



In situ monitoring of the phenomenon of electrochemical promotion of catalysis



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ARTICLE INFO

Article history:

Received 13 June 2017

Revised 25 September 2017

Accepted 26 November 2017

Keywords:

Electrochemical promotion

Spillover

Alkaline conductors

XPS

NAPP

Synchrotron analysis

Ni catalyst

Glancing angle deposition

ABSTRACT

In this work we investigate by in-situ near-ambient pressure photoemission (NAPP) spectroscopy the phenomenon of Electrochemical Promotion of Catalysis (EPOC). We studied the reduction and diffusion kinetics of alkaline ions in a solid electrolyte cell formed by a nickel electrode supported on K⁺-β-alumina electrolyte. Experiments in ultra-high vacuum and in the presence of steam showed that the amount of potassium atoms supplied to the surface is probably affected by nickel electronic modifications induced by adsorbed OH⁻ groups. It was also deduced that part of the segregated potassium would be adsorbed at inner interfaces where it would be inaccessible to the photoelectron analyzer. A migration mechanism of the promoter is proposed consisting in: (i) the electrochemical reduction of the alkali ions (potassium) at the Ni/solid electrolyte/gas interface; (ii) the spillover of potassium atoms onto the Ni gas-exposed surface; and (iii) the diffusion of potassium atoms to Ni inner grain boundary interfaces.

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1. Introduction

The Electrochemical Promotion of Catalysis (EPOC) concept has opened a new way of improving activity and selectivity of a heterogeneous catalytic reaction [1–3]. EPOC is based on the electrochemical activation of a catalyst film in contact with a solid electrolyte material (e.g., H⁺, Na⁺, K⁺, O²⁻ ionic conductors) that acts as a source of promoter ions. This phenomenon is not limited to a particular kind of catalyst, solid electrolyte material or chemical reaction and has been proved in a wide variety of systems [1]. To unravel its operating mechanisms, several experimental procedures have been utilized including adsorption-desorption techniques, work function measurements, isotope labeling, cyclic voltammetry, electronic microscopy, impedance spectroscopy and other spectroscopic techniques [1,4]. Of particular relevance for the present investigation are previous works using X-ray photoelectron (XPS) and Auger electron spectroscopies (AES) carried out by the group of Lambert et al., who analyzed EPOC systems

based on alkaline (Na⁺ and K⁺) ionic conductors and Pt [5–7], Rh [8,9] or Cu [10,11] catalyst films. In these studies, the solid electrolyte cells were initially exposed to EPOC reaction conditions in the pre-chamber of an electron spectrometer and then transferred to the ultra-high vacuum analysis chamber to collect the XP spectra. Although these works were not carried out under real “in operando” conditions, they showed that upon cathodic polarization the alkaline ions (M⁺) of the solid electrolyte migrate to the three-phase boundary (tpb), i.e., metal electrode/solid electrolyte/gas interface, where they become reduced to their elemental state (M) (i.e., reaction (1)), and then spill-over to the gas-exposed metal surface where they become adsorbed in neutral form.



The present work using Near Ambient Pressure Photoemission Electron Spectroscopy (NAPP) goes a step forward vs. these previous studies through the application of an experimental approach enabling the following:

- (i) To perform photoemission measurements under polarization in the same reactor chamber and conditions closer to those of an “operando” methodology [12].

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- (ii) To work at near ambient pressure, i.e. under reaction conditions similar to those encountered in EPOC electrochemical cell reactors.

The present study has been carried out in the context of previous EPOC works carried out by our group on catalytic hydrocarbon and alcohol reforming reactions [13–15]. Herein, by working under in-situ NAPP conditions we have gained a better understanding of the alkaline ion/metal diffusion processes by monitoring the potassium supply/removal under cathodic/anodic polarizations, i.e., in the course of the electric polarizations. Namely, we have found new evidences about potassium segregation onto the catalyst surface and back to the electrolyte when applying a negative/positive potential to the alkaline solid electrochemical cell. In particular, we have comparatively analyzed the kinetics of potassium surface segregation followed by NAPP as a function of atmosphere with the time evolution of the cell electrical signals (i.e., intensity and voltage) simultaneously measured with a potentiostat-galvanostat. The differences found between these two time-dependent signals have been rationalized with a three-step potassium reaction and migration mechanism during polarization. We propose that this systematic comparison can be a powerful methodology not only to understand the EPOC phenomenon, but also for other experiments in fields such as fuel cells, photovoltaic cells, batteries, corrosion and, in general, electrochemical systems where diffusion processes are key issues for device performance.

2. Experimental

2.1. Preparation of the electrochemical catalyst

The solid electrolyte cell was formed by a Ni film deposited on a side of a 19-mm-diameter, 1-mm-thick K- β -Al₂O₃ (Ionotec) disc (7.9 mm diameter, geometric area = 2.01 cm²) acting as electrolyte. The catalytically inert Au counter/reference (C/R) electrode was deposited on the other side of the electrolyte by applying a thin gold paste coat, followed by calcination at high temperature. Then, the active Ni catalyst film, which also behaves as a working electrode (W), was deposited on the other side of the electrolyte by a modification of the classical physical vapor deposition (PVD) technique, called oblique or glancing angle deposition (OAD or GLAD) [16,17]. By this method, the substrate (K- β -Al₂O₃) is placed in an oblique angle configuration with respect to the evaporated flux of deposited material (Ni) to enhance nanostructuring effects induced by the shadowing effects occurring during film growth [18]. As a result, a highly porous film, characterized by a high surface area and a controlled microstructure formed by tilted nanocolumns, was obtained. This kind of catalyst morphology can be of special interest in electrochemically assisted catalytic processes for H₂ production and storage [14]. In the present study, the Ni catalyst film was deposited at a zenithal evaporation angle $\alpha = 80^\circ$. As determined by Rutherford back scattering spectroscopy (RBS), these films presented an equivalent mass thickness of 900 nm (i.e., equivalent thickness if the film were compact). A SEM micrograph of the nanostructured Ni film is reported in Fig. 1a. This figure clearly shows that most nickel agglomerates in the form of nanocolumnar patches, while a continuous Ni layer also covers the substrate (see results). Additional characterization and electrocatalytic behavior of these electrode thin films can be found in previous works [14,16].

2.2. Near-ambient pressure photoemission spectroscopy measurements

For the NAPP experiments, the Ni/K- β -Al₂O₃/Au electrocatalytic cell was incorporated in a special sample holder (see scheme in

Fig. 1b). The sample, a circular pellet of K- β -Al₂O₃ with its top side coated with the porous Ni film and a gold dense film on the bottom, was silver glued to the sample holder through its back face. The sample holder consisted of a cylindrical stainless steel piece fully surrounding the back and lateral sides of the sample. It was connected with a thin silver thread (0.2 mm) to the active terminal of a potentiostat/galvanostat (Vertex model, Ivium Technologies). On the top side, a small drop of silver paste (4 mm² contact area) was deposited on the outer edge of the circular Ni electrode and then electrically contacted through a small spiral silver thread that was immersed in the silver paste till its drying and curing at room temperature. This second thread was connected to the second terminal of the potentiostat and grounded. This configuration means that, whatever the bias voltage applied to the Au counter electrode, the Ni electrode was always earthed, as required for referencing the binding energy scale of the photoelectron energy analyzer. A picture of this sample holder configuration is shown in Fig. 1c.

The NAPP spectrometer was located at the BL-24 CIRCE undulator beamline, in the ALBA synchrotron light source (Sant Cugat del Vallés, Spain); it is equipped with a Phoibos NAP150 XPS analyzer (SPECS) and a differential pumping system for operating at a given pressure in the analysis chamber. The beam spot size at the sample position was around 100 × 20 μ m². Samples were excited with photons of two different energies: 460 eV and 1170 eV. The emitted photoelectrons were analyzed with a pass energy of 10 eV. K/Ni atomic ratios were determined from the K2p and Ni3p spectra measured with $h\nu = 460$ eV, while C/Ni ratios were determined from the C1s and Ni2p spectra measured with $h\nu = 1170$ eV. For a semiquantitative evaluation of spectra, raw areas under the peaks were corrected for the photoionization cross sections of each electronic level [19] and the escape depth of photoelectrons [20].

Generally, spectra were recorded at the final state conditions of the experiments. In addition, the maximum of the K2p peak signal was continuously recorded as a function of time together with the current (I) and/or potential (V) applied and/or monitored with the potentiostat-galvanostat. All the experiments were carried out at the optimal temperature of 280 °C, as determined in previous studies [14], and two reaction atmospheres: under the presence of water vapor as an active adsorbate, denoted as “water conditions”, (water pressure of 10⁻² mbar), and under absence of any active adsorbate, denoted as “high vacuum” (residual pressure in the chamber of 10⁻⁷ mbar).

3. Results and discussion

A common feature of reforming reactions (for hydrocarbons or alcohols) is the use of water vapor as a second reactant. Water is also of paramount importance for the removal of deposited carbonaceous species on catalytic active sites [15,21]. Therefore, a first experiment was dedicated to condition the electrocatalyst surface and to monitor the evolution of the carbon residues on the Ni catalyst surface exposed to water vapor at 280 °C in the absence of any applied voltage, i.e., under open circuit conditions. Carbon residues were inevitably incorporated to the Ni catalyst surface during film preparation and afterwards during the manipulation of the cell in air. The collected NAPP spectra reported in Fig. 2 were obtained along 50 min and show that the intensity of the C1s signal of the adsorbed adventitious carbon progressively decreased up to reaching an almost negligible intensity in the steady state. This pre-treatment allowed obtaining an almost clean Ni catalyst film. The Ni2p signal of metallic nickel, characterized by a BE of 852.7 eV [22] did not undergo any significant modification in shape, although its intensity slightly increased as a result of this water vapor conditioning treatment. Meanwhile, a small O1s signal due to OH⁻ or similar functional groups was also recorded after that

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