

Electrochemical activation of Ru catalyst with alkaline ion conductors for the catalytic decomposition of ammonia

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ABSTRACT

This study reports the electrochemical activation (EPOC) of ruthenium catalyst film with alkaline ion conductors for hydrogen production via catalytic decomposition of ammonia. Two electrocatalysts, Ru/Na- β -Al₂O₃ and Ru/K- β -Al₂O₃ have been prepared, characterized, and tested under low temperature reaction conditions (250–350 °C). The electrochemically supply of moderate amounts of alkaline ions (Na⁺ and K⁺) from the solid electrolyte support to the ruthenium catalyst film, activated the hydrogen production rate. The promotional effect has been attributed to a strengthening of the chemisorptive bond of weakly adsorbed N surface species, which stabilizes N adsorbed molecules on the ruthenium catalyst surface and thus facilitating the ammonia decomposition reaction. Among the two alkali ions, the effect of potassium was stronger, increasing the hydrogen production rate above 230% at 300 °C under optimally conditions. Temperature programmed reaction experiments also confirms the interest of EPOC for the activation of the catalyst at low temperatures.

1. Introduction

An imminent decarbonization of the energy sector is needed in order to reduce the environmental damage caused by fossil fuel. As a result, clean, sustainable and renewable energy sources appear to be potential alternatives. In fact, the development of hydrogen-based technologies can help to reduce or eliminate greenhouse gas emission. In this sense, hydrogen (H₂) possesses the highest specific energy content among all conventional fuels and, it can be used as a green energy carrier using fuel cells and internal combustion engines by releasing only nontoxic by-products such as water [1]. However, the main drawback related to this compound is its low volumetric energy density which increases storage and transport costs [2]. An alternative to remove these issues is the use of hydrogen carrier compounds.

In this respect, liquid fuels generated from hydrogen (ammonia, methanol, metal amine salts, etc.) might be easily stored and transported to be in situ decomposed to produce clean hydrogen through suitable conversion processes [3,4]. Ammonia (NH₃) is a promising hydrogen carrier because of its high volumetric energy density and high hydrogen content, well-known technology for production and distribution and relatively low cost [5]. Moreover, its decomposition only produces hydrogen and nitrogen. Therefore, ammonia is an exceptional

carbon-free hydrogen vector. However, fuel cells which are very sensitive to ammonia concentration (<1 ppm), demand high purity hydrogen [6]. Thus, almost complete ammonia conversion is required at relatively low temperature (<500 °C). For that purpose, hydrogen production from ammonia decomposition requires efficient and low-cost catalysts to reduce the reaction temperature and the energy cost of the process.

Promising results of ammonia decomposition at low temperatures are achieved with ruthenium (Ru) catalysts [6–8]. Nevertheless, catalytic activity is very affected by other factors such as the size of metal particles since it is a structure-sensitive reaction [7,8]. Consequently, hydrogen production from ammonia has been widely studied using different types of active phases (Ni, Co, Rh, Pd, Pt, etc.) and supports such as Al₂O₃, SiC, ZrO₂, CeO₂, La₂O₃, MgO and carbonaceous materials [6–13]. Moreover, different types of promoters have been investigated to enhance the catalytic activity by adding alkaline species to the active phase [11–14]. In fact, these promoters increase the electron-donation to the active metals and stabilize the binding energy between metal and N atoms, favouring ammonia decomposition reaction.

In recent years, a novel route for adding promoters to heterogeneous catalyst has been developed through the phenomenon of Electrochemical Promotion of Catalysis (EPOC). This phenomenon discovered by Stoukides and Vayenas in 1981 [15] is a promising alternative way to

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explore the in-situ addition of electronic promoters to a heterogeneous catalyst and hence, to enhance catalytic reaction rates [16–18]. This phenomenon is based on the electrochemical supply of promoter ions from a solid electrolyte material (support) to a metal catalyst (working electrode) by the application of electrical currents or potentials. This electrochemical activation of the catalyst by using a solid electrolyte support allows the in-situ electrochemical addition or removal of a wide variety of promoters, anionic (O^{2-}) or cationic (Na^+ , K^+ , H^+) to different kinds of catalysts in a wide range of catalytic reactions [16,17,19–22].

The EPOC phenomenon has been widely investigated for different kinds of hydrogen production reactions, e.g., catalytic reforming of methane [20], water gas shift reaction [23–25] and reforming or partial oxidation of alcohols such as methanol and ethanol [16,26,27]. However, one can find in literature a unique previous study of EPOC in the catalytic decomposition of ammonia [17]. In this previous study an iron catalyst film deposited on both $K_2YZr(PO_4)_3$ (K^+ ionic conductor) and, $CaZr_{0.9}In_{0.1}O_{3-\alpha}$ (H^+ ionic conductor material), were electrochemically activated. Although very promising results were obtained, a high temperature range (500–600 °C) was explored probably due to the requirements for ionic conductivity of the solid electrolyte used.

In this work it has been explored for the first time in the literature, the effect of the electrochemical promotion for low temperature catalytic decomposition of ammonia (250–350 °C). For that purpose, a ruthenium catalyst and an alkaline solid electrolyte ($Na-\beta Al_2O_3$ and $K-\beta Al_2O_3$) have been used on the catalytic reaction. Very promising results have been obtained in a lower temperature range (250–350 °C) which have been discussed in terms of the EPOC rules and the mechanism of ammonia decomposition reaction. Hence, relevant findings are reported of great interest for the general catalysis field which could serve for the design of future novel catalyst formulations.

2. Experimental

2.1. Electrochemical catalysts preparation

$Na-\beta Al_2O_3$ and $K-\beta Al_2O_3$ (20 mm diameter and 1 mm thickness from Ionotec company) solid electrolyte discs were used as supports. First, thin coatings of gold paste (Gwent Electronic Materials) were deposited on the one side of the solid electrolyte disk as Au counter (CE) and reference (RE) electrodes, followed by calcination steps at 300 °C for 1 h ($5\text{ °C}\cdot\text{min}^{-1}$) and 800 °C for 2 h ($5\text{ °C}\cdot\text{min}^{-1}$). Blank experiments demonstrated the catalytically inactive properties of the prepared gold counter and reference electrodes for ammonia catalytic decomposition reaction. Then, an electrically continuous ruthenium catalyst film-working electrode (WE) (geometric area of 2.01 cm^2) was deposited on the other side of the disk as schematically shown in Figure S1 of the supporting information. An impregnation method described in detail elsewhere was used [28] by using a $RuCl_3$ solution. The precursor salt, $RuCl_3\cdot 3H_2O$ (Sigma Aldrich) was dissolved in 1:1 (volume) water: 2-propanol (Sigma Aldrich, 99.9% purity) solution, followed by a calcination step at 500 °C for 1 h ($5\text{ °C}\cdot\text{min}^{-1}$). Both obtained electrochemical catalysts ($Ru/Na-\beta Al_2O_3$ and $Ru/K-\beta Al_2O_3$) showed a similar final metal loading of $1.3\text{ mg}_{Ru}\cdot\text{cm}^{-2}$. Before the catalytic activity measurements, the metal catalyst film was reduced under 5 v/v% H_2/He gas mixture ($100\text{ mL}\cdot\text{min}^{-1}$) at 400 °C for 1 h ($10\text{ °C}\cdot\text{min}^{-1}$), in order to ensure the complete reduction of the active ruthenium particles, achieving a metal catalyst film with an in plane electrical resistance around 30 Ω .

2.2. Ex-situ characterization of the electrochemical catalysts

For the ex-situ characterization of the ruthenium catalyst film, X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) techniques were used. XRD diffractograms were obtained on a Philips X'Pert MPD with co-filtered Cu-K α radiation ($\lambda=1.54056\text{ \AA}$), after reduction under 5 v/v% H_2/Ar and for used catalyst. The XRD pattern were recorded from

$20 < 2\theta < 80^\circ$ with a scan rate of 0.02° step size and acquisition time of 4 s per step. The crystal size was determined by the Debye-Scherrer Eq. (1):

$$d = \frac{K\lambda}{\beta\cos\theta} \quad (1)$$

where d is the average particles size (nm), assuming particles are spherical, $K = 0.9$, $\lambda = 1.54056\text{ \AA}$, β is the full width at half the diffracted peak and θ is the Bragg angle.

SEM images of the ruthenium films were performed by ZEISS GeminiSEM 500 FE-SEM with a PIN-diode BSE detector. This instrument was equipped with an energy-dispersive X-ray spectroscopy (EDX) analyzer to verify the composition of the samples.

2.3. Electrocatalytic tests

Catalytic tests were carried out in a single chamber solid electrolyte cell reactor configuration (Figure S2 of the supporting information). The electrochemical catalyst was suspended in the reactor by using gold wires (Alfa Aesar, 99.95% purity) which also allow the electrical connections of the three electrodes (Counter (CE), Reference (RE) and Working electrode (WE)) with the potentiostat-galvanostat (Voltalab PGZ 301, Radiometer Analytical). The EPOC phenomenon was investigated by applying different electrical potentials between the WE and CE and measured between the WE and RE electrodes (V_{WR}), according to the technique generally used in conventional three-electrode electrochemical cells [29]. Reaction gasses (Air Liquide) were certified standards of helium (99.999% purity) and ammonia (5011.50 ppm) and the gas flows were controlled by a set of calibrated mass flow meters (Brooks 5850 E).

The ammonia decomposition reaction was carried out at atmospheric pressure operating at a temperature range from 220 to 350 °C, using an inlet composition of 1250 ppm ammonia with an overall gas flow rate of $200\text{ mL}\cdot\text{min}^{-1}$ (He balance). Gas effluents were analysed online with a dispersive IR Rosemount X-STREAM Enhanced XEGP continuous gas analyzer (EMERSON) for ammonia detection. The hydrogen formation rate ($\text{mmol } H_2\cdot\text{min}^{-1}\cdot g_{cat}^{-1}$) was calculated from balance of the ammonia content in the outgas stream, while conversion of ammonia (X_{NH_3}) was calculated as follows:

$$X_{NH_3} (\%) = \frac{F_{NH_3in} - F_{NH_3out}}{F_{NH_3in}} \cdot 100 \quad (2)$$

Where, F_{NH_3in} and F_{NH_3out} referred to the inlet and outlet ammonia molar flows ($\text{mmol gas}\cdot\text{min}^{-1}$), respectively. Furthermore, the apparent activation energy of the synthesized catalysts was calculated from the Arrhenius plot at low conversion values (<10%) in order to operate into differential conditions.

The electrochemical catalyst was also in-situ characterized in the single chamber cell reactor by cyclic voltammetry experiments. A cyclic voltammetry experiment with simultaneous ammonia recording was performed under ammonia catalytic decomposition reaction (1250 ppm ammonia and a gas flow of $200\text{ mL}\cdot\text{min}^{-1}$) at 280 °C and a scan rate of $5\text{ mV}\cdot\text{s}^{-1}$.

3. Results and discussion

3.1. Electrochemical catalyst characterization

Firstly, the catalytic activity of the ruthenium catalyst film was tested from 200 to 450 °C in the ammonia decomposition reaction under open circuit conditions (O.C.) for $Ru/Na-\beta Al_2O_3$ electrocatalyst (Figure S3 of the supporting information). This initial experiment demonstrated that the prepared metal catalyst film was active for the ammonia catalytic decomposition reaction under the explored reaction conditions. It shows a typical trend of ammonia conversion increasing with the reaction temperature due to the increase in the reaction kinetics [3]. However, it

can be observed that full conversion of ammonia was never reached (maximum conversion of 74% at 450 °C) due to certain bypass of the gas reactants flow to the ruthenium catalyst film. This behavior is typically observed with those kinds of solid electrolyte cells reactors and have been reported in previous studies [30].

The crystalline structure of the ruthenium catalyst film in the Ru/Na- β Al₂O₃ electrocatalyst after hydrogen reduction and after ammonia decomposition reaction was examined by XRD (Fig. 1). The reduced electrocatalyst showed the main diffraction peaks corresponding to hexagonal phase of Na- β Al₂O₃ (JCPDS: 19-1173) associated with the electrolyte support [31] and the hexagonal phase of metallic ruthenium (JCPDS: 06-0663) [7]. After catalytic activity measurements, the post-reaction ruthenium catalyst film showed the same crystalline phases than the reduced sample (metallic ruthenium and Na- β Al₂O₃) not showing crystalline phases derived from the EPOC experiments. Using the Scherrer equation at peak $2\theta=44^\circ$, the average particles size of ruthenium for both electrocatalyst, reduced and post reaction, was 15.7 and 21.4 nm, respectively. These results demonstrated certain sintering of the metal particles in the catalyst film during the catalytic activity measurements. This kind of sintering of metal particles are typical for conductive catalyst films and have been reported in previous studies of EPOC [28].

Fig. 2 shows SEM micrographs and EDX analysis of the metal film on reduced catalyst (a, b and c) and after ammonia decomposition reaction (d, e and f). Typically, the ruthenium film after reduction treatment was porous and continuous, which suggested that the preparation technique was adequate to synthesize ruthenium films for EPOC experiments [32]. It was observed from the EDX of the reduced sample (Fig. 2b), large concentrations of sodium (in blue) which were attributed to the thermal migration of alkaline ions from the solid electrolyte to the ruthenium catalyst film during the catalyst preparation procedure and reduction step [16,21]. From the SEM analysis of the post reaction sample, in agreement with the XRD, a sintering of the metal particles in the catalyst film could be observed. Furthermore, some cracks in the ruthenium catalyst film after catalysis were observed at microscopy level. However, these cracks did not affect the electrical conductivity of the ruthenium catalyst film as verified along the surface with a multimeter. In any case,

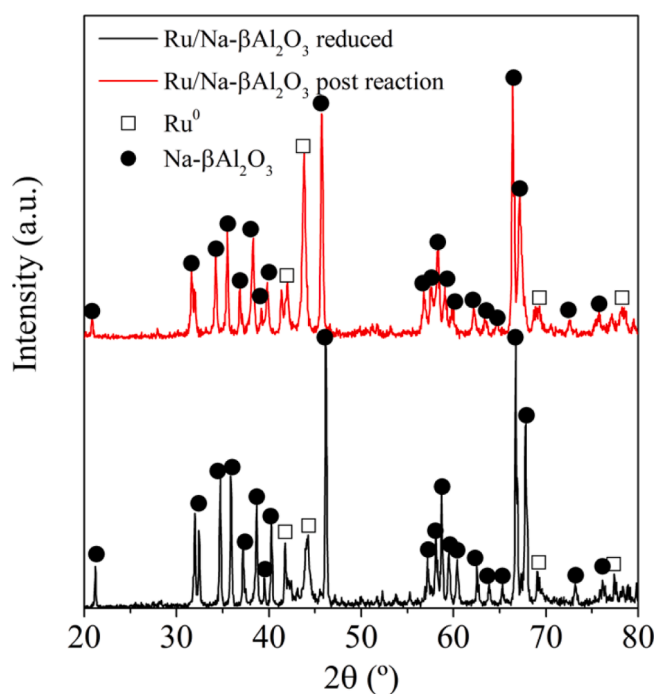


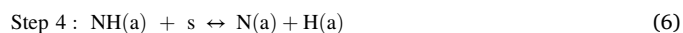
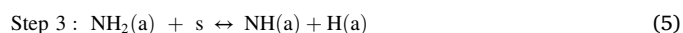
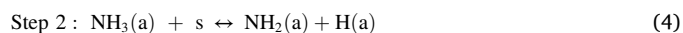
Fig. 1. XRD pattern for Ru/Na- β Al₂O₃ electrochemical catalysts reduced at 400 °C before and after ammonia decomposition reaction.

this sintering process of the metal particles shown in the sample after catalytic reaction probably occurred at the beginning of the experimental tests (initial experiment under open circuit conditions shown in Figure S3), since reproducible and stable catalytic activity values were obtained during EPOC experiments (as will be shown below).

3.2. Electrochemical activation of Ru catalyst with Na⁺ ions

Fig. 3 shows the variation of the hydrogen production rate vs. time at different applied potentials between 2 and -2 V at 300 °C. Each polarization was applied for 30 min in order to achieve a steady state catalytic behavior.

In agreement with previous EPOC studies and considering that the initial polarization at $V_{WR} = 2$ V allowed to obtain a metal catalyst film free of any sodium ions (reference state, i.e., un-promoted catalytic activity), the subsequent decrease in the applied potential led to the electrochemical supply of sodium ions to the catalyst surface. It was confirmed by the obtained measured negative electrical currents (not shown here) of higher magnitude as the applied potential decreased to more negative values, corresponding to a higher electrochemical supply of electropositive alkali sodium ions. This direct correlation has been recently confirmed by an Operando Near Ambient Pressure Photoemission Spectroscopy performed on Ni/K- β Al₂O₃ in a previous work of the research team [33]. Concerning the variation of the catalytic activity with the different applied polarizations, according to previous studies [22,24,25,34-37], one may rationalize the observed variation in the catalytic activity on the basis of the catalyst-electrode work function modification upon applied potential. A decrease in the catalyst potential below the open circuit conditions, and therefore, in the catalyst work function, led to an increase of the electronic density of ruthenium catalyst with a concomitant spillover of Na⁺ ions from the electrolyte onto the metal catalyst surface. This decreased work function, weakened the ruthenium chemical bond with electron-donor adsorbates and strengthened those with electron acceptors ones. In this work, the strong promotional effect, observed when lowering the catalyst potential below the open circuit conditions (50 mV), can be explained on the basis of a strengthening of the chemisorptive bond of weakly adsorbed N surface species, which stabilizes N on the catalyst surface. It facilitates the ammonia decomposition reaction, in good agreement with a previous EPOC study in the catalytic ammonia decomposition reaction on iron deposited on K₂YZr(PO₄)₃, a K⁺ conductor solid electrolyte [17]. This experimental observation is also in good agreement with the mechanism proposed in the literature for the catalytic ammonia decomposition reaction, which follows these six consecutive steps [38]:



where s represents a vacant site of the catalyst surface, (g) stands for gas and (a) stands for adsorbed molecules. Hence, a previous detailed kinetics analysis [8] has demonstrated that for the case of a ruthenium based catalyst under similar reaction conditions than our work, step 2 is the main rate determining step in the overall reaction mechanism. Then, the stabilization of NH₂(a) adsorbed species on the catalyst surface when the potential is decreased, might increase the kinetics of the dehydrogenation reactions (steps 2-4), leading to an overall activation of the process. On the other hand, the increase in the value of the applied potential above that of the open circuit conditions (50 mV), enhanced

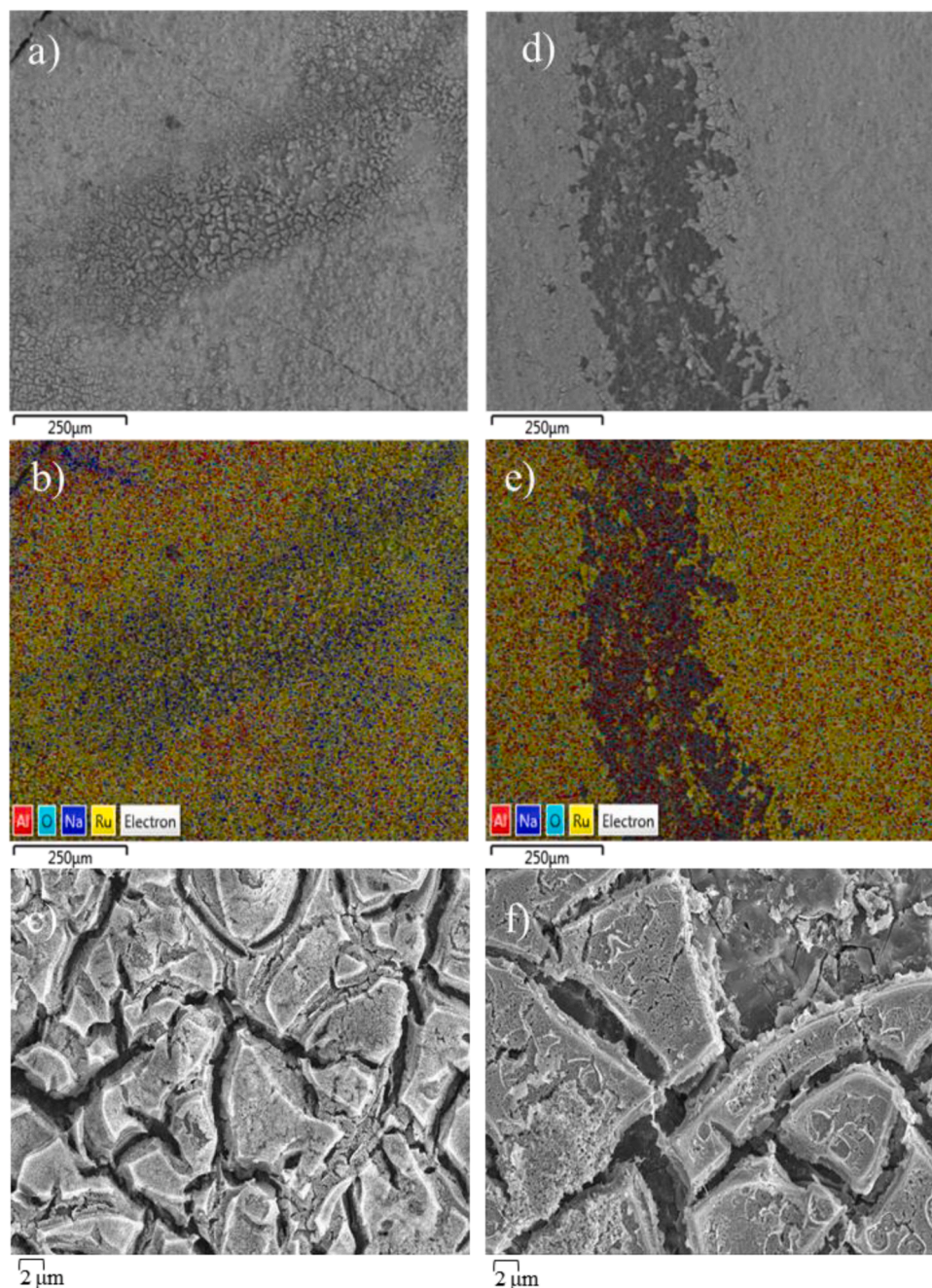


Fig. 2. SEM-EDX for Ru/Na-bAl₂O₃ electrochemical catalyst reduced at 400 °C before (a, b and c) and, after ammonia decomposition reaction (d, e and f).

the binding strength of the electron donor ammonia molecules (facilitating the ammonia adsorption, step 1 of the mechanism) [17]. It led to a slight increase in the catalytic activity, as can be observed under application of 2 V in Fig. 3, but much less important considering that a higher effect is produced when the electronic effect increases the kinetics of the rate determining step. Finally, it can also be observed that the final application of a potential of 2 V allowed to recover the initial un-promoted catalytic activity achieved at the beginning of the experiment, leading to a reversible EPOC phenomenon [16,25]. It implied that the same amount of sodium ions, initially transferred from the solid electrolyte to the catalyst during the previous polarizations, were returned from the catalyst to the solid electrolyte after the final application of 2 V. It also demonstrated the stability of the catalyst film under EPOC reaction conditions. Therefore, the sintering of the metal particles observed in Figs. 1 and 2 might occurred during the preliminary reaction

experiment under O.C. (Figure S3), stabilizing the ruthenium catalyst film for the subsequent EPOC experiments.

In order to study the influence of the reaction temperature, the same experiment performed at 300 °C was repeated at other reaction temperatures, i.e. 250 °C, 320 °C and, 350 °C. The steady state variation of the ammonia conversion vs. the applied polarization at the different reaction temperatures is shown in Fig. 4. Also, to quantify the magnitude of the EPOC phenomenon, Fig. 4 shows the maximum value calculated of the rate enhancement ratio (ρ), obtained by the following equation and typically used in EPOC studies [24,39]:

$$\rho = \frac{r}{r_0} \quad (9)$$

where r_0 is the un-promoted catalytic reaction rate ($V_{WR}=2$ V) and r is the promoted catalytic reaction rate at the explored potential.

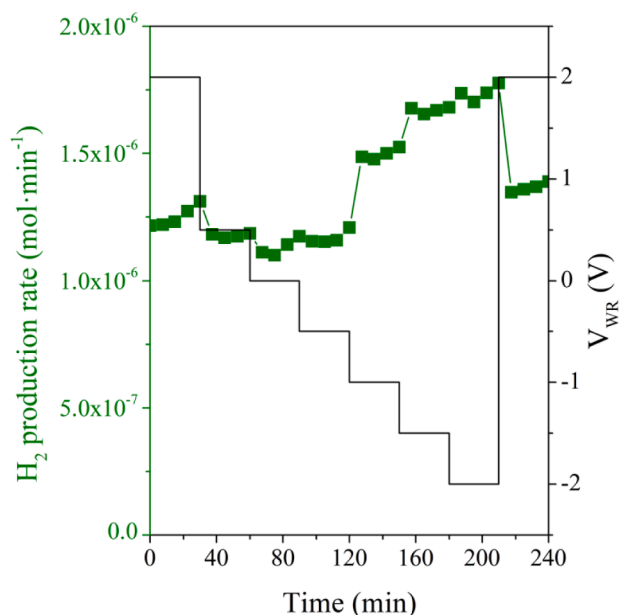


Fig. 3. Dynamic response of hydrogen production rate vs. applied potential at 300 °C for Ru/Na- β Al₂O₃.

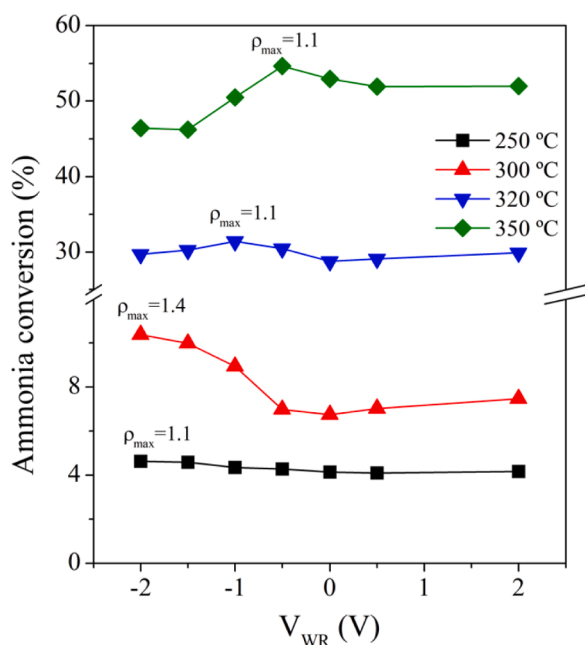


Fig. 4. Steady state of ammonia conversion vs. the applied potential for Ru/Na- β Al₂O₃ at different reaction temperatures.

Firstly, it could be observed a similar overall EPOC behavior, at the explored reaction temperatures, to the one already described in Fig. 3, with an increase in the catalytic reaction rate as the applied potential decreases from the open circuit potential values (typically around 50 mV). As typically found in previous EPOC studies with alkaline ion conductors [40], the highest value of the rate enhancement ratio was achieved at an intermediate reaction temperature, i.e. 300 °C, increasing the ammonia conversion 1.4 times vs. the un-promoted conditions (2 V). Hence, at low temperatures (i.e. 250 °C) the EPOC phenomenon is limited by the low ionic conductivity of the solid electrolyte which decreases the amount of electrochemically supplied ions. However, above certain reaction temperatures (e.g. 320 °C), the relative increase induced by the EPOC phenomenon, measured by ρ , is limited by the

initial higher value of the un-promoted catalytic activity (i.e. 30% at 320 °C). On the other hand, it is also interesting to note that, a poisoning effect can be observed at higher temperatures (above 320 °C), which led to an optimal value of the applied potential which maximized the catalytic activity at $V_{WR} = -1$ V at 320 °C and $V_{WR} = -0,5$ V at 350 °C. This behavior typically found in previous studies of alkaline EPOC can be attributed to an excess of promoting species on the catalyst surface which block the catalytic active sites [41]. In the present study, as already mentioned, the application of negative potentials decreased the relative coverage of electron donor molecules (ammonia) (step 1), causing a poisoning effect observed above certain temperatures and below certain applied potentials. Hence, above certain temperatures and above certain alkali coverage on the catalyst, the mechanism could be limited by the ammonia adsorption step, which may also justify the higher inhibiting effect observed at 350 °C vs. 320 °C at high negative potential (close to -2 V). On the other hand, it could be observed that higher optimal applied potential values (which maximized the catalytic activity) were obtained at higher reaction temperatures. It can be attributed to an increase in the solid electrolyte ionic conductivity with temperature leading to a higher supply of sodium ions for the same potential. Obtained results clearly demonstrated the interest of the EPOC phenomenon to electrochemically supply the optimal promoter amount at different reaction conditions (e.g. temperature), which is not possible with conventional heterogeneous catalyst doped with alkali, where a fix amount of promoter is added to the catalyst during the preparation step. This is one of the most interesting findings of EPOC which has been analysed in detail in a previous reviewed manuscript [42].

3.3. Electrochemical activation of Ru catalyst with K⁺ ions

In order to evaluate the electro-promotional effect of other type of alkali ions, the EPOC phenomenon was investigated on a Ru/K- β Al₂O₃ electrochemical catalyst. Fig. 5 shows the variation of the hydrogen production rate vs. time at different applied potentials (between $V_{WR} = 2$ V and -2 V) and reaction temperatures (300 and 320 °C). Each polarization was again applied for 30 min until a steady state catalytic behavior is achieved.

In good agreement with the results obtained with Ru/Na- β Al₂O₃, a

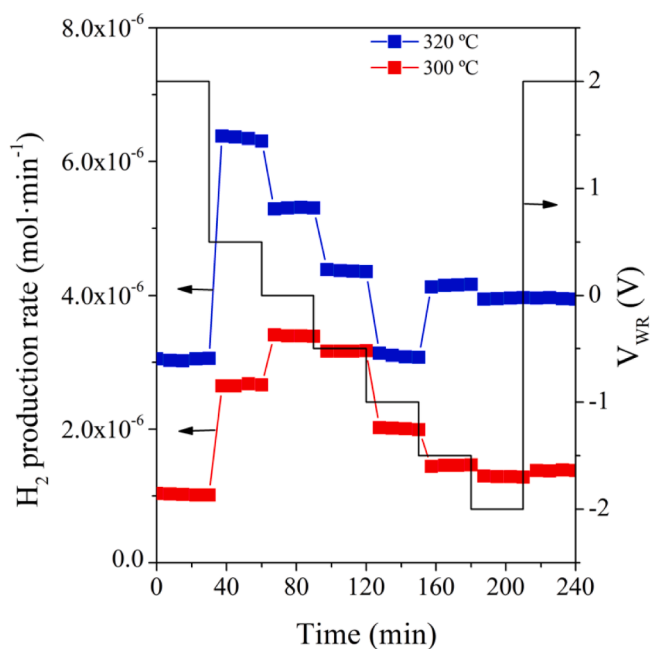


Fig. 5. Dynamic response of hydrogen production rate vs. applied potential at 300 °C and 320 °C for Ru/K- β Al₂O₃.

strong activation effect in the catalytic activity was observed under conditions of electrochemically supply of alkali ions (K^+). The observed promotional effect can be explained considering the influence of the alkali ions on the binding strength of chemisorbed reactants and intermediate molecules, as previously discussed for Ru/Na- β - Al_2O_3 . The electrochemical supply of potassium ions enhanced the chemisorption of electron acceptor molecules (weakly adsorbed N surface species) facilitating ammonia decomposition reactions, increasing the rate of the three consecutive steps 2, 3 and 4, on the previously mentioned reaction mechanism. In this case, it can be observed that an optimum applied potential of $V_{WR}=0$ V and $V_{WR}=0.5$ V was obtained at 300 °C and 320 °C, respectively. These optimal V_{WR} values were higher than the ones obtained for Ru/Na- β - Al_2O_3 , which can be justified considering the higher electronic effect on the catalyst of K^+ vs. Na^+ ions, attributed to the different ionic size of both cations ($Na^+=0.10$ nm and $K^+=0.13$ nm). In addition, some authors suggested that the higher dipole moment of potassium ion (~ 14 Debye) could increase the promotional effect of K^+ vs. Na^+ (whose dipole moment was ~ 6 Debye) and H^+ ions into the CO_2 hydrogenation reaction on Ru catalysts [43]. Hence, Lang et al. [44] clearly showed that the larger the alkali cation was, the greater the electric field suffered by co-adsorbed species located at an adjacent site. These higher promotional effect of K^+ vs. Na^+ ions have been observed in different chemical reactions through Electrochemical Promotion [35, 45, 46]. On the other hand, in a previous study of a conventional heterogeneous Ru catalyst doping with K^+ and Na^+ led to an increase in the ammonia conversion with respect un-doped catalyst at lower temperature, being the Ru-K the highest ammonia conversion due to the lower electronegative of potassium [47].

Thus, K^+ should perturb the Ru- NH_3 bond more strongly than Na^+ , leading to a higher activation effect. In fact, considering the lower ionic conductivity of K- β - Al_2O_3 (5.5 (ohm.m) $^{-1}$) vs. Na- β - Al_2O_3 (23.8 (ohm.m) $^{-1}$) at 300 °C provided by the supplier (Ionotec), lower values of potassium vs. sodium ions coverages on the metal catalyst surface would be attained for the same explored potential range (at the same temperature). Then, the higher effect on the reactants and intermediates chemisorption induced by K^+ vs. Na^+ can also explain the lower optimal potential values obtained, which maximized the hydrogen production rate. As already mentioned, the presence of an optimal V_{WR} value, and hence, an optimal alkali coverage on the catalyst, is probably due to an excessive decrease on the adsorption of electron acceptor ammonia molecules induced by potassium, which limits step 1 in the overall reaction mechanism. Results are in good agreement with a previous work of EPOC on catalytic ammonia decomposition reaction, in which moderate potassium coverages electrochemically supplied at $V_{WR}=1.3$ V were found to optimize the catalytic activity of an iron catalyst [17]. On the other hand, it is also interesting to note that a slight permanent EPOC effect was observed at 300 °C (the initial un-promoted catalytic rate was not reached after the final polarization of 2 V). This permanent effect is clearer at 320 °C in which larger differences between the initial and final polarization at $V_{WR}=2$ V were obtained. This kind of permanent EPOC effect has been also observed in previous studies above certain reaction temperatures working with K^+ ions conductor solid electrolytes [35]. It might be explained considering the possible formation of different kinds of promoting phases with higher stability on the catalyst surface, which cannot be electrochemically decomposed under the explored reaction conditions (temperature and electrical potential) [26]. Likely, an applied potential value higher than 2 V would be required for the decomposition of such promotional phases in order to reach the initial un-promoted state. At this point, it should be mentioned that under the explored reaction conditions, K^+ ions may also form different kinds of surface species (promotional phases) as a result of their reaction with the chemisorbed reactant and intermediates molecules. These species such as ammonia and nitrogen adsorbed molecules react with K^+ ions by distinct charge transfer electrochemical reactions (e.g., potassium nitrites, nitrates or nitrides among others) occurring at the different applied V_{WR} values. In fact, various kinds of promotional phases have

been already shown in other EPOC studies with potassium ions conductor electrolyte, verified by ex-situ FTIR [35] and XPS measurements [48]. This in-situ formation of different kinds of adsorbed species will be analysed with more detail in the next section by cyclic voltammetry measurements. Thus, the presence of distinct kind of promotional phases could also confirmed the presence of two local maximum on the hydrogen production rates observed at 320 °C at $V_{WR}=0.5$ V and -1.5 V. The formation and nature of different kind of promotional phases causing two optimal applied potential values have been reported in a previous work of hydrogen production via partial oxidation of methanol on platinum catalyst film deposited on K- β - Al_2O_3 [26]. Thus, the catalytic rates would be affected by the formation of several kinds of promoter phases as will be also lately confirmed by cyclic voltammetry. The higher promotional effect of potassium vs. sodium ions can be clearly observed also on Figure S4 of the supporting information, which compares the potentiostatic variation of ρ vs. V_{WR} at the two common explored reaction temperatures (300 and 320 °C). It can be observed that in both cases higher ρ values were obtained for Ru/K- β - Al_2O_3 vs. Ru/Na- β - Al_2O_3 at lower V_{WR} values. Hence, in the case of Ru/K- β - Al_2O_3 the catalytic hydrogen production rate via ammonia decomposition under optimal promoter coverage is multiplied by a factor close to 231.8% at 300 °C, which is one of the most important findings of the present work. It led to an overall higher ammonia conversion on the Ru/K- β - Al_2O_3 electrochemical catalyst vs. Ru/Na- β - Al_2O_3 as can be observed on Figure S5 of the supporting information. Considering the similar nature of both kinds of ruthenium catalyst films deposited on both, Na- β - Al_2O_3 and K- β - Al_2O_3 (same preparation procedure and same geometric area of the catalyst working-electrode), the observed difference in the ammonia conversion is clearly due to a higher promotional effect of potassium. Therefore, considering that the most interesting results were obtained by the Ru/K- β - Al_2O_3 electrochemical catalyst, this sample was selected for further reaction and characterization experiments as will be shown below.

Fig. 6 shows the ammonia conversion on Ru/K- β - Al_2O_3 electrochemical catalyst through temperature programmed reaction experiments (2 °C \cdot min $^{-1}$) under application of three different potentials ($V_{WR}=2, 0$ and -1 V).

In first place it can be observed that under the three explored V_{WR}

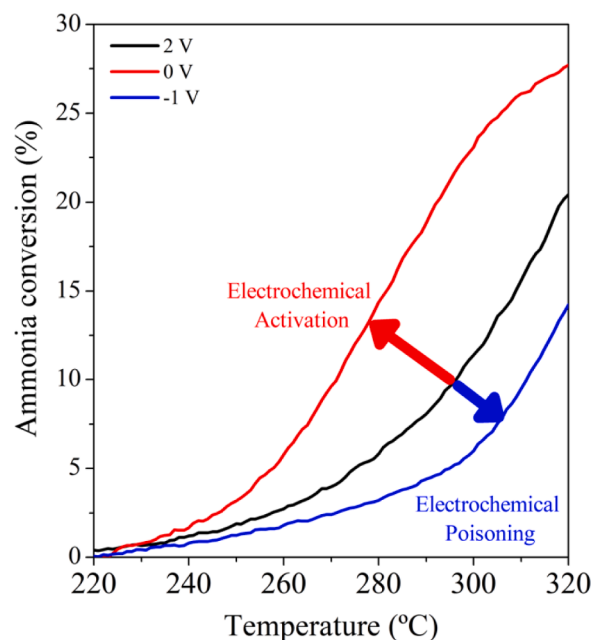


Fig. 6. Ammonia conversion variation under temperature programmed reaction experiments (2 °C \cdot min $^{-1}$) under different applied potentials for Ru/K- β - Al_2O_3 electrochemical catalyst.

values, ammonia conversion increased with the reaction temperature due to an increase in the reaction kinetics and the endothermic nature of the reaction. In good agreement with previous results, it can be observed that the application of a mild potential value ($V_{WR} = 0$ V) enhanced ammonia conversion at the whole explored temperature range vs. the un-promoted potential value (2 V). Under these conditions, a moderate amount of potassium ions was supplied to the catalyst leading to an electrochemical activation of the metal catalyst film. This catalyst potential ($V_{WR} = 0$ V) was selected from the results obtained in Fig. 5 in order to improve the catalytic activity in a wide temperature range (220–320 °C). However, it can be observed again that, a decrease in the potential to $V_{WR} = -1$ V decreased ammonia conversion in the whole temperature range. It was related to a strong increase on the K^+ coverage, which weakens the binding strength of ammonia, decreasing the reaction rate. Moreover, the excess of promoter over catalyst surface, induced by a negative potential, led to the blockage of ruthenium active sites causing electrochemical poisoning, similarly to a previous EPOC study on ammonia decomposition using an Fe electrochemical catalyst under potassium coverages [17]. This kind of poisoning behavior has been also observed in previous studies of catalytic ammonia decomposition on ruthenium catalysts chemically doped with potassium [47] and cesium [49].

In any case, results shown in Fig. 6 demonstrate the interest of EPOC phenomenon to activate the catalyst at lower reaction temperatures, which may be of great interest for energy saving, especially for endothermic reactions as the one explored here. In this sense, Figure S6 of the supporting information shows the reaction temperature necessary to achieve a specific ammonia conversion (5 and 10%) as a function of the three explored potentials ($V_{WR} = 2, 0$ and -1 V) used in the experiment of Fig. 6. It can be observed an activation by means of a reduction of 20 °C to achieve 5% of ammonia conversion and 30 °C for 10% ammonia conversion induced by EPOC under $V_{WR} = 0$ V. At this point it should be mentioned that a further optimization could be performed (out of the scope of the present study), applying the optimal potential value at each explored temperature to maximize the hydrogen production rate.

The apparent activation energy values (E_a) were calculated from these experiments via the Arrhenius plot at each applied potentials ($V_{WR} = 2, 0$ and -1 V) as shown in Figure S7 of the supporting information. The obtained values, which were in the range of previously obtained ones with ruthenium catalysts [7,50], decrease from $E_a = 80.9$ $\text{kJ}\cdot\text{mol}^{-1}$ at $V_{WR} = 2$ V to $E_a = 74.6$ $\text{kJ}\cdot\text{mol}^{-1}$ at $V_{WR} = 0$ V. This decrease in the E_a induced under electrochemical activation conditions is in good agreement with the promotional mechanism explained above. Hence, the optimal potassium coverages achieved at $V_{WR} = 0$ V allowed an activation of the chemisorption of electron acceptor molecules (N adsorbed molecules), which promotes the rate determining step of ammonia decomposition reaction, decreasing the E_a [17]. In addition, a similar decrease in the apparent activation energy of 5–20 $\text{kJ}\cdot\text{mol}^{-1}$ was observed for ruthenium catalysts chemically doped with potassium species on ammonia decomposition reaction [47].

3.4. Cyclic voltammetry measurements

Fig. 7 shows the cyclic voltammetry experiment (CV) of Ru/K- $\beta\text{Al}_2\text{O}_3$ with the simultaneous recording of ammonia signal during ammonia catalytic decomposition reaction at 280 °C, from $V_{WR} = 2$ V to -2 V and a scan rate of 5 $\text{mV}\cdot\text{s}^{-1}$. Before the cyclic voltammetry experiment, the electrochemical catalysts were kept at 2 V for 30 min in order to define an initial reference state.

Starting from 2 V, during the initial forward scan from 2 V to -2 V, it can be observed negative current values attributed to the electrochemical supply of K^+ ions from the solid electrolyte to the metal catalyst film with the simultaneous formation of surface promotional phases between the K^+ ions and the chemisorbed reactant and product species [51]. According to the obtained CV curve one could envisage different kinds of charge transfer reactions evidenced by the different

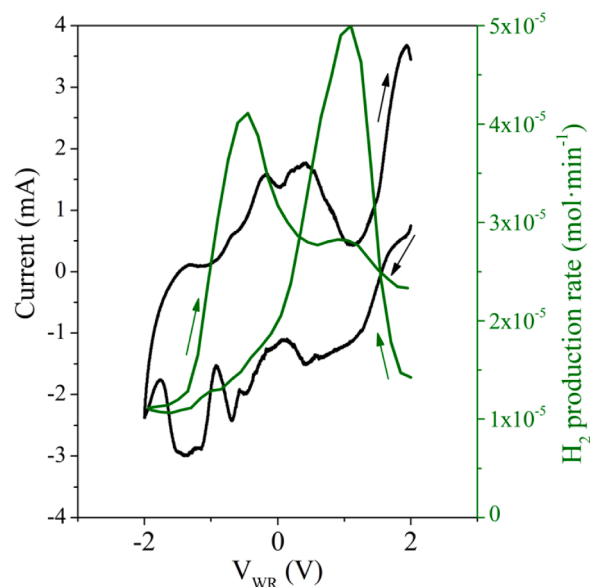


Fig. 7. Current variation and hydrogen production rate vs. applied potential during cyclic voltammetry between +2 V and -2 V for Ru/K- $\beta\text{Al}_2\text{O}_3$. $T = 280$ °C and scan rate = 5 $\text{mV}\cdot\text{s}^{-1}$.

obtained cathodic peaks vs. other CV curves obtained in EPOC systems where single cathodic peaks were typically observed [51]. It demonstrates the formation of different kinds of promotional phases between the K^+ ions and chemisorbed molecules, in good agreement with the different observed promotional effects already discussed in Fig. 5. During the forward CV scan, an increase in the hydrogen production rate was also observed due to the electrochemical supply of K^+ ions. In good agreement with the previous results shown in Fig. 5, an optimal potential value was attained corresponding to an optimal alkali coverage on the catalyst surface. During the positive scan from -2 V to 2 V (backward scan) the different promotional phases previously formed on the metal catalyst film were electrochemically decomposed, returning the K^+ ions to the solid electrolyte and leading to the appearance of different anodic current peaks. It is interesting to note that during this positive scan a new promotional state is again reached at $V_{WR} = -0.5$ V maximizing the hydrogen production rate. In addition, during the backward scan a second local maximum in the hydrogen production rate was also observed at $V_{WR} = 1$ V. Considering the dynamic character of the experiment, these results again confirmed the presence of different kinds of promotional phases which locally optimize the hydrogen production rate at different potentials. Some of these species were likely formed from the partial electrochemical decomposition of the promotional phases initially formed during the forward scan. The existence of a permanent EPOC effect is also clear at the end of the cyclic voltammetry experiment at 2 V which showed a higher hydrogen production rate in the backward vs. the forward scan. At this point ($V_{WR} = 2$ V), positive current values were obtained showing that certain promotional phases were still present on the catalyst surface and were not completely removed (via electrochemistry). It supports the origin of the permanent EPOC phenomenon observed in Fig. 5 and previously discussed in the case of the Ru/K- $\beta\text{Al}_2\text{O}_3$ electrochemical catalyst.

4. Conclusions

The electrochemical supply of alkaline ions (Na^+ and K^+) to a ruthenium catalyst film activates the hydrogen production rate via catalytic ammonia decomposition reaction. The promotional effect is due to the strengthening of the chemisorptive bond of weakly adsorbed N surface molecules which stabilizes N adsorbed species on the ruthenium catalyst surface. This stabilization increases the kinetics of the

ammonia decomposition reaction leading to the overall activation of the process.

A higher promotional effect of K^+ ions was found vs. Na^+ ions. It is attributed to the higher electronic effect induced by K^+ which allows to increase the hydrogen production rate above 230% under optimal potential conditions. However, a large amount of alkali ions supplied to the catalyst at very negative potentials, led to a poisoning effect on the catalytic activity. It is associated with a strong decrease in the chemisorption of the electron donor molecules (ammonia).

Temperature programmed reaction experiments show the interest of EPOC for the electrochemical activation of the catalyst at lower temperatures, which may contribute to decrease on the overall energy requirements of the process.

A permanent EPOC effect was also found for the case of $Ru/K\text{-}\beta\text{-Al}_2\text{O}_3$ which led to a permanent activation of the catalyst under the explored conditions. It was attributed to a higher stability of some promotional phases formed during the negative polarization as supported by cyclic voltammetry.

CRedit authorship contribution statement

M. Pinzón: Investigation, Methodology, Validation, Visualization, Writing – original draft. **E. Ruiz-López:** Investigation, Methodology. **A. Romero:** Conceptualization, Visualization, Writing – review & editing, Supervision, Funding acquisition. **A.R. de la Osa:** Conceptualization, Visualization, Writing – review & editing, Supervision, Funding acquisition. **P. Sánchez:** Conceptualization, Visualization, Writing – review & editing, Supervision, Funding acquisition. **A. de Lucas-Consuegra:** Conceptualization, Visualization, Writing – review & editing, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:[10.1016/j.mcat.2021.111721](https://doi.org/10.1016/j.mcat.2021.111721).

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