

## On the Role of Electronic Properties of Nanostructured Catalysts on the Reaction Pathways of Ethanol Oxidation

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### ABSTRACT

Studies of the distribution of reaction products carried out by *in situ* FTIR and the evaluation of the Pt 5d band vacancy by *in situ* XAS measurements performed around the Pt  $L_3$  edge were combined aiming to unravel the influence of electronic properties on the reaction mechanism of ethanol electrooxidation on PtSn-based catalysts. These studies were carried out for nanocatalysts containing PtSn nanoparticles supported on carbon and on carbon-TiO<sub>2</sub> nanocomposites. All catalysts were prepared with 20 wt.% load of PtSn nanoparticles and characterized by several *ex situ* techniques (X-ray diffraction, transmission electron microscopy and X-ray photoelectron spectroscopy). The catalytic activities for ethanol oxidation were determined by linear potential sweeps and chronoamperometry, while the ability of the catalysts for promoting the bifunctional mechanism was evaluated by measuring the stripping curves of adsorbed CO. It was observed that the presence of TiO<sub>2</sub> has little effect on the activity for CO oxidation, which remains nearly unchanged, at the time that it produces an enhancement of the ethanol oxidation current density. *In situ* FTIR results indicate that larger amounts of acetaldehyde (and therefore smaller quantities of acetic acid) are produced on PtSn/TiO<sub>2</sub>-C catalysts than on PtSn/C. At first glance an increase in the yield of acetaldehyde, which involves the exchange of a lower number of electrons per ethanol molecule than the formation of acetic acid, may seem inconsistent with an enhancement of the measured currents. However, data can be rationalized based on the increase in the turnover frequency for the acetaldehyde formation pathway, which would result from an easier acetaldehyde desorption caused by the decrease of the Pt 5d band vacancy promoted by the oxide.

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**Keywords:** electronic effects; reaction mechanism; ethanol oxidation.

