

# Electrochemical characterization of the Pt/ $\beta''$ -Al<sub>2</sub>O<sub>3</sub> system under conditions of in situ electrochemical modification of catalytic activity for propane combustion

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**Abstract** Linear sweep and cyclic voltammetry were used for electrochemical characterization of the Pt/sodium- $\beta''$ -Al<sub>2</sub>O<sub>3</sub> system and investigation of the phases formed upon electrochemical pumping of sodium ions to the Pt catalyst-electrode under conditions of propane combustion or under mixtures of O<sub>2</sub> or CO<sub>2</sub> with helium, at temperatures between 320 and 480 °C. The number, position and magnitude of the peaks in the obtained voltammograms were found to depend on gas phase composition, temperature, and pre-scan (initial polarization) conditions. The results showed that under conditions of propane combustion more than one sodium phases can be formed as a result of electrochemical pumping of sodium ions to the Pt catalyst. The related electrochemical reactions and the identity of these sodium phases, which correspond mainly to carbonate or bicarbonate phases but also to oxide phases, are discussed on the basis of the obtained results and those of former studies.

**Keywords** Alkali doping ·  $\beta''$ -Al<sub>2</sub>O<sub>3</sub> · Electrochemical promotion · Cyclic voltammetry · Linear sweep voltammetry · NEMCA · Platinum · Propane combustion

## 1 Introduction

Sodium- $\beta''$ -Al<sub>2</sub>O<sub>3</sub> is a Na<sup>+</sup> conductor which has been widely used in the past as electrolyte in sodium-sulfur batteries. Since 1991 [1] it has been known that sodium- $\beta''$ -Al<sub>2</sub>O<sub>3</sub> can also be used as electro-active catalyst

support to induce pronounced catalytic activity changes of metal catalyst films via the effect of electrochemical promotion [2, 3] or non-faradaic electrochemical modification of catalytic activity (NEMCA effect) [2–4]. Electrochemical promotion corresponds to the reversible alteration of the catalytic behaviour of metal and metal-oxide catalyst-electrode films deposited on solid electrolytes or mixed ionic–electronic conductors via polarization of the catalyst-electrode and concomitant pumping of mobile promoter species to or from the catalyst-electrode surface under reaction conditions. This electrochemically induced catalytic effect allows for in situ tuning of catalyst performance and has been reported [2, 3] for over sixty catalytic reactions on a large number of catalyst-electrodes (Pt, Rh, Pd, Ag, Fe, Ni, IrO<sub>2</sub>, RuO<sub>2</sub>, etc.) interfaced to a variety of solid electrolytes and mixed electronic–ionic conductors. Work in this area has been thoroughly reviewed relatively recently [3].

Alkali metal compounds are commonly employed as promoters of metal catalysts, a fact that has stimulated the use of potassium and sodium ion conductors, namely  $\beta''$ -Al<sub>2</sub>O<sub>3</sub> and NaSiCon, in a large number of electrochemical promotion studies [2, 3, 5–13]. It is well documented in literature that when sodium- $\beta''$ -Al<sub>2</sub>O<sub>3</sub> is used in electrochemical promotion studies the chemical state of the electro-pumped sodium on metal catalyst surfaces is determined by the reactive gas environment [14–16]. The promoter or poisoning phases in the case of electrochemical promotion by sodium of the platinum-catalyzed combustion of propene [16] or ethylene [15] have been found spectroscopically to contain mainly sodium carbonate species. At high sodium coverage these sodium phases can form three dimensional crystallites partially blocking the Pt catalyst surface which, however, also exposes sodium-modified Pt sites [15].

Electrochemical techniques have also been employed to investigate the reactions occurring at the metal/ $\beta''$ -Al<sub>2</sub>O<sub>3</sub>

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or metal/NaSiCon interface and the resulting sodium phases under various gaseous environments. Staikov et al. [17] used cyclic voltammetry to study the electrochemical processes taking place at the Pt/ $\beta''$ -Al<sub>2</sub>O<sub>3</sub> interface under oxygen–argon mixtures (oxygen partial pressure ranging from 10<sup>-5</sup> to 0.1 atm) at temperatures 150–350 °C. They observed a number of anodic peaks, which they attributed to decomposition of different states of sodium oxide formed during the cathodic scan via electrochemical reaction of Na<sup>+</sup> with oxygen or surface platinum oxides. Vernoux et al. [8] observed cathodic and anodic cyclic voltammetric peaks in the reaction of propene combustion on Pt/NaSiCon at 200 °C which they attributed to the formation and decomposition of sodium carbonate and bicarbonate species. Kotsionopoulos and Bebelis [18] using linear sweep voltammetry under conditions of in situ electrochemical modification of catalytic activity for propane combustion of a Pt catalyst-electrode interfaced to  $\beta''$ -Al<sub>2</sub>O<sub>3</sub>, at temperatures between 320 and 480 °C, concluded that more than one sodium phases, depending on temperature, are formed at the Pt/ $\beta''$ -Al<sub>2</sub>O<sub>3</sub> interface following electrochemical pumping of sodium ions to it. Dorado et al. [13], studying the selective catalytic reduction (SCR) of NO by propene in presence of oxygen, performed cyclic voltammetry experiments to investigate the chemisorption of reactant species in the Pt/ $\beta''$ -Al<sub>2</sub>O<sub>3</sub> system at 240 °C and under different gas atmospheres, namely He, C<sub>3</sub>H<sub>6</sub>/He, NO/He, C<sub>3</sub>H<sub>6</sub>/O<sub>2</sub>/He, C<sub>3</sub>H<sub>6</sub>/NO/He and C<sub>3</sub>H<sub>6</sub>/NO/O<sub>2</sub>/He mixtures with different concentrations of O<sub>2</sub>. Under NO, C<sub>3</sub>H<sub>6</sub>/O<sub>2</sub> or NO/C<sub>3</sub>H<sub>6</sub>/O<sub>2</sub> atmospheres they observed two peaks, one cathodic and one anodic, which they associated with the formation/decomposition of sodium compounds, possibly a mixture of sodium nitrate/nitrite under NO atmosphere and a mixture of sodium carbonate and bicarbonate under C<sub>3</sub>H<sub>6</sub> + O<sub>2</sub>. In agreement with previous studies [6] they suggested that the chemical identity of sodium compounds depends on the species more strongly adsorbed on the metal catalyst. Cyclic voltammetry experiments were also performed recently by de Lucas-Consuegra et al. [19] in the Pt/K- $\beta$ -Al<sub>2</sub>O<sub>3</sub> system under wet SCR conditions (C<sub>3</sub>H<sub>6</sub>/NO/O<sub>2</sub>/H<sub>2</sub>O/He mixture) at 350 °C along with NO<sub>x</sub> analysis. They observed more than one peaks both in the cathodic and anodic scan, which they attributed to the formation/decomposition of different surface compounds originating from the interaction of chemisorbed NO<sub>x</sub> with Pt and potassium promoting species.

In continuation of the previous studies, mainly linear sweep voltammetry but also cyclic voltammetry experiments were carried out in the present study to further elucidate the electrochemical reactions and corresponding formation of phases taking place in the Pt/ $\beta''$ -Al<sub>2</sub>O<sub>3</sub> system upon electrochemical pumping of sodium ions to the Pt

catalyst-electrode under conditions of propane combustion as well as under O<sub>2</sub>/He and CO<sub>2</sub>/He mixtures.

## 2 Experimental

The atmospheric pressure continuous flow experimental apparatus used in this study has been described previously [1, 3]. Gases were certified standards of propane in He, O<sub>2</sub> in He and CO<sub>2</sub> in He (L'Air Liquide and Messer), which could be further diluted by mixing with He (99.999%, L'Air Liquide). The flow of gases was controlled by a set of calibrated mass flowmeters (MKS 1259C controlled by an MKS 247C controller), while the total flow rate was also measured by using a bubble flowmeter. The composition of the gas mixtures entering and leaving the reactor was determined using an on-line gas chromatograph (Model 14B, Shimadzu), while CO<sub>2</sub> concentration in the effluent from the reactor was also continuously monitored by means of an infrared (IR) analyzer (Model Binos 100, Emerson Process Management) as described in detail elsewhere [20]. The electrochemical measurements were carried out using a Princeton Applied Research 263A potentiostat–galvanostat controlled by the PowerSuite electrochemical software. The catalyst potential values reported in this work under closed circuit conditions can be considered essentially ohmic-drop-free potential values as the uncompensated ohmic drop component, determined by AC impedance spectroscopy, was insignificant.

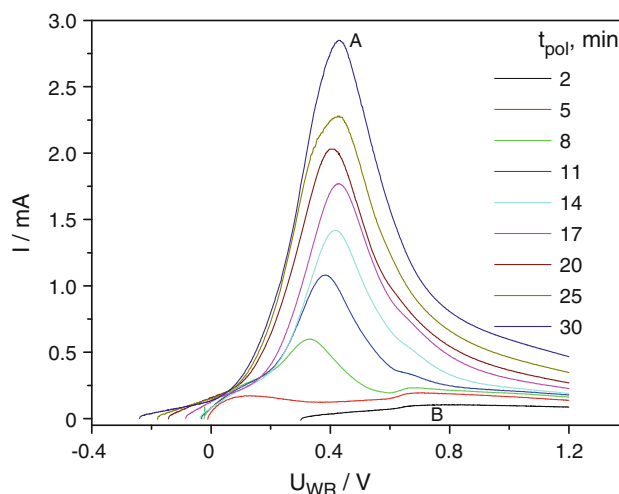
The atmospheric pressure continuous flow reactor was a “single chamber” reactor [2, 21]. A sodium  $\beta''$ -Al<sub>2</sub>O<sub>3</sub> disc (Ionotec Ltd, 20 mm diameter and 1 mm thickness), on the two sides of which a Pt catalyst-electrode and two auxiliary (counter and reference) Au electrodes were deposited, was suspended in the interior of a closed at one end quartz tube of volume approximately 50 cm<sup>3</sup>, where the gas mixture was fed, via three wires mechanically pressed on the three electrodes. These wires were also used as electron collectors or suppliers. The deposition of the Pt catalyst-electrode (1.3 mg Pt) on the  $\beta''$ -Al<sub>2</sub>O<sub>3</sub> disk was performed by application of thin coatings of an Engelhard-CLAL M603B Pt paste followed by drying and calcination in air, first at 400 °C (4 °C min<sup>-1</sup>) for 2 h and then at 800 °C (7 °C min<sup>-1</sup>) for 20 min. Details concerning the morphology of the Pt electrode (scanning electron microscopy characterization) can be found elsewhere [18]. The surface mol (mol of active sites) N of the Pt catalyst-electrode, which had a geometric (superficial) area of 1.55 cm<sup>2</sup>, was equal to 2.5 × 10<sup>-7</sup> mol Pt, as measured [18] using the technique of isothermal titration [1, 3] of adsorbed CO at 350 °C assuming an 1:1 CO to Pt adsorption stoichiometry. The Au counter electrode had the same geometric (superficial) area with the Pt working electrode and was deposited

exactly opposite to it, on the other side of the  $\beta''$ -Al<sub>2</sub>O<sub>3</sub> disk. The Au reference electrode was deposited at a distance of 0.5 cm from the counter electrode and had a geometric area of 0.5 cm<sup>2</sup>. The deposition of the porous Au auxiliary electrodes on the  $\beta''$ -Al<sub>2</sub>O<sub>3</sub> disk was performed using a Au paste, as described in detail elsewhere [18].

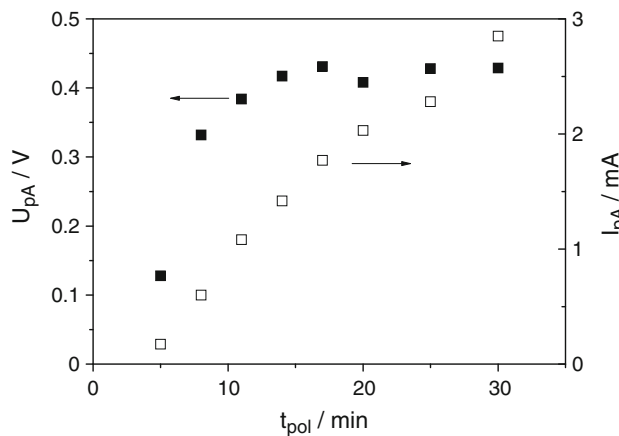
### 3 Results and discussion

The experiments were carried out in the temperature range 320–480 °C. They included linear sweep and cyclic voltammetry measurements under conditions of propane combustion as well as under O<sub>2</sub>/He and CO<sub>2</sub>/He mixtures. Before each run the catalyst-working electrode surface was electrochemically cleaned by pumping sodium species away from the Pt film via holding the catalyst potential at 1.2 V for 10–15 min. At the end of this time the current fell to practically zero.

Figure 1 shows linear sweep voltammograms obtained at 360 °C and potential scan rate  $v = 20 \text{ mV s}^{-1}$  under propane combustion conditions, specifically for  $P_{\text{O}_2} = 1 \text{ kPa}$  and  $P_{\text{C}_3\text{H}_8} = 0.2 \text{ kPa}$  (stoichiometric conditions) in the reactor, after previous application of a current of  $I_{\text{pol}} = -50 \mu\text{A}$  between the Pt catalyst and the Au counter electrode for polarization times  $t_{\text{pol}}$  ranging from 2 to 30 min. Following current application, the catalyst-electrode potential  $U_{\text{WR}}$  versus the Au reference electrode is increased linearly from its value  $U_{\text{WR,start}}$  to 1.2 V at a rate equal to  $20 \text{ mV s}^{-1}$  and the resulting current  $I$  is recorded as a function of  $U_{\text{WR}}$ . During current application (polarization)  $-\frac{I_{\text{pol}} t_{\text{pol}}}{F}$  mol of sodium ions are electrochemically transferred to the catalyst-electrode surface and establish there a corresponding coverage  $\theta$  of sodium species. In view of the surface mol of the Pt catalyst ( $N = 2.5 \times 10^{-7} \text{ mol Pt}$ ), a monolayer coverage of sodium species is approximately established after application of  $-50 \mu\text{A}$  for  $t_{\text{pol}} = 8 \text{ min}$ . As shown in Fig. 1, for  $t_{\text{pol}} = 2 \text{ min}$  only a current peak (peak B) appears in the voltammogram at  $\sim 0.74 \text{ V}$ . For higher polarization times, a second current peak (peak A) also appears at lower potentials becoming the dominant feature of the voltammograms for  $t_{\text{pol}}$  larger or equal than 8 min. The height of this peak increases with increasing  $t_{\text{pol}}$  while its position shifts to higher potentials, reaching a practically constant value for  $t_{\text{pol}}$  higher than 14 min. This is better shown in Fig. 2, where is presented the effect of polarization time  $t_{\text{pol}}$  on the potential  $U_{\text{pA}}$  and current  $I_{\text{pA}}$  corresponding to current peak A. The position of peak B, which appears only up to  $t_{\text{pol}} = 11 \text{ min}$ , shifts to lower potentials with increasing  $t_{\text{pol}}$ , while its height seems to pass through a maximum for  $t_{\text{pol}} = 5 \text{ min}$  (Fig. 1). In Fig. 3 is plotted the electric charge  $Q_{\text{int}}$  corresponding to each voltammogram versus the charge  $Q_{\text{pol}} = -I_{\text{pol}} t_{\text{pol}}$  corresponding to the galvanostatic polarization preceding the

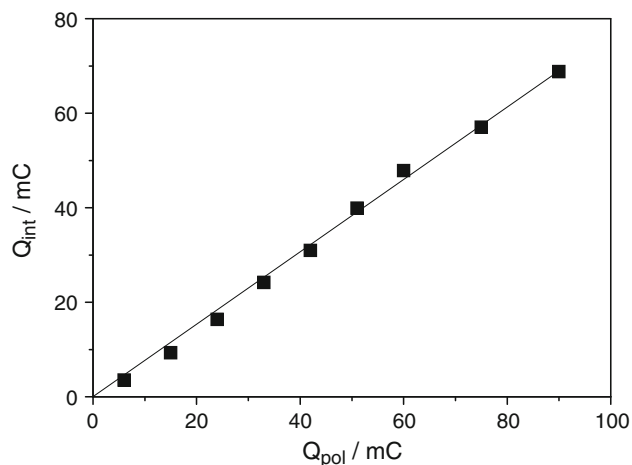


**Fig. 1** Linear sweep voltammograms obtained at 360 °C under propane combustion conditions after previous application of  $-50 \mu\text{A}$  for different time  $t_{\text{pol}}$ .  $P_{\text{O}_2} = 1.0 \text{ kPa}$ ,  $P_{\text{C}_3\text{H}_8} = 0.2 \text{ kPa}$ . Scan rate:  $20 \text{ mV s}^{-1}$ . Flow rate:  $83 \text{ cm}^3 \text{ (STP) min}^{-1}$

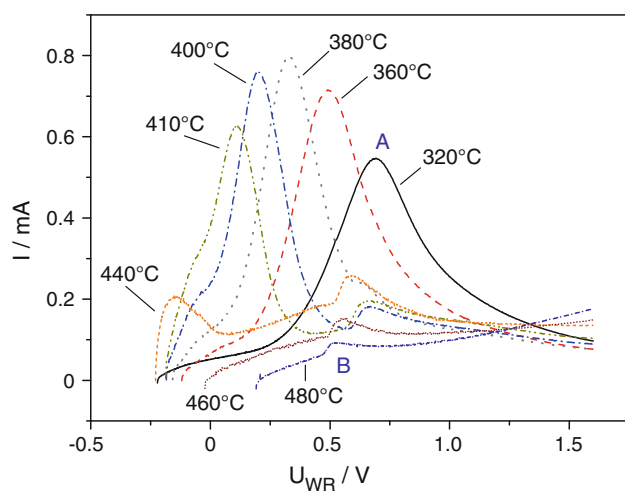


**Fig. 2** Effect of polarization time  $t_{\text{pol}}$  on the potential  $U_{\text{pA}}$  and current  $I_{\text{pA}}$  corresponding to current peak A in the linear sweep voltammograms shown in Fig. 1

potential scan.  $Q_{\text{int}}$  is calculated by integration of the current with respect to time or, equivalently, with respect to voltage and division by the potential scan rate. As shown in the figure, the  $Q_{\text{int}}$  vs.  $Q_{\text{pol}}$  plot corresponds practically to a straight line passing through the origin with a slope equal to 0.76, which corroborates the fact that most of the amount of sodium electrochemically pumped to the Pt catalyst participates in the formation of phases which are decomposed during the linear sweep of the potential from  $U_{\text{WR,start}}$  to 1.2 V. It is also noted that the starting potential  $U_{\text{WR,start}}$  shifts to lower values with increasing polarization time  $t_{\text{pol}}$  (Fig. 1), as increase in the coverage of the electropositive sodium species results in decrease of the Pt catalyst work function [1–4] which relates directly to catalyst potential [1–4].

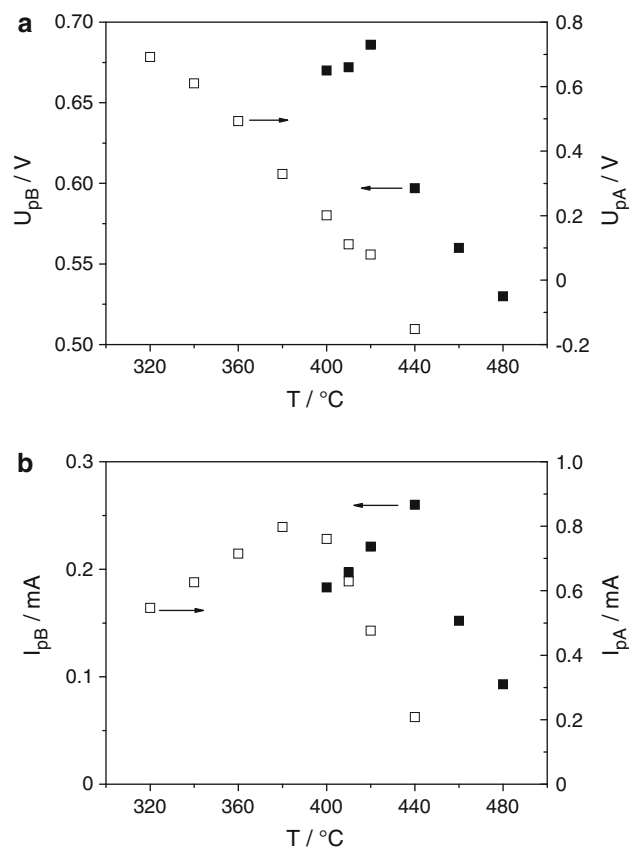


**Fig. 3** Electric charge  $Q_{\text{int}}$  corresponding to each voltammogram in Fig. 1 versus the electric charge  $Q_{\text{pol}}$  corresponding to polarization preceding the potential scan



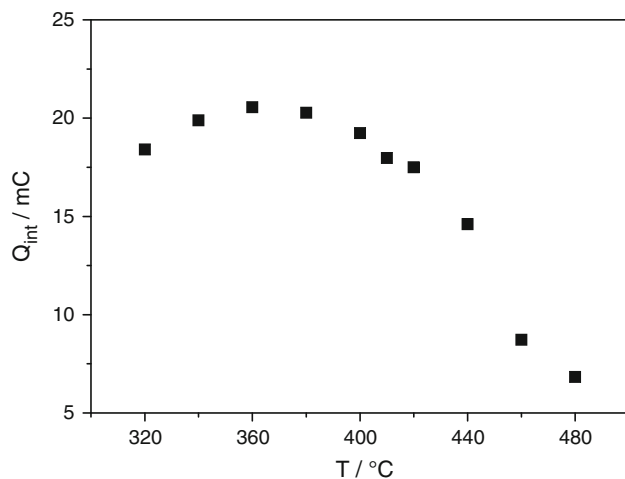
**Fig. 4** Linear sweep voltammograms obtained at different temperatures under propane combustion conditions after previous application of  $-50 \mu\text{A}$  for 8 min [18].  $P_{\text{O}_2} = 1.0 \text{ kPa}$ .  $P_{\text{C}_3\text{H}_8} = 0.2 \text{ kPa}$ . Scan rate:  $20 \text{ mV s}^{-1}$ . Flow rate:  $84 \text{ cm}^3 (\text{STP}) \text{ min}^{-1}$

Figure 4 shows linear sweep voltammograms obtained under propane combustion conditions, specifically for  $P_{\text{O}_2} = 1 \text{ kPa}$  and  $P_{\text{C}_3\text{H}_8} = 0.2 \text{ kPa}$  in the reactor, by linearly scanning the catalyst-electrode potential up to 1.6 V at a rate equal to  $20 \text{ mV s}^{-1}$ , after previous application of  $-50 \mu\text{A}$  for 8 min corresponding to electrochemical pumping of  $2.49 \times 10^{-7} \text{ mol}$  of sodium ions to the Pt catalyst. As already mentioned, this amount of sodium corresponds practically to a monolayer of sodium species ( $N = 2.5 \times 10^{-7} \text{ mol Pt}$ ). Figure 4 has appeared in an earlier work [18] however it is also shown here as the presented data are further analyzed and discussed. As shown in the figure, at temperatures below  $380^\circ\text{C}$  only one current peak appears (peak A) which shifts to lower



**Fig. 5** Effect of temperature on the potential (a) and current (b) corresponding to current peaks A and B in the linear sweep voltammograms shown in Fig. 4

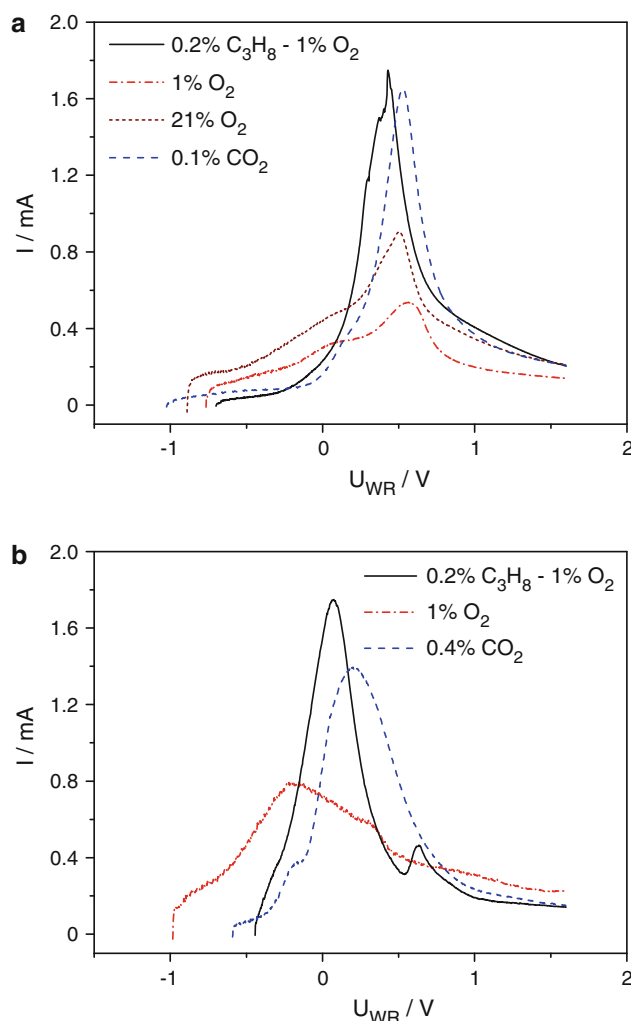
potentials with increasing temperature while its height increases. This peak most probably corresponds to the dominant peak in Fig. 1, i.e., peak A, as it is concluded by comparing Figs. 1 and 4 concerning the linear sweep voltammograms obtained at  $360^\circ\text{C}$  and  $t_{\text{pol}} = 8 \text{ min}$ . At higher temperatures the height of the aforementioned peak decreases, a shoulder appears on its left side and a second, more anodic, peak (peak B) appears gradually. This peak, which is the only one remaining above  $440^\circ\text{C}$  could correspond to the small peak observed at  $360^\circ\text{C}$  after application of  $-50 \mu\text{A}$  for  $t_{\text{pol}}$  less than 8 min (peak B in Fig. 1) in view also of the fact that it also corresponds to a low coverage of sodium, as described below. The height of this peak seems to increase with increasing temperature up to  $440^\circ\text{C}$  and then gradually decrease. The effect of temperature on the potential and current corresponding to the peaks A and B appearing in Fig. 4 (which, as discussed, presumably correspond to peaks A and B in Fig. 1) is shown also in Fig. 5a, b, respectively. It is noted that data points corresponding to linear sweep voltammograms obtained at  $340^\circ\text{C}$  and  $420^\circ\text{C}$ , which are not presented in Fig. 4 for clarity, are also shown in Fig. 5a, b as well as in Fig. 6 below. The electric charge  $Q_{\text{int}}$  corresponding to



**Fig. 6** Effect of temperature on the electric charge  $Q_{\text{int}}$  corresponding to each voltammogram in Fig. 4

each voltammogram in Fig. 4 is shown as a function of temperature in Fig. 6. At temperatures below 410 °C, the electric charge corresponding to the voltammograms does not change significantly with temperature (interestingly, a shallow local maximum is observed at 360 °C), being lower by less than 25% compared to the charge  $Q_{\text{pol}} = 24$  mC which corresponds to the initial current application before the onset of the potential scan. This again corroborates the fact that the current peaks appearing in the linear sweep voltammograms can be associated with the decomposition of sodium compounds formed during current application and concomitant migration of sodium ions to the catalyst surface. As shown in Fig. 6, above 420 °C a significant decrease of  $Q_{\text{int}}$  with increasing temperature is gradually observed. This decrease can be attributed to the increase of the rate of sodium desorption from the catalyst surface with increasing temperature and to the fact that the sodium surface compounds formed during initial polarization are thermally unstable and cannot be retained on the catalyst surface [15].

Figure 7a, b shows linear sweep voltammograms obtained under different gas atmospheres, at 360 °C and 440 °C respectively, after previous application of  $-50$   $\mu\text{A}$  for 20 min. During current application  $6.22 \times 10^{-7}$  mol of sodium ions are electrochemically transferred to the Pt catalyst. This amount of sodium corresponds approximately to 2.5 monolayers ( $N = 2.5 \times 10^{-7}$  mol Pt). As shown in Fig. 7a, b, the features of the obtained voltammograms depend on temperature and, mainly, on gas phase composition. Under propane combustion conditions, specifically  $P_{\text{O}_2} = 1$  kPa and  $P_{\text{C}_3\text{H}_8} = 0.2$  kPa in the reactor, only one current peak is observed at 360 °C (Fig. 7a), in agreement with the results presented in Fig. 1, while at 440 °C two current peaks appear (Fig. 7b), the more cathodic one being dominant. On the basis of the results



**Fig. 7** Linear sweep voltammograms obtained under different gas phase compositions after previous application of  $-50$   $\mu\text{A}$  for 20 min. (a)  $T = 360$  °C; (b)  $T = 440$  °C. Scan rate:  $20$   $\text{mV s}^{-1}$ . See text for discussion

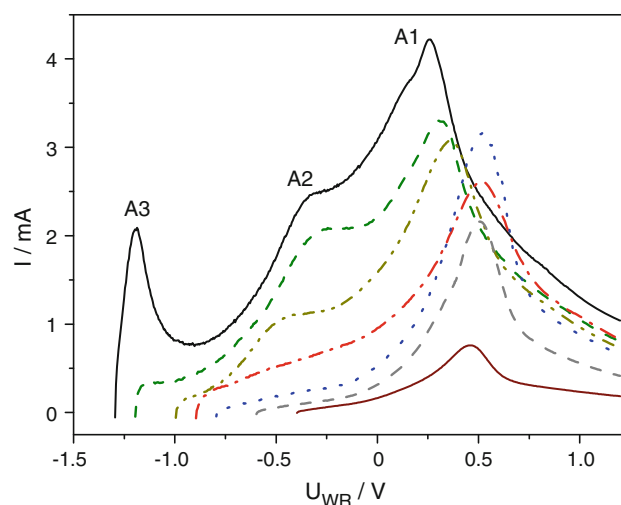
presented in Fig. 4 and the corresponding discussion, the larger, more cathodic, peak corresponds to the current peak obtained at 360 °C (peak A) shifted to lower potentials, while the second peak corresponds to the smaller, more anodic, peak observed above 380 °C after application of  $-50$   $\mu\text{A}$  for 8 min (peak B, Fig. 4). The difference in the relative height of these two peaks in Figs. 4 and 7b, for the same temperature, can be attributed to the difference in the corresponding polarization times before the onset of the linear sweep of the potential. In order to validate the formation of carbonate species as a result of sodium pumping, the linear sweep voltammograms obtained under propane combustion conditions were compared with those obtained when a mixture of  $\text{CO}_2$  in He was fed in the reactor, with  $\text{CO}_2$  concentration close to that in the reactor under reaction conditions, specifically  $P_{\text{CO}_2} = 0.1$  kPa at 360 °C and  $P_{\text{CO}_2} = 0.4$  kPa at 440 °C. At 360 °C one current peak is



obtained under CO<sub>2</sub>/He mixture with height and position close to those of the peak obtained under propane combustion conditions (Fig. 7a). At 440 °C and under flow of 0.4% CO<sub>2</sub> in He mixture a current peak is also observed (Fig. 7b), with a small shoulder on its left side, its position shifted by approximately 0.3 V to lower potentials compared to that of the corresponding peak observed at 360 °C. This shift is practically the same with the corresponding shift in the position of the dominant peak observed under propane combustion conditions (Fig. 7a, b). The comparison between the voltammograms obtained under propane combustion conditions and under CO<sub>2</sub>/He mixtures implies that both at 360 and 440 °C the main phases formed under conditions of propane combustion as a result of electrochemical sodium transport onto the Pt electrode are sodium carbonate (or, possibly, bicarbonate) phases, in agreement with the results of earlier spectroscopic studies [15, 16].

The formation of oxide phases during sodium pumping under propane combustion conditions cannot be excluded; however, as described below, their contribution in the dominant current peak is small, at least under the conditions of the present experiment. When the feed in the reactor is O<sub>2</sub> in He mixture with oxygen partial pressure corresponding to that in the reaction mixture (P<sub>O<sub>2</sub></sub> = 1 kPa), a peak is obtained at 360 °C with a shoulder (or a not well resolved peak) also appearing on its left side (Fig. 7a). This peak is located near the peaks observed under reaction conditions and under CO<sub>2</sub> in He mixture, but has a significantly smaller height. At 440 °C (Fig. 7b) and P<sub>O<sub>2</sub></sub> = 1 kPa a wide peak is obtained, which has also a height smaller than that of the corresponding peak observed under reaction conditions (Fig. 7b), being centered not very far from it. By increasing at 360 °C the oxygen partial pressure in the O<sub>2</sub>/He mixture feed to P<sub>O<sub>2</sub></sub> = 21 kPa a peak larger than that observed under P<sub>O<sub>2</sub></sub> = 1 kPa is obtained, centered at a potential lower by approximately 65 mV. In spite of the large increase in oxygen partial pressure, the height of this peak is also significantly smaller than that of the corresponding peaks observed under propane combustion conditions and under CO<sub>2</sub> in He mixture. The above observations indicate clearly the formation of oxidic phases during pumping of sodium ions to the Pt catalyst in the presence of oxygen. Furthermore, they imply that the dominant peak observed in the linear sweep voltammograms under propane combustion conditions (Fig. 7a, b) is mainly due the decomposition of carbonate (or bicarbonate) phases formed upon interaction of CO<sub>2</sub> with the sodium species electrochemically supplied to the catalyst-electrode, although it may also contain a contribution corresponding to decomposition of oxidic phases.

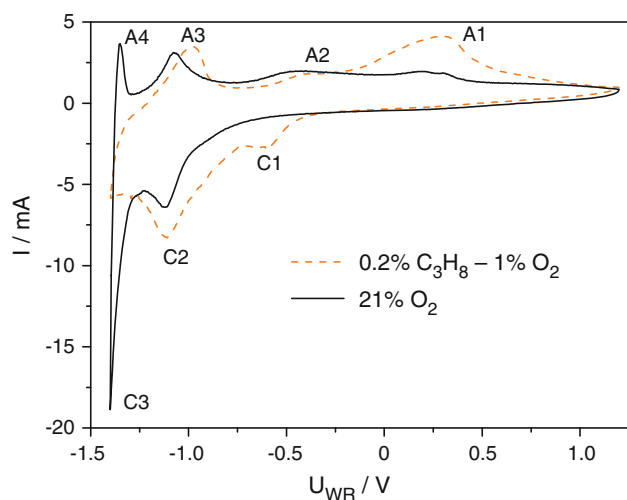
Figure 8 shows the effect of starting potential on the features of linear sweep voltammograms obtained at



**Fig. 8** Linear sweep voltammograms obtained at 360 °C under propane combustion conditions after previous application of different starting potentials, ranging from  $-0.4$  to  $-1.3$  V, for 5 min. P<sub>O<sub>2</sub></sub> = 1.0 kPa, P<sub>C<sub>3</sub>H<sub>8</sub></sub> = 0.2 kPa. Scan rate: 50 mV s<sup>-1</sup>. Flow rate: 85 cm<sup>3</sup> (STP) min<sup>-1</sup>

360 °C under reaction conditions (P<sub>O<sub>2</sub></sub> = 1 kPa and P<sub>C<sub>3</sub>H<sub>8</sub></sub> = 0.2 kPa in the reactor). The catalyst potential is held at a starting potential U<sub>start</sub> for 5 min (U<sub>start</sub> ranges from  $-0.4$  to  $-1.3$  V) and then the potential is linearly scanned up to 1.2 V, at a scan rate equal to 50 mV s<sup>-1</sup>. As shown in the figure, for starting potentials ranging from  $-0.4$  to  $-0.9$  V only one peak is observed (peak A1). Although direct comparison with the voltammograms presented in Fig. 1 is not possible in view of the difference in the experimental procedure, the position of this peak at  $\sim 0.5$  V implies that it most probably corresponds to peak A in Fig. 1. In view of the discussion concerning Fig. 7a, b it could be attributed to decomposition of carbonate and/or bicarbonate phases formed in the presence of the propane combustion products. For starting potentials  $-1$  and  $-1.2$  V a second more cathodic peak is observed (peak A2), although not well-developed, while for starting potential equal to  $-1.3$  V a third peak (peak A3) is clearly observed at  $-1.2$  V. The position of the not-well developed peak A2 shifts to higher potentials with decreasing starting potential, while, in parallel, the position of the more anodic peak A1 shifts to lower potentials. It is evident from the figure that the electric charge Q<sub>int</sub> which corresponds to the voltammograms increases with decreasing (absolutely increasing) starting potential. This is expected by the enhancement of sodium doping in view of the fact that application of a more negative (absolutely larger) potential yields to absolutely higher transient currents, i.e. to a higher average rate of sodium ion pumping to the catalyst-electrode.

Figure 9 shows cyclic voltammograms obtained at 360 °C under reaction conditions (P<sub>O<sub>2</sub></sub> = 1 kPa and



**Fig. 9** Cyclic voltammograms obtained at 360 °C under reaction conditions ( $P_{O_2} = 1.0$  kPa,  $P_{C_3H_8} = 0.2$  kPa) and under 21%  $O_2$  in He mixture. Scan rate: 50  $mV s^{-1}$ . Starting potential:  $-1.4$  V. Holding time at the starting potential: 5 min. Flow rate: 85  $cm^3$  (STP)  $min^{-1}$

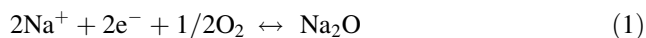
$P_{C_3H_8} = 0.2$  kPa in the reactor) and under 21%  $O_2$  in He mixture. The potential was linearly scanned between  $-1.4$  V (starting potential) and 1.2 V at a scan rate 50  $mV s^{-1}$ , after previously holding the electrode at the starting potential for 5 min. The voltammograms shown in the figure correspond to the 5th cycle after which practically no changes were observed. Under reaction conditions the main features of the voltammogram are three peaks appearing during the forward (anodic) scan, denoted as A1, A2 and A3 and two peaks appearing during the backward (cathodic) scan, denoted as C1 and C2. It is evident that the anodic peaks in this voltammogram correspond to the peaks in the linear sweep voltammogram shown in Fig. 8 for starting potential equal to  $-1.3$  V, being also centred very close to them. Under 21%  $O_2$  in He mixture peak C1 and, practically, peak A1 disappear, while two additional peaks, an anodic peak (denoted A4) and a cathodic peak (denoted C3), appear near the starting potential. The appearance of peaks A1 and C1 practically only under reaction conditions implies that these peaks are mostly related with the formation during the cathodic sweep and decomposition during the anodic sweep of carbon containing species, most probably sodium carbonate and/or bicarbonate species and that the contribution of oxidic phases in the formation of these peaks is minimal, in agreement with the conclusions drawn from the results presented in Fig. 7a, b. As already mentioned, peak A1 corresponds to the dominant peak A observed at 360 °C in the linear sweep voltammograms shown in Fig. 1. From Fig. 9 it can be concluded that peaks A3 and C2 are related mostly to decomposition/formation of oxidic phases, as their height increases with increasing oxygen partial

pressure, while peaks A4 and C3 are related exclusively with the decomposition/formation of oxidic phases as they do not appear under reaction conditions.

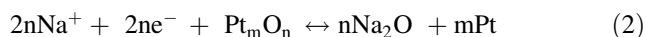
The observed features of the voltammograms in the present study can be discussed and explained on the basis of results of former spectroscopic and electrochemical studies, especially those concerning the identity of the promoting or poisoning species when  $\beta''$ - $Al_2O_3$  is used as active catalyst support for in situ electrochemical modification of the catalytic activity of metal catalyst-electrodes. In view of the preceding discussion, especially concerning the effect of gas phase composition on the voltammograms, the dominant peak (peak A) observed under reaction conditions in the linear sweep voltammograms shown in Fig. 1, obtained at 360 °C for polarization times  $t_{pol}$  higher than 2 min, as well as in the linear voltammograms shown in Fig. 4, obtained for temperatures lower or equal to 440 °C, can be related to the decomposition of sodium carbonate and/or bicarbonate species. Sodium carbonate species have been identified spectroscopically as the main constituent of the promoter or poisoning phases in the case of electrochemical promotion by sodium of the platinum-catalyzed combustion of propene [16] or ethylene [15]. Formation and decomposition of sodium carbonate and bicarbonate (formed in the presence of  $H_2O$ ) species has been related to the appearance of cathodic and anodic cyclic voltammetric peaks in the reaction of propene combustion on Pt/NaSiCon at 200 °C under  $C_3H_6/O_2$ : 0.04%/8.3% mixture [8] and on Pt/sodium- $\beta''$ - $Al_2O_3$  at 240 °C under  $C_3H_6/O_2$ : 2000 ppm/5% mixture [13]. The fact that more than one voltammetric peaks related to carbon containing sodium phases were observed under reaction conditions depending on temperature (Fig. 4) and sodium doping level (Figs. 1, 8) can be related to the co-existence of different sodium carbonate phases and/or the change in their nature with changing conditions.

As concluded from Fig. 9 as well as from Fig. 7a, b, the formation of sodium oxide phases during electrochemical pumping of sodium to the Pt catalyst and their contribution in the appearance of voltammetric peaks cannot be excluded. However, the extent of this contribution depends on the experimental conditions. It is clear from the aforementioned figures, that at 360 °C and below a certain level of sodium doping the contribution of the oxidic phases is minimal (Fig. 7a, b and peak A1 in Fig. 9), however it can become significant with increasing sodium doping (peak A3 in Fig. 9). Interaction of electrochemically pumped sodium species with oxygen or surface platinum oxides can result in the formation of various sodium oxide phases to a different extent depending on temperature, oxygen partial pressure and electrode potential [17]. Peaks C2 and A3 which appear in the cyclic voltammograms presented in Fig. 9 may be attributed to  $Na_2O$  formation during the

cathodic sweep followed by decomposition during the anodic sweep, according to the reaction



Peaks C3 and A4 in Fig. 9, which appear under 21% O<sub>2</sub> in He mixture but not under reaction conditions, may be attributed to Na<sub>2</sub>O formation and decomposition via the electrochemical reaction



This reaction is possible as surface platinum oxides (Pt<sub>3</sub>O<sub>4</sub>, PtO<sub>2</sub>, PtO) may be present on the electrode surface under 21% O<sub>2</sub> in He mixture in view of the affinity of platinum towards oxygen, which is enhanced by lowering platinum work function as a result of sodium pumping onto its surface [1–3]. Formation of binary oxides of sodium and platinum, e.g. Na<sub>x</sub>Pt<sub>3</sub>O<sub>4</sub> [22–24], via an electrochemical reaction similar to Reaction 2 may also contribute to the appearance of these peaks. It is noted that the multiplicity of peaks related to decomposition of sodium oxide phases (Figs. 7a, 9) has been also attributed by Staikov et al. [17] to the gradual decrease of the activity of the sodium oxide formed during the cathodic scan via Reaction 1 in the ceramic electrolyte in the vicinity of the electrode.

Under the conditions of the present study, i.e., in the temperature range 320–440 °C and for stoichiometric oxygen to propane ratio, it has been reported [18] that electrochemical pumping of sodium ions to the Pt catalyst results in decrease of the catalytic rate (electrophobic NEMCA effect), with the relative change in the rate being up to 60 times larger than the corresponding change in sodium coverage. This behavior, which implies a pronounced electronic poisoning effect of sodium, was explained by taking into account the propane combustion mechanism and the induced decrease in the work function of the gas exposed catalyst surface by increasing sodium coverage [1–4, 18] which in turn results in strengthening of the chemisorptive bond of oxygen (electron acceptor) and loosening of the chemisorptive bond of propane (electron donor) [18]. The results of the present study can be considered complementary to those presented in ref. [18] as they give an insight into the nature of the different sodium phases which are formed upon electrochemical pumping of sodium ions to the Pt catalyst, under different conditions. Combining electrochemical characterization with in situ or operando spectroscopic analysis could further clarify the exact chemical state of these phases.

#### 4 Conclusions

The formation/decomposition of the phases created on a Pt catalyst-electrode interfaced to sodium-β''-Al<sub>2</sub>O<sub>3</sub>, a Na<sup>+</sup>

conductor, upon electrochemical pumping of sodium ions to the Pt catalyst under conditions of propane combustion or under mixtures of O<sub>2</sub> or CO<sub>2</sub> in He was investigated using mainly linear sweep voltammetry as well as cyclic voltammetry, at temperatures between 320 and 480 °C. It was found that under these conditions different sodium phases can be formed, corresponding to current peaks in the obtained voltammograms. The number, position and magnitude of these peaks depended on gas phase composition, temperature, starting potential and pre-scan (initial polarization) conditions. The results of the voltammetric characterization indicate that under propane combustion conditions sodium carbonate or bicarbonate phases are mainly formed while formation of oxide phases is also possible via interaction of sodium species with gas phase oxygen, being enhanced by increasing sodium doping or, equivalently, decreasing the starting potential of the voltammetric scan. Under oxygen in He mixtures the formation of sodium oxide phases via interaction of sodium species with surface platinum oxides is also possible. These conclusions are in agreement with literature. However their validation as well as the detailed investigation of the exact nature of the phases which are related with the appearance of the current peaks in the voltammograms requires combining electrochemical characterization with in situ or operando spectroscopic analysis.

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