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Studies of the reaction products resulted from glycerol electrooxidation on Ni-based materials in alkaline medium

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ABSTRACT

In this work, nickel oxy-hydroxide was shown as active catalytic specie for the glycerol oxidation reaction in alkaline medium. As the formation of cobalt and iron oxy-hydroxides occurs at lower potentials than those of nickel, cobalt and iron amounts were added to modify the Ni material. Carbon supported Ni-M (M = Co, Fe) nanomaterials were thereby synthesized by the impregnation method with metal loadings of wt. 20% and heat-treated in reducing H_2 atmosphere. Physical characterizations of the materials were performed with TGA-DTA and XRD to assess their metallic charge and the crystallite size, respectively. Cyclic voltammetry was mainly used to evaluate the electrochemical activity of the catalysts towards the oxidative transformation of glycerol. In a selected potential chronoamperometry experiments were then carried out and the glycerol oxidation products on the Ni-based anodes were analyzed with liquid chromatography. The glycerol conversion depends on the catalyst composition and the distribution of the products was well correlated with those identified with infrared reflectance spectroscopy which supported the proposed simplified mechanism.

1. Introduction

Fossil fuel consumption continues to increase because of the growing global energy demand. To face the programmed scarcity of these energy sources and to satisfy the growing energy demand, the use of alternative fuels from renewable sources should not be overlooked. Although glycerol is currently used as starting material in cosmetic, pharmaceutics, food and tobacco industries, its availability could exceed the demand due to the growing production of biodiesel [1–10]. Glycerol is regarded as an attractive alternative to conventional fuels. It has a theoretical energy density of 5 kWh kg^{-1} and a high theoretical number of exchanged electrons (14 electrons/glycerol molecule) [11–14], which means that its oxidation can be doubly motivated by providing sustainable energy source and cogenerating added-value chemicals [15–20]. Two of the more important chemicals that can be obtained are glyceric acid and dihydroxyacetone [6,16,21,22], although other oxygenates, as tartronic acid, glycolic acid, mesoxalic acid or hydroxypyruvic acid can be obtained [11,17,23]. These products are potentially valuable chelating agents which can be used as intermediate compounds for the synthesis of fine chemicals and polymers [24,25]. The glycerol oxidation reaction was mainly investigated on precious electrode metals (Pt, Au and Pd) [6,14,24,26–33]. As many oxidation products can be formed it requires controlling selectivity by careful catalytic design. In general Pd catalysts were found to be more selective than Pt and high selectivities to dihydroxyacetone [21,22,30,34], glyceraldehyde [35] or hydroxypyruvic acid [36] were obtained on PtBi catalysts by controlling the reaction conditions and particularly, the pH of the solution. However, formic acid was also noted as reaction product, probably issued from the formation of oxalic acid. It was also reported that glycerol could be oxidized with 100% selectivity to glyceric acid on AuC [32]. Most reports discussed a bifunctional mechanism where the metallic modifier added to a basic noble metal provides oxygen species to aid in the removal of adsorbed CO and other incomplete oxidation products [18,37–40]. Tin and ruthenium have also been described in the literature as beneficial modifiers of platinum catalysts for biomass oxidation by helping to improve catalytic activity and decrease adsorbed oxidation intermediates [41–44]. Many reports concerning the feasibility of these metallic systems applied to fuel cells have mostly focused on acid electrolyte, while alkaline media presents many advantages for electrochemical reactions such as improvements in reaction kinetics at the anode and cathode [38,45,46]. A number of studies were carried out in alkaline medium because of the

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reduced poisoning effect by the catalyst in such electrolyte, which improves the kinetics of the reaction and the degree of fuel oxidation [18,41,47]. Hydroxypyruvate, glycerate, mesoxalate, glycolate, tartronate, oxalate and formate ions and dihydroxyacetone are the main products observed during the glycerol oxidation reaction in alkaline medium on noble electrodes [22–24,27,47,48].

As pointed out above, to date the best and most frequently used electrocatalysts for alcohol oxidation processes are Pt, Au and Pd-based materials. Efforts are under way for reducing the scarce metal loadings by using non-precious metals such as cobalt, nickel and iron in alkaline medium [49–53]. Nickel based electrocatalysts are promising due to competitive price and their high catalytic activity to convert selectively glycerol in high added-value chemicals [49,52,54]. There are few reports about glycerol oxidation reaction on Ni-based electrodes that were used in the oxidative conversion of various alcohols [15,51,52,55,56]. This study looks into the chromatographic analysis and identification by in situ IR reflectance spectroscopy of the reaction products obtained on Ni, Ni-M (M = Co, Fe) anode catalysts. The results indicate that the distribution of the products depends on the nature of the M content in the catalyst composition.

2. Experimental

2.1. Synthesis of nickel based catalysts by impregnation-reduction method

Carbon supported nickel Ni/C was prepared by mixing $Ni(NO_3)_2.6H_2O$ (Aldrich P.A.) and a suitable amount of carbon Vulcan (XC-72) in ultra-pure water to obtain an expected metal loading. The mixture was sonicated for 1 h. After heating at 80 °C to evaporate water, the resulting residue was ground to a fine powder. A heat-treatment was performed under H_2 flow at 300 °C with a temperature rate of 5 $^\circ C\ min^{-1}$ for 2 h. The same procedure was used to prepare CoNi/C, FeNi/C and FeCoNi/C with the addition of $CoCl_2.6H_2O$ solution (Alfa Aesar P.A.) or $FeCl_2.6H_2O$ solution (Alfa Aesar P.A.) and both, respectively. The metal loading for each catalyst sample was 20 wt. % and the nominal atomic ratio was 1:1 to bimetallic materials and 1:1:1 for the ternary material. The Ni-based catalysts with Fe and Co contents were heat-treated at 700 °C for 2 h, which allowed the homogenization of the composition. Vulcan XC 72 carbon black (CABOT) used as a supporting substrate was previously treated under argon at 850 °C for 5 h.

The metal loading of the tailored catalyst was evaluated by Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) using a TA Instruments SDT Q600 Apparatus. A few milligrams of catalytic powder were put in alumina crucible and heat-treated under air atmosphere (flow, 100 $mL\ min^{-1}$) from 25 to 900 °C with a temperature rate of 5 $^\circ C\ min^{-1}$. An empty alumina crucible with a punctured lid was used as reference.

The X-ray diffraction powder patterns of the catalytic powders were carried out with a Rigaku model Ultima IV diffractometer. Cu K_α incident radiation ($\lambda = 1.5418$ Å) was used at 40 kV and 30 mA. The scan speed was $1^\circ\ min^{-1}$ with a diffraction angle (in 2θ) from 20 to 90°.

2.2. Electrochemical measurements

All the electrochemical measurements were performed at room temperature (21 °C). A Reversible Hydrogen Electrode (RHE) and a glassy carbon slab were used as reference and counter electrode, respectively. The solutions were prepared from NaOH (Sigma-Aldrich 97%), Glycerol (Sigma-Aldrich $\geq$ 99%) and ultrapure water. The electrolytic solution was purged with N_2 for 30 min to expel dissolved oxygen and during the experiment, a nitrogen stream was maintained over the electrolyte.

A two-compartment Pyrex cell was used for the voltammetric measurements of the catalysts and for long-term electrolysis of glycerol. The compartments were separated with an anion-exchange membrane (35 µm thickness, from Fumatech). The working electrode consisted of catalytic powders deposited on a Carbon Toray paper used as conductive carrier with a geometric surface area of 3 cm^2. A conducting carbon paste was used to connect the carbon Toray substrate and a gold wire. A catalytic ink was prepared from the metal/C powder (2 mg) added to a mixture of 425 µL of Nafion solution (Aldrich) and 75 µL of water. 50 µL of the catalytic ink was then deposited onto each face of the carbon Toray paper and the solvent was evaporated at room temperature. The metal loading in the working electrode represents 133 $\mu g\ cm^{-2}$.

Cyclic Voltammetry (CV) in 0.1 $mol\ L^{-1}$ NaOH was performed to characterize the activity of the electrocatalyst in the absence and presence of glycerol. Measurements were conducted with a computer controlled Autolab Potentiostat (PGSTAT 302 N) which was connected to an Electrochemical Interface (Metrohm). Next, the glycerol oxidation in NaOH (0.1 $mol\ L^{-1}$ glycerol + 0.1 $mol\ L^{-1}$ NaOH) and chronoamperometry analyses (1.6 V vs. RHE) were performed in potential domains where the CV curves showed the formation of metal oxy-hydroxides at the electrode surface.

2.3. In situ FTIRS experiments

FTIR experiments were performed under external reflection conditions on a Bruker IFS66 v spectrometer, modified for beam reflectance at 65° incident angle, equipped with a globar MIR source and a liquid N_2-cooled MCT narrow-band detector. Data acquisition and processing was performed with OPUS 5.5 software. In order to avoid IR bands from atmospheric CO_2 and H_2O, the system is kept under vacuum. All the experiments were performed in a special three-electrode spectroelectrochemical cell fitted at the bottom with a CaF_2 window, allowing the beam to pass through a thin electrolyte layer. For the measurements, 3 µL of the catalyst ink were deposited onto a vitreous carbon disk previously polished with alumina (working electrode). The counter electrode was a plate of vitreous carbon and the reference electrode was a RHE. Spectra were given in the 800–2400 cm^{-1} range with a spectral resolution of 8 cm^{-1}. For Chronoamperometry/FTIRS experiments, spectra were collected every 5 min for 4 hours, with the electrode potential set at 1.5 V *vs* RHE. The reflectance spectra were calculated for the different potential values as changes in the reflectivity (R_i) relative to a reference single-beam spectrum (R_{ref}) as follows: $\Delta R/R = (R_i - R_{ref})/R_{ref}$. The reference spectrum was taken at the beginning of the experiment at t = 0 for Chronoamperometry/FTIRS experiments. Positive and negative going bands represent respectively the decrease and increase of species.

2.4. High Performance Liquid Chromatography (HPLC) measurements

The separation and analysis yields of the products from the glycerol oxidation were performed using a High Performance Liquid Chromatography (HPLC) with the Dionex system (P680 HPLC). It works with an isocratic elution and mainly includes a sample loop (20 µL) and an ion-exclusion column (Aminex HPX-87H) which separates by ascending pKa [53]. The chromatograph was equipped with an UV-vis detector followed by a differential refractometer (IOTA2). The column operated at room temperature and the analytes were separated with diluted sulfuric acid (3.3 $mmol\ L^{-1}$ H_2SO_4) used as eluent and a flow rate of 0.6 $mL\ min^{-1}$. The assignments of the different peaks and the quantitative determination of the products were done by comparing the