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Enhancement of ethanol oxidation on Pd nanoparticles supported on carbon-antimony tin oxide hybrids unveils the relevance of electronic effects

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ABSTRACT

A comparative study of activity toward ethanol oxidation was carried out for catalysts having the same loading of identical Pd nanoparticles supported on carbon-oxide hybrids containing antimony tin oxide (Sb_2O_5/SnO_2 – ATO) in different amounts (20, 30 and 40 wt.%). Enhanced catalytic activity was observed for Pd nanoparticles supported on C-ATO hybrids. X-ray absorption spectroscopy experiments carried out around the Pd L_3 edge evidenced an increase in the electronic occupancy of the Pd 4d band indicating an electronic transfer from the hybrid supports to the Pd particles. A strong correlation between ethanol oxidation currents and X-ray absorption data reveals the importance of electronic effects in the electrocatalysis of ethanol oxidation on Pd. In addition, FTIR data show that C-ATO hybrid supports promote a decrease in the onset potential and an increase in carbonate/CO_2 production.
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1. Introduction

Power for vehicles and portable devices could be generated with low or zero CO_2 emissions using Direct Ethanol Fuel Cells (DEFC) [1], but that prospective depends essentially on developing catalysts for the ethanol oxidation reaction (EOR) substantially more active than those currently available. Numerous studies were dedicated to the search for more efficient catalysts over the last decades, mostly in acid environments and mainly involving alloying Pt with transition metals [2]. Some studies also demonstrated that transition-metal oxides as co-catalysts or supports can enhance the activity of Pt nanoparticles for the oxidation of small organic molecules in acid media [3–6]. These effects were often interpreted as associated with the presence of OH groups on the oxide surface [7], which would favor the bifunctional mechanism [5,6]. On the other hand, ligand effects can also explain enhanced activities because charge transfer between the transition-metal oxide and Pt particles would shift the Fermi level of Pt, which, in turn, could modify adsorption energies [8,9].

As development of anion-exchange membranes progressed [10,11], the interest in alkaline fuel cells [12] was renewed and resulted in a rapid increase in the number of studies of the EOR in base [13–15]. Recent studies demonstrated the relevance of metal-support interactions on the EOR catalytic activity in alkaline medium for Pt nanoparticles on hybrid supports containing different transition-metal oxides [16]. The increased attention given to studies in alkaline environments also boosted the search for Pt-free catalysts. In particular, Pd and Pd-based catalysts were widely studied [17–20]. Although the number of published papers regarding the effects of transition-metal oxides is not as large as for Pt and Pt-based catalysts, enhancing effects of TiO_2 [21–26], CeO_2 [27–29] and other oxide supports [30–35] were reported for Pd.

Studies of the influence of antimony tin oxide (Sb_2O_5/SnO_2 – ATO) on the activity of Pt nanoparticles were carried out for alcohol oxidation [36–39] and oxygen reduction [40–42]. For Pd nanoparticles, the effect of ATO was investigated only for hydrogen peroxide reduction [43] and acid formic oxidation [44]. To best of our knowledge, neither studies regarding the impact of adding ATO to Pd nanocatalysts on ethanol oxidation nor systematic evaluations of ligand effects have been published. In this work, a comparative study of activity for ethanol oxidation was carried out on catalysts having the same loading of identical Pd nanoparticles supported on carbon-oxide hybrids containing different amounts (20–40 wt.%) of antimony tin oxide. In addition, X-ray absorption spectroscopy (XAS) experiments were carried out around the Pd L_3 edge to assess the way in which interactions between metal nanoparticles and C-ATO hybrids perturb the Pd d band and *in situ* FTIR experiments were performed to analyze adsorbed ethanol oxidation reaction intermediates and products.

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2. Experimental

2.1. Preparation of supports and catalysts

Hybrid supports contained carbon (Vulcan XC-72, Cabot Corp.) and varying amounts of commercial antimony tin oxide nanopowder (Aldrich, Sb_2O_5/SnO_2 – ATO; 7–11% Sb_2O_5, particle size <50 nm). Carbon and ATO nanopowders were separately dispersed in isopropanol, keeping the mixtures in an ultrasonic bath for 10 min. The suspensions were then mixed to obtain the C-ATO hybrids, which were prepared with 20, 30 and 40 wt.% oxide content.

Pd nanoparticles were prepared in a liquid two-phase system [45] modified by the addition of oleic acid and oleylamine as capping agents. Briefly, 6.26 mL of aqueous solution of $PdCl_2$ (0.03 M) was added to a solution of a phase-transfer agent (tetraoctylammonium bromide – ToABr) in toluene (0.4562 g of ToABr in 16.7 mL of toluene). Thus, the ratio ToABr/metal was 4.4/1. After stirring for 2 h, the aqueous phase was separated from the toluene phase and discarded. Then, the capping agents were added (50 µL of oleic acid and 54 µL of oleylamine). To reduce the Pd^{2+} ions, 9.4 mL of 0.2 M solution of $NaBH_4$ was slowly added (10/1 final reducer/metal ratio). After that, the system was stirred for 12 h. At the end of this process, the toluene phase contains the Pd colloidal particles, the compound used to transfer the Pd ions from the aqueous to the organic phase (ToABr) and reducer residues. Therefore, after obtaining the Pd particles the toluene phase was washed with dilute solution of H_2SO_4 (5 mM), dilute solution of KOH (5 mM) and ultrapure water. Because surface properties as well as electronic effects are important in electrocatalysis [46], in order to evaluate the influence of the support on EOR activity it is indispensable to warrant that the only difference between catalysts is the support. Therefore, to prepare catalysts with identical Pd nanoparticles, each support was mixed with one fraction of the same Pd colloidal suspension. The main steps of the preparation procedure are depicted schematically in Fig. 1.

After adding the supports to the different portions of colloidal Pd nanoparticles, the resulting mixtures were stirred during 12 h and then the powders were filtered, and washed exhaustively with ethanol, acetone, toluene, and chloroform. The washing steps with ethanol and acetone allow removing traces of ToABr and reducer that might have remained in the toluene phase and remove, at least partially, the capping agents. The two following washings (one with toluene and another with chloroform) were done aiming to further remove the capping agents, as oleic acid and oleylamine are both highly soluble in these solvents [47]. After this sequence of washing steps, the filtered catalyst powder was dispersed in dilute solution of KOH in ethanol (5 mM), and this dispersion kept in an ultrasonic bath for 40 min. After filtering again, the final step of the cleaning procedure involved thoroughly washing the catalyst powder with ethanol, acetone and water. All materials were dried at 70 °C in air. For simplicity, we shall refer to the catalysts as Pd/C-ATO (wt.%). A Pd/C reference sample was prepared with one of the fractions of the same Pd colloid used to prepare Pd/C-ATO materials. All catalysts were prepared with 20 wt.% Pd loading. Chemicals were purchased from Sigma-Aldrich, and used as received.

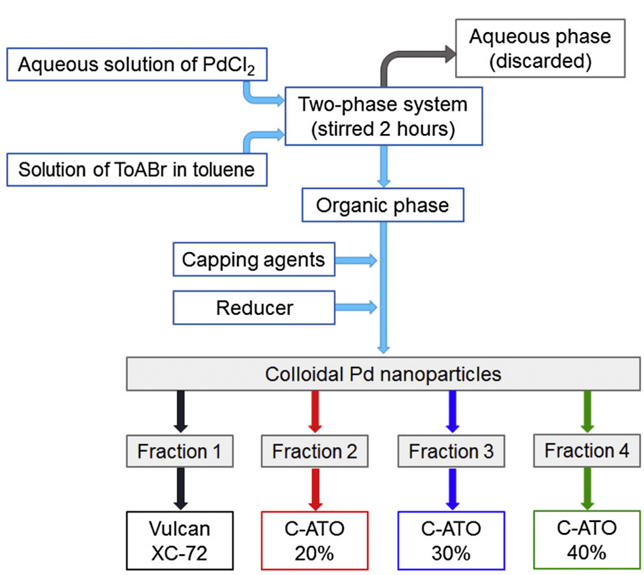

Fig. 1. Scheme of main steps of catalysts preparation procedure.

2.2. Catalyst characterization

X-ray diffraction measurements were carried out in a Rigaku DMax 2500 PC equipment at 2° min^{-1} in the 2θ range 20–100 using Cu Kα radiation (λ = 1.5406 Å). Data were also collected in step scan mode (0.02° step and 5 s/step) in the 2θ range 60–80. Transmission electron microscopy in scanning mode (STEM) was performed with a FEI TECNAI G^2 F20 HRTEM instrument.

The electronic properties were studied by X-ray absorption spectroscopy (XAS) around the Pd L_3 edge (3.173 eV) at the Soft X-ray Spectroscopy (SXS) beamline of the Brazilian Synchrotron Light Laboratory (LNLS). For these measurements, the dried catalyst powder was adhered on a double-sided carbon tape fixed on an aluminum holder. Experiments were carried out in a high-vacuum chamber using a InSb(1 1 1) monochromator. Photon energies were calibrated using a Mo foil and spectra were collected in total electron yield mode (TEY), with resolution of 2.2 eV. Spectra were taken on three different points of each sample.

2.3. Electrochemistry

Measurements were performed in a three-electrode cell, with a reversible hydrogen reference electrode (RHE) and a platinized Pt wire auxiliary electrode in a separate compartment. The working electrode was an ultra-thin layer of catalyst (28 µg cm^{-2} Pd loading) obtained depositing 10 µL of catalysts ink on a previously polished glassy carbon disk (0.196 cm^2 area). The ink was prepared dispersing 2.9 mg of catalyst in 1 mL of isopropyl alcohol and 15 µL of Nafion solution (5 wt.% in a mixture of lower aliphatic alcohols and water). The Pd electrochemically active surface area was evaluated from the charge of PdO reduction determined from cyclic voltammetry (CV) curves measured in 0.5 M H_2SO_4. Experiments done for different high potential limits allow establishing the potential at which a full monolayer of PdO was completed [48,49]. All other CV experiments were made in alkaline medium (argon-saturated 0.1 M KOH). Chronoamperometry (CA) curves were measured in deoxygenated 0.5 M ethanol in 0.1 M KOH solution. All experiments were performed at 25 °C.

2.4. In situ FTIR

In situ multi-stepped FTIR spectroscopy experiments [50] were performed in a three-electrode spectroelectrochemical cell with a CaF_2 window and using a Nicolet 6700 infrared spectrometer. The catalyst ink was deposited on a previously polished Au disk (8 µg cm^{-2} Pd loading), which was pressed against the optical window to form the thin-layer of electrolyte. A gold foil was used as counter-electrode and a reversible hydrogen electrode as reference electrode. The base spectrum was collected at 0.050 V. Data are

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