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Electrochemical and *in situ* FTIR study of the ethanol oxidation reaction on PtMo/C nanomaterials in alkaline media

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ABSTRACT

In this work, the catalytic activity of PtMo/C catalysts for the Ethanol Oxidation Reaction (EOR) in 0.5 mol L^{-1} KOH electrolyte was evaluated by electrochemical and *in situ* Fourier Transform Infrared Spectroscopy (FTIR) measurements. The alloys having 1:1, 2:1 and 3:1 Pt:Mo atomic ratios were synthesized by the formic acid method. X-ray diffraction analyses (XRD) showed the crystalline features of the catalysts, with crystallite sizes between 2.5 and 3.2 nm. Cyclic voltammograms (CVs) indicated the alloys mass catalytic activity in the order: $Pt_1Mo_1/C > Pt_3Mo_1/C > Pt_2Mo_1/C$, in all cases higher that Pt/C. For specific catalytic activity, the performance was in the order $Pt_3Mo_1/C > Pt_1Mo_1/C–Pt/C > Pt_2Mo_1/C$. Two CO-like species namely CO^{I}_{ads} and CO^{II}_{ads} were evidenced from CO-stripping measurements on the alloys. *In situ* FTIR characterization showed that the alloys promote the oxidation of ethanol in the alkaline media mainly through a 4 electrons transfer route. CO_2 was produced probably from the break-up of the C—C bond and the oxidation of C1 species. Pt_3Mo_1/C produced moreCO^{I}_{ads}, followed by Pt_1Mo_1/C, oxidizing carbon monoxide more easily. These two alloys also had a higher CO_2/CH_3CHO ratio, due to a high efficiency for oxidizing C2 and C1 species to CO_2. Such capabilities promoted a higher catalytic activity of Pt_1Mo_1/C and Pt_3Mo_1/C for the EOR, related to the other catalysts.

1. Introduction

Over the last decades, the Direct Alcohol Fuel Cells (DAFCs) have been widely investigated as power sources for stationary and portable applications. These electrochemical devices present energetic advantages such as simple fuel handling, low operating temperature, high energy conversion efficiency and reduced environmental impact [1–5]. Among the different liquid fuels proposed for DAFCs, ethanol is particularly interesting because of its relevant energy density and also its large production from agricultural raw materials and biomass [6,7].

For several decades, the research on DAFCs focused on the use of acid polymer electrolytes [8]. Nevertheless, the recent advances in the development of chemically stable alkaline polymer electrolytes have prompted an increased interest in Alkaline Direct Alcohol Fuel Cells (A-DAFCs) [9,10]. Having the advantage of being devices with a less corrosive environment than that found in their acid counterparts, thus ensuring a longer life-cycle, A-DAFCs are rapidly becoming the subject of study and development worldwide [11–15]. Moreover, A-DAFCs present facile anode and cathode kinetics, compared to acid fuel cells [16–18].

Besides that, it is acknowledged that even in the alkaline media, the complete oxidation of ethanol into CO_2 proceeds through a complex reaction mechanism that involves dissociative adsorption of the molecule, C—C bond cleavage and dehydrogenation. Consequently, it is observed the formation of reaction intermediates that in turn are poison for Pt-alone anode catalysts [19–24]. Nonetheless, it has been reported that at high pH values, the C—C bond breakage, *i.e.*, the so called C1-pathway, is more facile than its acid counterpart [25]. Further reactions induced after the C—C cleavage at ethanol or acetaldehyde, such as the oxidation of $CH_{x,ads}$ and CO_{ads} species leading to CO_2, proceed at more low potentials in alkaline media [25,26]. On the other hand, in the C2-pathway (*i.e.*, no C—C breakage of the ethanol molecule), the rate of acetaldehyde oxidation to acetate increases at high pH [25]. According to Koper et al., the formation of acetaldehyde leads to an increase of the current density during the EOR in alkaline electrolyte [25].

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In spite of that, it is well known also that due to the multi-step reaction mechanism, plurimetallic Pt-based anodes are needed, in order to enhance the tolerance to intermediate species and increase the catalytic activity for the EOR [21,22]. Zhao and co-workers have demonstrated that Pt-Rh/C anodes activate the EOR in KOH solution, improving the C—C bond cleavage and accelerating the oxidation of CO_{ads} species to CO_2, leading to an increase of the catalytic activity compared to Pt/C [21]. The report by Assumpção and co-workers has showed that PtAu/C alloys have a higher catalytic activity than Pt/C for the EOR due to an extension of the Pt lattice parameter, promoting as well the C—C bond breaking [22]. Moreover, Zhu and co-workers have developed hollow Au/Pt core-shell nanostructures, with enhanced catalytic activity and stability for the EOR, in part due to a higher Pt utilization factor at the nanoporous materials [27].

On this regard, the study of an element like Mo in PtMo/C alloys for the EOR in alkaline media has been ignored or at least limited. Mo is an oxophilic metal that has been incorporated as co-catalyst for increasing the catalytic activity for the oxidation of alcohols in acid solutions and also for improvement of the tolerance towards CO, compared with pure Pt anodes [28–32]. It has the advantage of being inexpensive and widely available [19]. In acid electrolyte, PtMo/C is more active than Pt/C for the EOR, even though its performance is lower compared to PtRu/C [32]. In *situ* FTIR and DEMS studies have indicated that the incorporation of Mo to PtRu/C catalysts results in a higher tolerance to CO, leading to acetaldehyde and acetic acid formation [33]. Precisely, the study of the EOR at PtMo/C catalysts in alkaline media and identification of reaction intermediates by *in situ* FTIR is not reported in the literature, to the best of the authorís knowledge.

With the aim to evaluate their catalytic activity for the EOR in alkaline media, this work presents the synthesis of PtMo/C catalysts (Pt:Mo atomic ratios of 1:0, 1:1, 2:1 and 3:1) with formic acid as reducing agent. XRD and EDS analyses were performed in order to assess the crystalline structure and the chemical composition of the materials. Their electrochemical characterization has been studied through cyclic voltammetry (CV), the chronoamperometry and the CO stripping measurements. The identification of reaction intermediates and products was carried out by *in situ* FTIR spectroscopy technique.

2. Experimental

2.1. Materials

Chloroplatinic acid hexahydrate ($H_2PtCl_6{\cdot}6H_2O$), ammonium molybdate tetrahydrate ($(NH_4)_6\ Mo_7O_{24}$), formic acid (HCOOH), ethanol (C_2H_5OH) and potassium hydroxide (KOH) were obtained from Sigma-Aldrich. CO and N_2 gases were of UHP grade (Praxair). Vulcan XC-72 from Cabot® was used as the support.

2.2. Physical and chemical characterization

XRD measurements were performed with a Phillips-Xípert diffractometer using CuKα radiation source, in a scan from 10 to 100° (2θ). The data was refined by using the Savitzky-Golay algorithm. The crystallite size was calculated with the Scherrer equation by analyzing the Pt (220) reflection of each sample. The chemical composition was obtained by a Phillips XL30 SEM microscope equipped with an Energy Dispersive X-ray Spectroscopy (EDS) analyzer operating at 20 kV.

2.3. Synthesis of the electrocatalysts

PtMo/C catalysts with metal loading of 20 wt.% were synthesized by simultaneous reduction of chloroplatinic acid and ammonium molybdate in aqueous medium. An appropriate amount of Vulcan was dispersed by ultrasound in 0.1 mol L^{-1} formic acid for 30 min. The mixture was heated at 80 °C under magnetic stirring and the appropriate quantities of Pt and Mo precursors were added drop by drop, maintaining the temperature for 2 h. The solution was allowed to cool down to room temperature and the final products were filtered, washed, and dried. The same procedure was used with chloroplatinic acid alone for preparing the pure 20 wt.% Pt/C catalyst.

2.4. Electrode preparation and electrochemical measurements

The catalytic activity of the electrocatalysts for the EOR was studied in a three electrode cell (from Pine Inst.), using a Voltalab PGZ 301 potentiostat/galvanostat. The counter electrode was a platinum sheet and the reference electrode was an Ag/AgCl electrode. For simplifying the comparison all potentials reported in this paper were referenced to the RHE scale. The working electrode was a thin catalytic film on glassy carbon (5 mm diam) which is inserted in a Teflon support (Pine Inst.). This catalytic layer was prepared by deposition of 10 μL of a catalytic ink composed of 5 mg of catalyst in a mixture of 0.5 mL isopropyl alcohol and 25 μL Nafion®.

CVs were acquired in N_2-saturated 0.5 mol L^{-1} KOH electrolyte in the potential range between 0.05 V to 1.2 V/RHE at a scan rate of 20 mV s^{-1}, based on the geometrical area of the glassy carbon. The electrochemically active surface area $\left(ECSA_{H_{UPD}}\right)$ of the anodes was calculated from the charge corresponding to the hydrogen desorption, considering a charge of 210 μC cm^{-2} due to the adsorption of a hydrogen monolayer on Pt. Afterwards, the mass and specific catalytic activities for the EOR were evaluated in an electrolyte containing 0.5 mol $L^{-1}C_2H_5OH$. In the first case, the amount of Pt at each catalysts (from EDS analysis) was considered. In the second case, the real Pt areas, obtained from the hydrogen desorption regions at the CVs, were taken into account. Chronoamperometric tests were performed by polarizing the electrode at 0.66 V/RHE for 20 min in the presence of ethanol. CO-stripping was carried out as follows: at a constant applied potential of 0.26 V/RHE at the working electrode, CO was bubbled for 10 min. Then the electrolyte was saturated with N_2 for 10 min and CVs were recorded at 20 mV s^{-1}. The electrochemically active surface area ($ECSA_{CO}$) of the electrocatalysts was determined by assuming a charge of 420 μC cm^{-2} due to the adsorption of a CO monolayer at the Pt surface [34].

2.5. In situ *FTIR spectroscopy measurements*

In situ FTIR measurements were carried out under external reflections conditions on a Bruker-IFS66 v spectrometer interfaced with the OPUS 5.5 software (Bruker) and modified for beam reflectance at a 65° incident angle and equipped with a liquid N_2-cooled MCT (HgCdTe) detector. In order to avoid vibration bands from air the system is maintained under vacuum. The experiments were carried out in a three electrode spectroelectrochemicall cell equipped with a CaF_2 window on the bottom and connected to a potentiostat Autolab (PGSTAT-30) interfaced with the Nova 1.8 software. A reversible hydrogen electrode and a glassy carbon slab were respectively used as reference and counter electrodes. The working electrode consisted of a glassy carbon disk of 6 mm diameter (0.282 cm^{-2}) that was polished using alumina powder prior to each experiment. The spectra were acquired using the single potential alteration IR reflectance spectroscopy (SPAIRS) method in the range of 0.1–1.2 V *vs* RHE at 50 mV intervals at a scan rate of 1 mV s^{-1}.The spectra resolution was 4 cm^{-1}, and the FTIR spectra were recorded in the 1000 cm^{-1} and 4000 cm^{-1} MIR region. 512 interferograms were co-added and IR spectra were calculated for each potential values as changes in the reflectivity (R) relative to a