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Effect of molybdenum content on the morphology and electronic characteristics of Pd–MoO_x nanomaterials and activity evaluation for ethylene glycol electro–oxidation

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ABSTRACT

In this work, Pd–MoO_x nanomaterials were developed changing the Mo/Pd precursor ratio and tested for ethylene glycol electro–oxidation reaction (EGOR) in alkaline medium. Mo atomic % compositions of 0, 15, 35, 45 and 75 at. % were evaluated. The increase of Mo at. % resulted in morphology changes due to the directing effect of hexadecyltrimethylammonium bromide (CTAB) on molybdenum passing from hemispheres to nanobelts + hemispheres (15 at. % Mo denoted as $Pd_{85}Mo_{15}$), then only nanobelts (35 at. % Mo, $Pd_{65}Mo_{35}$), and nanosheets (45 at. % Mo, $Pd_{55}Mo_{45}$), and hemispheres were newly obtained at the higher Mo concentration (75 at. % Mo, $Pd_{25}Mo_{75}$). The activity evaluation of EGOR at 60 °C indicated that $Pd_{25}Mo_{75}$ supported on Vulcan carbon ($Pd_{25}Mo_{75}$/C) displayed the highest current density (63.80 mA cm^{-2}), and according with X–ray photoelectron spectroscopy (XPS) the highest activity of $Pd_{25}Mo_{75}$/C can be related to the abundance of Mo^{5+} species, which have oxygen vacancies with a single positive charge. Additionally, the analysis of O 1s core–level corroborated the abundance of oxygen with high number of defects sites. Thereby, it was found that Pd loading can be decreased without comprising the activity by increasing oxygen vacancies of MoO_x as co–catalyst.

1. Introduction

Ethylene glycol is a cheap, non–volatile, and abundant raw material for plenty industrial applications [1]. Ethylene glycol (EG) is undoubtedly a promising fuel for energy conversion applications as has been stablished in many reviews [2–4]; the electrocatalysis of EG has been studied on platinum [5], palladium [6], and gold [7] noble metals. Nonetheless, the successful use of EG on energy conversion applications requires the decrease of the noble metal loading, which can be achieved by combining precious metals with non–noble metals or by designing a) non–precious metal based or b) metal–free catalysts. The latter two options have been widely used for the oxygen reactions (oxygen reduction/evolution) [8–10]; however, for fuel oxidation, it has been difficult to overcome the energy barriers to start the reaction [11,12]. Thus, for alcohols oxidation, the most reported strategies to decrease the noble metal loading are based on the mixture of the noble metal with cheap transition metals in their oxide or zero–valent form [13–15] or conductive polymers such as poly(3,4–ethylenedioxythiophene) (PEDOT) [16].

Transition metal oxides (TMOs) have been extensively used to develop mixtures of transition metal oxides (MTMOs) ordered typically in a spinel-like structure ($A_xB_{3-x}O_4$; A, B = Co, Ni, Cu, Mn, etc.) [17]. The smart design of these MTMOs together with the multiple valences of the cations in the spinel structure have resulted beneficial for the development of highly active materials for oxygen reduction/evolution reactions (ORR/OER) [17–20]. Going further the typical 3*d*–metals that composed TMOs/MTMOs, 4*d*– and 5*d*–TMOs have also displayed excellent electrocatalytic properties for oxygen reactions [21,22]. Among 4*d*–metals, molybdenum is found to be an excellent material for energy conversion. Mo has been tested in form of oxides and sulphides for the hydrogen evolution reaction [23,24], and this attention has been attracted due to molybdenum oxides (MoO_x) are low cost, non–toxic,

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