments as previously reported [22]. The surface acidity of the as-prepared support materials was estimated by titration following the procedure developed by Tamele [24]. TiO₂ and TiO₂-Ce powders (300.0 mg) were dispersed in 40 mL of benzene by sonication for 30 min and stirring for another 30 min. After that, five drops of 0.05 N methyl red (H₀ ≤ 4.8) solution in benzene were added to the beaker. Then N-butylamine (0.01 N) was titrated against the powder, and the amount of titer required to effect the color change on the surface of the powder was registered. The procedure was repeated three times taken precautions to handle the powders to ensure that the results were reproducible and comparable between them. The surface acidity of the samples was expressed in milimole per gram of sample.

The morphology, size and particle distribution of supported PtSn catalyst were analyzed using transmission electron microscopy (TEM, JEOL 100CX II operated at 200 keV). Whereas, the bulk composition of the electrode materials was determined by energy dispersive X-ray (EDX) coupled to a SEM microscope (JEOL 100) and the analysis was done with the incident electron beam energies ranging from 0.1 to 20 keV. The analysis was carried out in five different areas of each sample. The samples were prepared by placing 20 μL of catalyst ink onto a copper grid and over the surface of a polished glassy carbon rod (GC, 3 mm diameter) for TEM and EDX analysis, respectively. After that, the supports were dried to ensure that the catalyst was firmly adhered to the substrate surface.

X-ray diffraction (XRD) patterns of as-synthesized PtSn/TiO₂-Ce catalysts were recorded by means of a Rigaku Dmax III C diffractometer with monochromated Cu-Kα radiation source (λ = 0.15418 nm) operated at 40 keV and 30 mA at a scan rate of 0.05° s⁻¹ with 2θ angles in the range of 20–80°. The peak profiles in XRD patterns of the supported catalysts were fitted with the pseudo-Voigt function, using non-linear least-squares refinement procedures based on a finite difference Marquardt algorithm. The lattice parameters were estimated using Bragg's law and the crystallite sizes estimated using Scherrer's equation.

The platinum and tin metal loadings of the different catalysts were determined by ICP-AES (Shimadzu 1000 model III). The platinum loading of the samples expressed per unit of GC geometric area was 50.0 ± 0.3 μg cm⁻².

2.4. Electrochemical characterization

Electrochemical experiments were performed in three-electrode glass cells with a PAR 273 potentiostat/galvanostat. A platinum spiral was used as the counter electrode, and a saturated calomel electrode (SCE, +0.241 V vs. RHE) located in a Luggin capillary was used as reference electrode. The potentials mentioned in this work are referred to the SCE reference electrode. The electrodes were prepared by placing 20 μL of catalyst ink on the surface of a mirror-like

Table 1
Composition of Ce-doped TiO₂ materials determined by EDX analysis.

Catalyst	Ce(Val) ₃ wt.%	Ce wt.%	Ce at.%	Ti wt.%	Ti ¹ at.%	O ¹ wt.%	O ¹ at.%
CT2	0.17	0.71	0.13	56.63	30.95	41.31	67.58
CT3	0.86	2.09	0.39	54.31	29.41	42.84	69.47
CT4	2.13	11.1	2.14	37.99	21.41	42.08	71.00

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