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Review

A Review of Surface Analysis Techniques for the Investigation of the Phenomenon of Electrochemical Promotion of Catalysis with Alkaline Ionic Conductors

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Abstract: Electrochemical Promotion of Catalysis (EPOC) with alkali ionic conductors has been widely studied in literature due to its operational advantages *vs.* alkali classical promotion. This phenomenon allows to electrochemically control the alkali promoter coverage on a catalyst surface in the course of the catalytic reaction. Along the study of this phenomenon, a large variety of *in situ* and *ex situ* surface analysis techniques have been used to investigate the origin and mechanism of this kind of promotion. In this review, we analyze the most important contributions made on this field which have clearly evidenced the presence of adsorbed alkali surface species on the catalyst films deposited on alkaline solid electrolyte materials during EPOC experiments. Hence, the use of different surface analysis techniques such as scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning photoelectron microscopy (SPEM), or scanning tunneling microscopy (STM), led to a better understanding of the alkali promoting effect, and served to confirm the theory of electrochemical promotion on this kind of catalytic systems. Given the functional similarities between alkali electrochemical and chemical promotion, this review aims to bring closer this phenomenon to the catalysis scientific community.

Keywords: electrochemical activation; EPOC; alkali promotion; surface analysis; ionic conductors; active catalyst supports; sodium; potassium

1. General Features of Alkaline Electrochemical Promotion

Promoters are widely used in the heterogeneous catalysis field [1,2]. Structural promoters improve the dispersion and stability of the active phase on the catalyst support, while electronic ones enhance the catalytic properties of the active phase itself. This latter kind of promoters can be added to the catalyst *ex situ*, *i.e.*, during the catalyst preparation step, or *in situ*, *i.e.*, in the course of the catalytic reaction, through the phenomenon of Electrochemical Promotion Of Catalysis (EPOC). This phenomenon, also known in literature as "Non-faradaic Electrochemical Modification of Catalytic Activity" (NEMCA effect) [3], is based on the modification of the performance of a catalyst by the electrochemical pumping of promoter ions from an electro-active catalyst support, which is a solid electrolyte material, e.g., H^+, Na^+, K^+, O^{2-}, or F^- ionic conductors [4]. Although the first works on electrochemical promotion were carried out by using yttria-stabilized zirconia (YSZ), *i.e.*, an O^{2-} ionic conductor material, as solid electrolyte [5], alkaline conductors such as the β-alumina family or NASICON-like compounds (e.g., $Na_3Zr_2Si_2PO_{12}$, $K_2YZr(PO_4)_3$, or $Li_{14}ZnGe_4O_{16}$), among others, have also been widely studied on the electrochemical promotion field [6,7].

In the case of electrochemical catalysts based on alkali (M^+)-conductors, the application of a cathodic polarization (*i.e.*, negative current or overpotential) between the catalyst film-working electrode, which is deposited on one side of the electrolyte, and an inert counter electrode (typically gold) located at the opposite side (see Figure 1) leads to the migration of promoter (M^+) ions to the catalyst film, which is also called as back-spillover phenomenon. Once located over the catalyst surface, as in chemical (classical) promotion, these ionic species modify its chemisorption properties and hence its catalytic performance [3]. Thus, some of the main advantages of electrochemical promotion *vs.* classical promotion in heterogeneous catalysis are the capability of optimizing the amount of promoter coverage under changing reaction conditions and the possibility of *in situ* tuning the catalyst performance to maximize its activity and selectivity toward the desired product, even preventing catalyst deactivation or allowing its regeneration. These operational advantages *vs.* classical promotion, among others, have recently been revised by A. de Lucas-Consuegra [6]. It should also be noted that there are important differences in operating EPOC systems depending on the nature of the employed electro-active catalyst support. When using ionic conductor materials where the supplied ions can also participate in the catalytic reaction under study (e.g., O^{2-} ions in the case of catalytic oxidations or H^+ ions in catalytic hydrogenations) then these ions act as "sacrificial promoters" and present a finite mean residence time on the catalyst surface. In these cases, both galvanostatic and potentiostatic operations allow to obtain a steady-state catalytic reaction rate at each applied current or potential, respectively. However, when using solid electrolytes where the ionic conducting species are not involved in the catalytic reaction (e.g., Na^+ or K^+ ions) then only potentiostatic operation leads to steady-state reaction rates and, under galvanostatic operation, the coverage of the M^+ promoter, θ_{M^+}, increases with time as long as a constant electric current is maintained [3]. However, in these cases, as will be shown later, these alkali ions typically react with co-adsorbed reactant molecules on the gas-exposed catalyst surface leading to the formation of a large variety of promotional species.

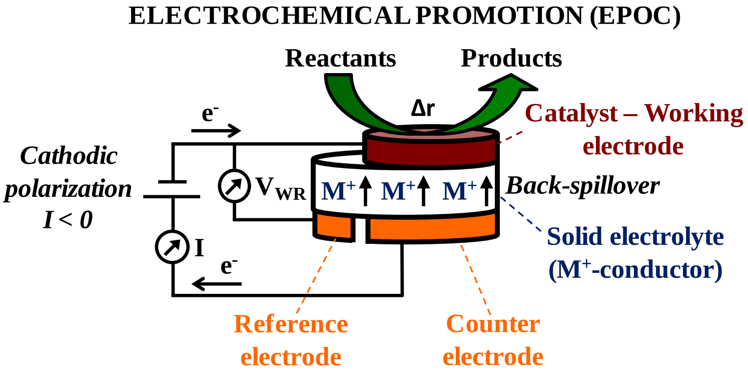

Figure 1. Scheme of the electrochemical cell used in electrochemical promotion studies with an alkaline ionic conductor (generally indicated as M^+-conductor) solid electrolytes.

Vayenas *et al.* performed the first electrochemical promotion study with alkaline solid electrolyte (Na-βAl_2O_3) in 1991 [8]. From this pioneer work, Na^+-conductors have been widely employed in many catalytic systems such as ethylene [9,10], CO [11], propane [12] and propylene oxidation [13], NO reduction [14–16], Fischer Tropsch synthesis [17], or hydrogenation of benzene [18] and CO_2 [19]. On the other hand, the first EPOC study using a K^+-conductor electrolyte ($K_2YZr(PO_4)_3$) dates from 1997 and addressed the Fe-catalyzed ammonia decomposition [20]. Urquhart *et al.* used other K^+-conductor solid electrolyte (K-βAl_2O_3) in Fischer-Tropsch reaction studies under both atmospheric [21] and high pressure [22], and de Lucas-Consuegra *et al.* introduced the use of this kind of ion-conducting catalyst support for the electrochemical promotion of Pt in CO [23] and propylene [24] oxidation, as well as in NO_x reduction reactions [25,26]. More recent alkaline electrochemical promotion studies on CO_2 hydrogenation [27–30] and methanol conversion reactions [31–33] should also be highlighted. Additionally, in order to understand the mechanism of the phenomenon of electrochemical promotion of catalysis with both anionic and cationic conductors, a wide variety of characterization techniques have been used in the fields of catalysis (e.g., TPD, TPO, or work function measurement), electrochemistry (e.g., cyclic/linear sweep voltammetry or impedance spectroscopy), and surface science (e.g., XPS, UPS, SPEM, or STM) [3]. This paper aims to summarize the most relevant contributions relative to the latter techniques carried out in literature on electrochemical promotion with alkaline conductors. For this purpose, the surface characterization studies summarized in the next two sections have been divided into two categories, depending on whether they were performed under potentiostatic/galvanostatic control (*in situ* analysis) or not (*ex situ* analysis), as schematically shown in Figure 2. All these techniques have contributed to the further understanding of the alkali electro-promotional effect in good agreement with the general rules of chemical and electrochemical promotion, valid for the different kinds of electronic promoters (both anionic and cationic ones) [3].

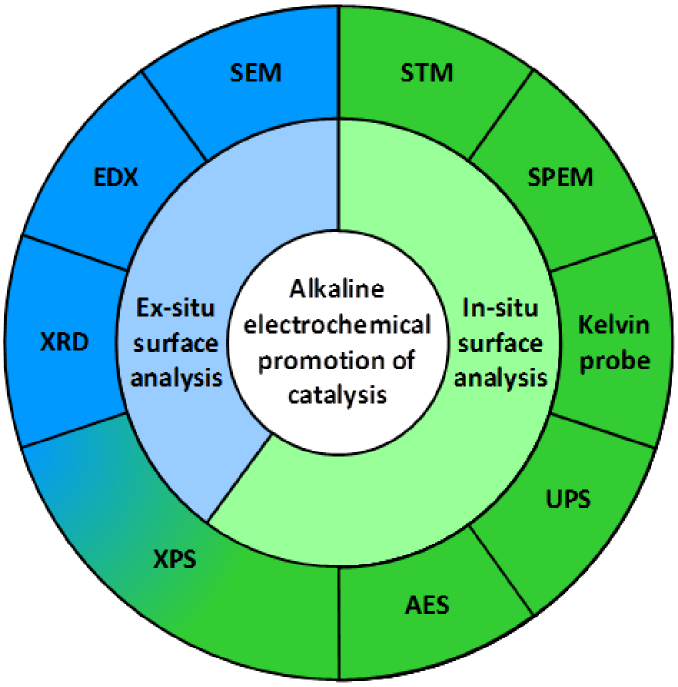

Figure 2. Scheme of the different surface analysis techniques used for investigating alkaline Electrochemical Promotion effect.

2. *Ex Situ* Characterization of Alkali-Promoted Catalyst Surfaces

The post-reaction characterization and analysis of the surface state of a catalyst film, previously subjected to given electrochemical promotion conditions, can be carried out *ex situ* by the following generic procedure. In the first place, the catalyst film is exposed to the reaction mixture while applying a certain positive or negative overpotential (for establishing an unpromoted or electropromoted state, respectively). After a given time, the reactor is cooled down to room temperature at the same applied overpotential. Then, the reactor and pipe lines are swept with inert gas and open-circuit conditions are established when the temperature is below 373 K (approximately), *i.e.*, when alkali ions mobility is too low. Finally, the electrochemical catalyst is transferred, under inert atmosphere, from the reactor to the characterization equipment. The aim of this procedure is to “freeze out” the catalyst surface state pertaining to the desired unpromoted/electropromoted state.

SEM and other microscopy techniques are widely employed in catalysis field to evaluate the structure and morphology of the catalysts. In EPOC studies, this technique, together with Energy-dispersive X-ray (EDX) spectroscopy, has also been employed to identify the arrangement and nature of the promoter phases present on the catalyst surface. For instance, Figure 3 shows the SEM micrograph, along with the corresponding elemental mapping and spectra by EDX, of a selected region of a Cu catalyst film deposited on a K-βAl$_2$O$_3$ pellet (K$^+$-conductor) used for the electrochemical promotion of the methanol partial oxidation reaction [32]. Prior to the surface analysis, the catalyst was subjected to certain reaction conditions and an applied potential, $V_{WR} = -0.5$ V, such that K$^+$ promoter ions were electrochemically supplied to the catalyst surface. As a consequence, in these micrographs, a large concentration of potassium (in blue) was found on the Cu catalyst surface (in green). This demonstrated that K$^+$ ions were able to migrate through the catalyst film and reached the gas-exposed catalyst surface. As also revealed by the EDX analysis taken from different areas of the micrograph (Figure 3c1,c2), oxygen- and potassium-containing surface compounds seemed to be formed on the metal catalyst film during the EPOC experiments, probably in form of some potassium oxides or carbonate molecules. In fact, an excess of these surface species (supplied under high cathodic polarization) could block the Cu active sites causing a decrease in the catalytic reaction rate in agreement with conventional chemical promotion [32]. Furthermore, some nitrogen (in red) was also noticed, homogeneously distributed on the catalyst surface, which was attributed to the K$^+$-promotional effect on the ammonia formation via reaction of hydrogen and nitrogen, both of them present in the gas reaction atmosphere.

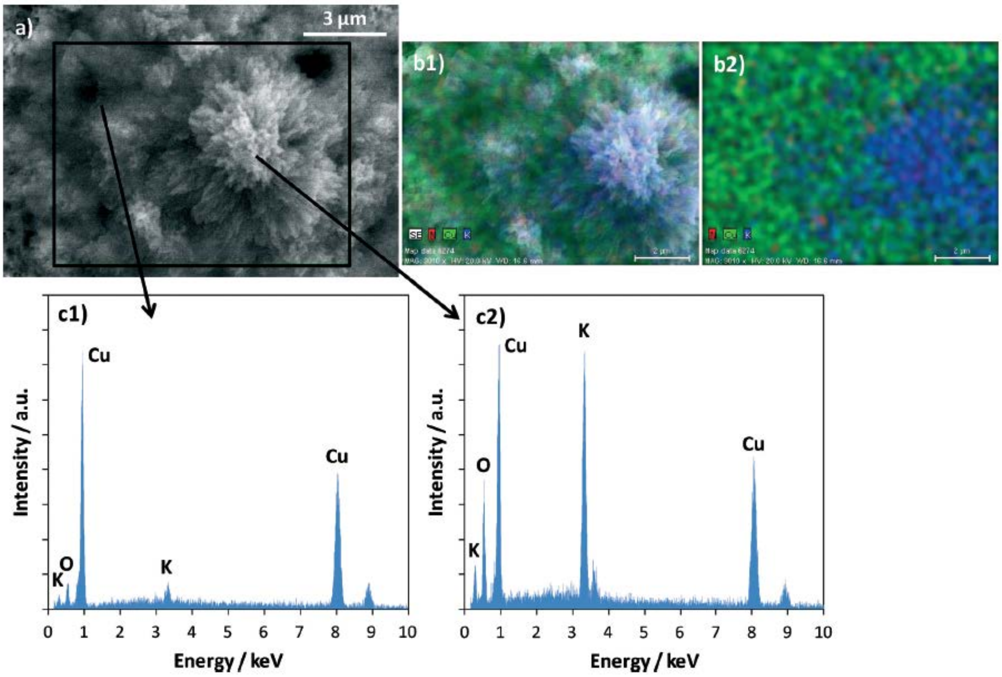

Figure 3. Top view SEM image of a selected area of a Cu/K-βAl$_2$O$_3$ electrochemical catalyst (**a**) after the EPOC experiments (593 °C, CH$_3$OH/O$_2$ = 4.4%/0.3%, $V_{WR} = -0.5$ V for 1 h), along with the corresponding elemental mapping (**b1** and **b2**) of Cu (green), K (blue), and N (red) and the EDX spectra from different regions (**c1** and **c2**). Reprinted with permission from Ref. [32].

The presence of potassium carbonate/bicarbonate species was also identified on the surface of a promoted Pt/K-βAl$_2$O$_3$ electrochemical catalyst employed in a methanol partial oxidation reaction [31]. In this study, these kinds of promoter-derived compounds were also detected *ex situ* by X-ray diffraction analysis after EPOC experiments, as shown in Figure 4. As in the case of the electropromoted Cu catalyst film, a poisoning effect derived from an excess of K$^+$-derived surface species was found on this Pt film [31]. Furthermore, in both mentioned studies [31,32], the obtained electropromotional effect was completely reversible since all the promoter phases were decomposed and the alkali ions were transferred from the catalyst back to the solid electrolyte after applying a positive enough potential at the end of the experiments. In this way, a clean, un-promoted catalyst surface, free of any promoter species, was achieved. These surface species were also observed by SEM-EDX analysis on Pt catalyst films deposited on K-βAl_2O_3 solid electrolyte for propene oxidation reaction [24]. In this case, the presence of potassium oxides and superoxides, along with carbon deposited fragments were observed after catalytic experiments. Moreover, these K^+-derived species seemed to induce a permanent EPOC effect and showed to be more stable than potassium carbonates or bicarbonates, since the latter needed lower positive potentials to be decomposed. These results demonstrated that the nature of the final form of alkali promoter species and their chemical structure (e.g., oxides, superoxides, carbonates, *etc.*) strongly influence the final electropromotional behavior.

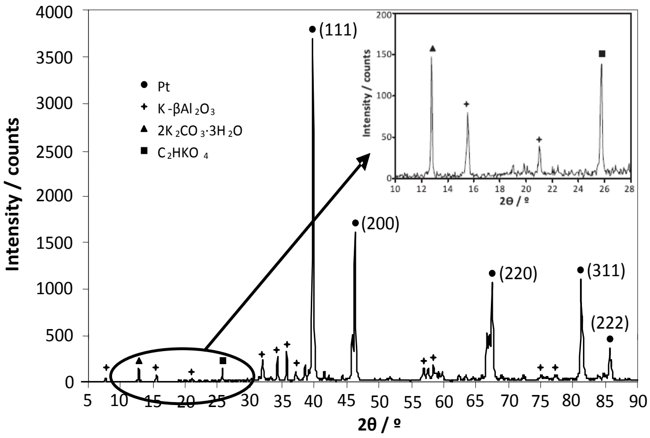

Figure 4. XRD spectra after EPOC experiments (CH_3OH/O_2 = 7.2%/4.6%, 593 K, overnight at −2 V) of a Pt film prepared by impregnation on a K-βAl_2O_3 solid electrolyte. Reprinted with permission from Ref. [31].

It should be noted that other characterization techniques such as X-ray photoelectron (XPS) [32] and Fourier transform infrared (FTIR) [24] spectroscopies have also been *ex situ* employed in the past to study the chemical state of the different alkali promoter species formed on the catalyst surface under EPOC conditions, obtaining similar information about the nature of the different promotional species.

3. *In Situ* Characterization of Alkali-Promoted Catalyst Surfaces

During the alkaline electrochemical promotion of a catalyst film, the influence of the applied potential on the promoter coverage, as well as the nature and stability of the alkali-derived surface species, can be *in situ* evaluated by different techniques. Indeed, the progress made in the development and understanding of the phenomenon of electrochemical promotion over the years could not be conceived without the *in situ* spectroscopy studies performed by the group of professor Lambert and co-workers [34–45]. In all cases, the spectra were obtained immediately after exposing the appropriately polarized catalyst film (either unpromoted or electrochemically promoted) to conditions of temperature and reactant partial pressures similar to those encountered in the electrochemical promotion reactor, in order to simulate the different surface conditions of interest. For this purpose, spectrometers equipped with a reaction cell (under galvanostatic/potentiostatic control) and an ultra high vacuum chamber were used, in such a way that the electropromoted sample was mounted on a manipulator that allowed its translation between both chambers.

X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) measurements have been carried out on Pt [34–38,40], Rh [39,41–43] and Cu [41,44,45] catalyst films used in alkaline electrochemical promotion studies for the oxidation of ethylene [34] or propene [37], hydrogenation of acetylene [38], and reduction of NO by CO [36,40–45] or by propene [35,39,42,43]. In first place, all these studies demonstrated that the mode of operation of the electrochemically promoted catalyst films involves reversible pumping (backspillover) of Na^+ or K^+ ions from the solid electrolyte in agreement with the theory and rules of Electrochemical Promotion of Catalysis. For instance, Figure 5a shows the Na 1s XPS spectra obtained on a Rh catalyst supported on Na-βAl_2O_3, at 580 K, as a function of catalyst potential (V_{WR}) under ultra-high vacuum conditions [41]. The +1 V spectrum corresponds to the clean (unpromoted) sample, while increasingly negative values of V_{WR} correspond to increasing amounts of electropumped Na^+ on the catalyst surface. As typically observed in these studies [35,38,40–42,44,46], the Na 1s emission comprises two components. The first one exhibits invariant binding energy (BE) and its intensity increases with decreasing V_{WR}, *i.e.*, as Na^+ ions are electropumped to the catalyst. This is ascribed to sodium at the surface of the (grounded) Rh catalyst film. The second (shaded) component exhibits constant intensity and a systematic shift in apparent BE. This shift is numerically equal to the change in catalyst potential, strongly suggesting that this emission arises from the underlying solid electrolyte, whose electrostatic potential differs from that of the Rh film by the change in V_{WR}. This interpretation was confirmed by the experimental results obtained by grazing exit synchrotron photoemission, where the signal from the electrolyte vanished [46]. As also stated in the other referenced studies, the spectral behaviour was reversible and reproducible as a function of V_{WR}, consistent with the reversible and reproducible catalytic response observed during the electrochemical promotion of the Rh catalyst for the NO reduction reaction with both CO and C_3H_6 [41]. Hence, as it can be drawn from Figure 5b, the decrease in the catalyst potential to -1 V leads to a linear increase in the Na^+ coverage (θ_{Na^+}), up to around 0.025 monolayers, which may be estimated from the integrated Na 1s intensity of the component associated with the metal surface [47]. Moreover, the catalyst work function (ϕ) also shows to vary linearly with V_{WR} in such a low θ_{Na^+} range. In this case, work function changes were determined by ultraviolet photoelectron spectroscopy (UPS), by measuring the change in secondary electron cutoff in the spectrum relative to the Fermi edge [41], although it can also be *in situ* measured with a Kelvin probe [48]. Very interestingly, XPS data also allowed verifying that electrochemically pumped sodium is identical in behavior and in chemical state with Na supplied by vacuum deposition from a Na evaporation source [35], which is in very good agreement with the close similarities found between electrochemically-promoted catalysts and conventionally-promoted ones [35,49].

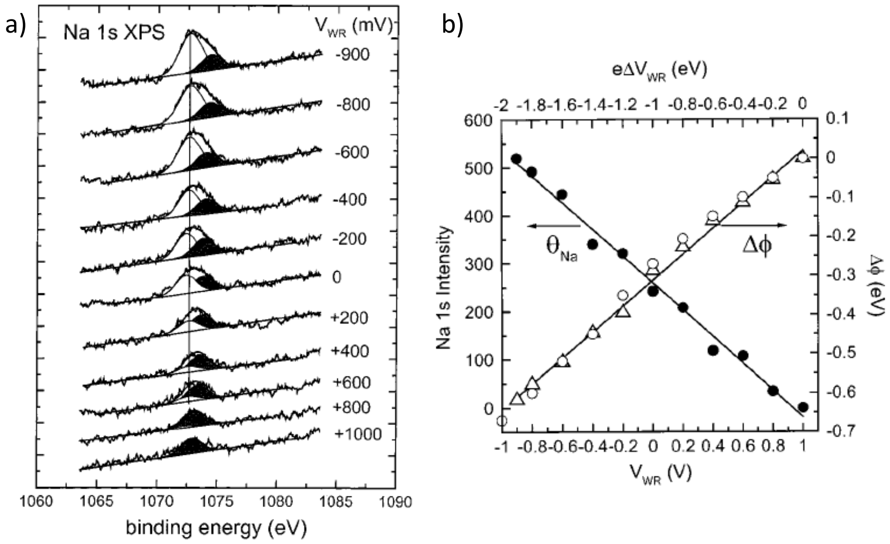

Figure 5. Na 1s XPS spectra taken on a Rh/Na-βAl_2O_3 electrochemical catalyst (580 K, UHV conditions), showing the effect of catalyst potential (V_{WR}) on sodium coverage (**a**). Invariant component due to Na on Rh; shifting component due to Na in solid electrolyte. Influence of V_{WR} on the integrated Na 1s XPS intensity due to Na on the Rh surface and associated work function change of the catalyst film (**b**). Reprinted with permission from Ref. [41]. Copyright 2000 American Chemical Society.

XPS is also a very useful technique for the in-situ identification of alkali-derived surface compounds and for the study of their formation/decomposition on the catalyst surface during the electrochemical promotion experiments. In this way, depending on the reaction atmosphere, $NaNO_2$ [40], $NaNO_3$ [40,43–45] and Na_2CO_3 [34,37,39,43] were found on the electropromoted catalyst surface which, in excess, induced a poisoning effect on the catalytic activity [34,37,40]. A very illustrative example is the work carried out by Filkin *et al.* on propene oxidation reaction with a Pt/Na-βAl_2O_3 catalyst, where not only XPS but also X-ray excited AES and X-ray absorption near edge structure (XANES) were performed [37]. Figure 6a,b show the Na KLL Auger and Na 1s XPS spectra obtained after exposure of the catalyst to the reaction mixture and to an applied potential (V_{WR}) such that the Pt film was either poisoned ($V_{WR} = -0.6$ V, spectrum 1), promoted ($V_{WR} = -0.1$ V, spectrum 2) or electrochemically clean ($V_{WR} = +0.5$ V, spectrum 3). The Na KLL auger data show that the catalyhst surface promoted at slightly negative potential presents a lower amount of Na-containing compounds than the poisoned surface (*i.e.*, at higher negative potential), and that these promoter phases are stable at reaction temperature (588 K) but decomposed by pumping the Na^+ ions back to the solid electrolyte. Moreover, as the authors stated, during the positive polarization, the pressure in the vacuum system increased, denoting that gaseous molecules released upon decomposition of the alkali-derived compounds. The Na 1s XPS spectra confirm the stability of the Na^+-derived compounds at reaction conditions and their decomposition under positive polarization. However, this kind of spectrometry technique does not allow distinguishing the Na loading obtained under promoted and poisoned conditions, in contrast to Auger electron spectroscopy (Figure 6a). This feature can be explained according to the different electron escape depths related to the AE and XPS spectra (with sampling depths of around 25 and 8 Å, respectively [37]). On the other hand, the carbon 1s XPS spectra (Figure 6c) not only confirm that the poisoned surface presents a much higher amount of Na^+-derived compounds formed under reaction conditions, but also provide some proof concerning the chemical nature of these species, which likely consist of sodium carbonates, as also verified by the XANES results (Figure 6d).

In two of the previously mentioned studies [38,46], scanning photoelectron microscopy (SPEM) was also used to *in situ* analyze the surface of Cu [46] and Pt [38] catalysts promoted by Na^+ and K^+, respectively. For instance, Figure 7 shows the results obtained on this latter work for the alkali-promoted acetylene hydrogenation reaction. Specifically, 6.4 µm × 6.4 µm Pt $4f_{7/2}$ (raw data), K $2p_{3/2}$ (raw data) and topography corrected [50] K $2p_{3/2}$ intensity maps were taken under different applied potentials (V_{WR}) from +0.4 V (unpromoted state) to −0.8 V (electropromoted state). These micrographs show that the Pt signal does not attenuate as K^+ ions are electrochemically supplied to the catalyst film and that a very small thermal drift takes place during the experiment. On the other hand, after correcting the intensity modulations derived from topography, the K $2p_{3/2}$ maps show that the alkali promoter is relatively uniformly distributed on the Pt surface, and that its concentration clearly increases upon decreasing V_{WR}.

Furthermore, it should be mentioned that the back-spillover phenomenon with alkaline ions has also been confirmed by scanning tunneling microscopy (STM) over Pt catalysts [51–53]. In these studies, unfiltered STM images were firstly obtained from an air-exposed Pt(111) catalyst film deposited on a Na-βAl_2O_3 solid electrolyte, under open circuit conditions, *i.e.*, before applying any electric current or potential. In this way, a Pt(111)-(2×2)-O adlattice (interatomic distance of 5.6 Å) was found along with an overlapping Pt(111)-(12×12)-Na adlattice (interatomic distance of 33.2 Å) in some regions, the latter being attributed to thermal diffusion of sodium from the Na-βAl_2O_3 during the deposition of the Pt(111) film [51–53]. Then, STM was carried out under both unpromoted and electropromoted established conditions. In the first case, after the application of a positive current or potential, only the Pt(111)-(2×2)-O adlattice remained on the micrograph, thus denoting a Na-free catalyst surface. This demonstrates that an unpromoted (reference) state can be defined by applying a positive enough potential on the catalyst film supported on an alkaline solid electrolyte. In the second case, after applying a negative current (of the order of −1 µA) for a few minutes, the Pt(111)-(12×12)-Na adlattice reappeared [51–53]. Then, all these studies show that the origin of alkali-EPOC is clearly due to the reversible migration (back-spillover) of alkali ions to the catalyst surface. These ions may interact with co-adsorbed reactant molecules depending on the reaction conditions forming a wide variety of surface compounds and altering the chemisorption properties of the catalyst in a pronounce and controllable way.

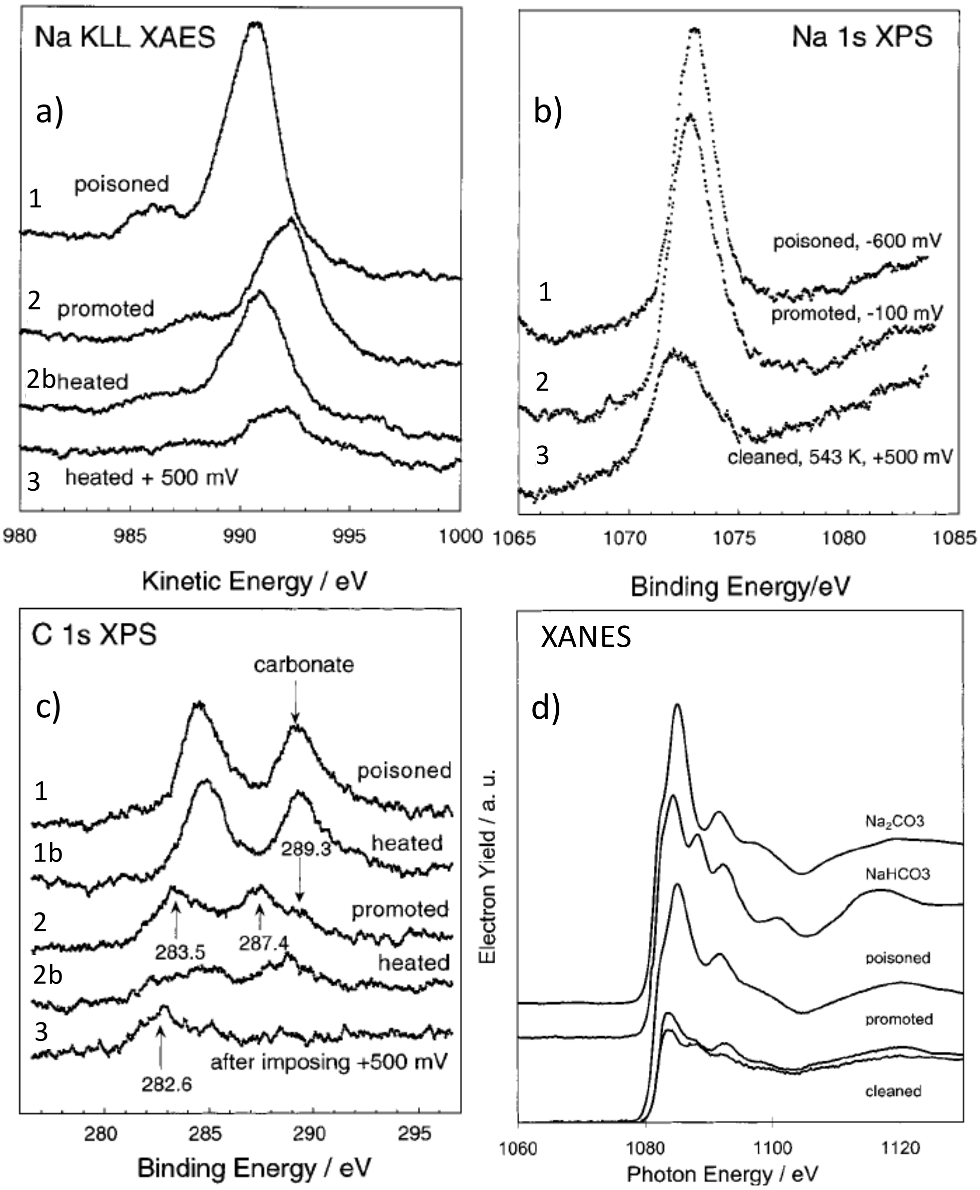

Figure 6. (**a**) Sodium KLL XAES, (**b**) Sodium 1s XPS and (**c**) Carbon 1s XPS analysis of a Pt/Na-βAl_2O_3 electrochemical catalyst under propene combustion atmosphere (0.6 kPa propene, 2.5 kPa oxygen). All spectra acquired at room temperature, open circuit, after exposure to different un-promoted and electropromoted conditions: *1*, poisoned conditions, $V_{WR} = -600$ mV; *1b*, as *1* but after heating to 588 K; 2, promoted conditions, $V_{WR} = -100$ mV; *2b*, as 2 but after heating to 588 K; *3*, as 2 but after imposing $V_{WR} = +500$ mV. (d) XANES spectra after exposure to propene and oxygen at 500 K under promoted and poisoned conditions (See Ref. [37] for temperature and partial pressures conditions). Reference XANES spectra for the cleaned surface, Na_2CO_3 and $NaHCO_3$ are also shown. Reprinted with permission from Ref. [37].

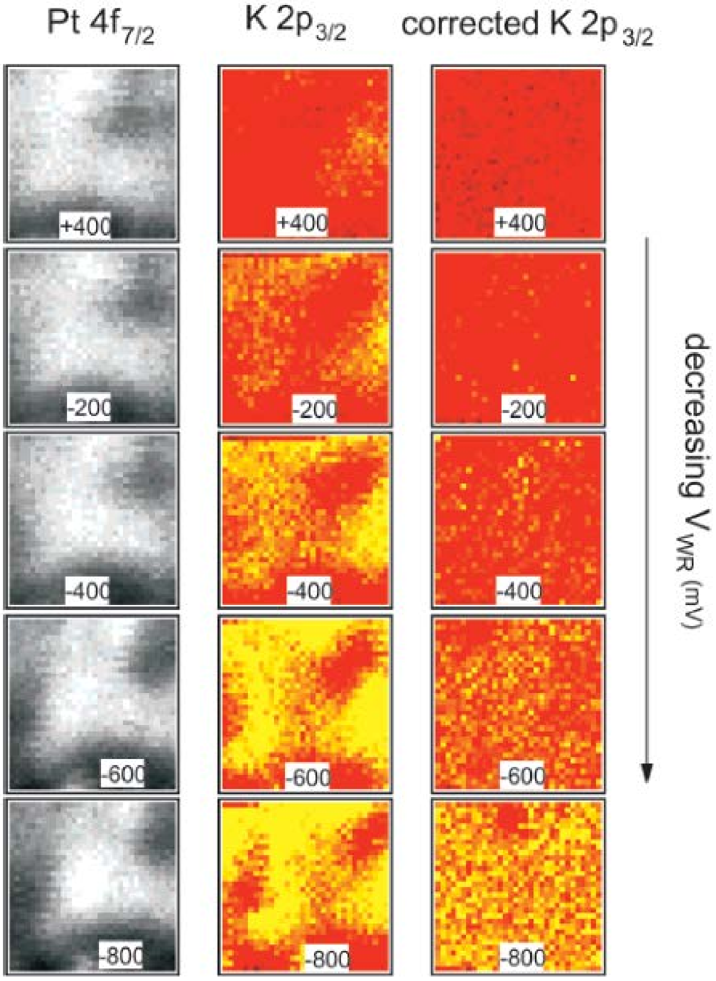

Figure 7. Pt 4f7/2 and K 2p3/2 photoelectron intensity maps taken on a Pt/K-βAl_2O_3 catalyst as a function of V_{WR} at 473 K during the selective hydrogenation of acetylene. Reprinted with permission from Ref. [38].

Finally, it should be noted that there is a kind of *in situ* characterization methodology called operando which is acquiring increasing interest in the catalysis scientific community and could be also very helpful in the study of the alkaline electrochemical promotion. This methodology is based on the *in situ* characterization of the catalyst surface while the catalytic activity is simultaneously measured, under real working conditions. However, the perfect correlation between the catalytic activity measurement and the surface analysis is very difficult mainly due to problems arising from the operando cell reactor design. This reactor cell must operate under specific pressure and temperature conditions while keeping the three-electrode configuration and allowing the spectra collection under such reaction conditions. Moreover, the presence of spectator species in the reaction and void volumes in the reactor, which are typically high for gas phase reactions, may affect the obtained spectra. Thus, new insights in the *in situ* characterization of the EPOC phenomenon could be opened in so far as the operando reactor design is improved and such limitations are overcome.

4. Conclusions and Prospects

It is well known that alkali promoters play a key role in heterogeneous catalysis with special emphasis on catalytic reactions of large scale industrial application such as ammonia or hydrocarbons synthesis. As classical alkali promotion, the phenomenon of electrochemical promotion of catalysis (EPOC) is based on the addition of promoting species to the catalyst active surface in order to modify its chemisorptive properties and, hence, its activity and selectivity. However, in the case of EPOC, the electrically induced back-spillover of the promoter species enables the straightforward study of the promoting role of certain alkali coverage and the *in situ*, controlled, enhancement of the catalytic performance under dynamic reaction conditions. For this reason, it becomes essential the employment of proper surface analysis techniques which allow monitoring the amount and state of the promoter phases as well as a deep understanding of the back-spillover phenomenon. In this sense, several *ex situ* and *in situ* characterization techniques have been carried out for the last two decades that have been described on this paper.

Although the *ex situ* surface analysis techniques involve a series of inaccuracies derived from the necessary handling and transfer of the electrochemical catalyst to the characterization equipment, they may constitute a useful and easy tool to determine the stability of the electrochemical catalyst and to obtain qualitative information about the different species adsorbed on the catalyst surface. On the other hand, the *in situ* characterization techniques provide detailed information about the mechanism of alkali ions backspillover, the nature of the promoter-derived surface compounds and their influence on the catalytic properties, as a function of both the catalyst potential variation and the reaction conditions. Hence, the implementation of surface analysis techniques herein mentioned and other possible such as fourier transform infrared (FTIR) spectroscopy, photoelectron emission microscopy (PEEM), or atomic force microscopy (AFM), in conjunction with the development of alkaline electrochemical promotion experiments, is of paramount importance not only for better understanding of this phenomenon, but also for the design of more efficient and competitive conventional heterogeneous catalysts.

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Author Contributions: Jesús Gonzalez Cobos was the primary author of this review, selecting and discussing the most important results published on the field. Antonio de Lucas Consuegra provided assistance in writing, revising the case studies and updating the article in response to the reviewers.

Conflicts of Interest: The authors declare no conflict of interest.

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