Ammonia Selective Oxidation on Pt(100) Sites in an Alkaline Medium

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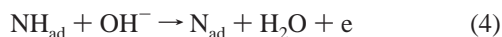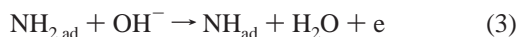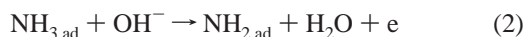
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The oxidation of ammonia on platinum surfaces is a structure sensitive reaction that takes place almost exclusively on Pt(100) sites. This report shows how dependent the activity is on different arrangements of (100) sites of platinum. The effect of two-dimensional domains has been addressed by using stepped surfaces having terraces with (100) geometry, either with (111) and (110) steps. The results were compared with those obtained from stepped surfaces having terraces with (111) or (110) symmetry and monatomic (100) steps, thus representing monodimensional (100) domains. The observed behavior confirms the extreme sensitivity of the reaction to the different arrangement of this type of square sites.
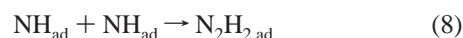
Introduction

Ammonia oxidation has been widely studied for many years. Among others, the aim of these studies has been applied to the development of fuel cells, the fabrication of electrochemical sensors for water analysis and for environmental purposes, trying to develop a method for its electrochemical destruction, due to the fact that ammonia is a common water pollutant in industrial wastewaters and in continental waters (it is extensively used as fertilizer). For elimination purposes, ammonia can be oxidized to different products, with nitrogen being the most suitable one, due to its ecologically friendly properties. In this way, the study of the electrochemical oxidation of ammonia is an important issue in environmental electrochemistry.

The most widely accepted mechanism for the ammonia oxidation in basic media on rough platinum surfaces was proposed in 1969 by Gerischer and Mauerer.[1] Tafel slopes were determined and shown to be temperature dependent. From this study, the active intermediates in the selective oxidation to N_2 were postulated to be NH_{ads} and $NH_{2,ads}$ that recombine to form N_2H_y ($y = 2-4$) species. Nitrogen is obtained after the oxidation of the intermediate N_2H_y, which happens in hydrazine oxidation on platinum.[2,3] The intermediates are obtained through a sequential series of reactions that can be simplified as

$$NH_{3,soln} \rightarrow NH_{3,ad} \tag{1}$$

$$NH_{3,ad} + OH^- \rightarrow NH_{2,ad} + H_2O + e \tag{2}$$

$$NH_{2,ad} + OH^- \rightarrow NH_{ad} + H_2O + e \tag{3}$$

$$NH_{ad} + OH^- \rightarrow N_{ad} + H_2O + e \tag{4}$$

$$2N_{ad} \rightarrow N_{2,soln} \tag{5}$$

These reactions generate a series of adsorbed intermediates that could react on the electrode surface in parallel steps:

$$NH_{2,ad} + NH_{2,ad} \rightarrow N_2H_{4,ad} \tag{6}$$

$$NH_{2,ad} + NH_{ad} \rightarrow N_2H_{3,ad} \tag{7}$$

$$NH_{ad} + NH_{ad} \rightarrow N_2H_{2,ad} \tag{8}$$

that finally lead to nitrogen through fast processes ($y = 4-2$):

$$N_2H_y + yOH^- \rightarrow N_2 + yH_2O + ye \tag{9}$$
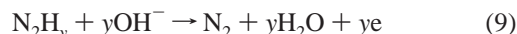
In all of these reactions, adsorbed OH was postulated as reaction partner[1] through the reaction

$$OH^- \rightarrow OH_{ads} + e \tag{10}$$

In agreement with this general behavior, hydrazine oxidation on platinum in alkaline solutions takes place at lower potentials than that of ammonia.[2] It was accepted, however, that dehydrogenation of NH_{ad} through reaction 4 implies surface blocking by the formation of strongly chemisorbed N_{ad}. Strongly adsorbed nitrogen atoms play the role of a surface poison, and reaction 5 is not convenient for nitrogen evolution. Tafel slopes as low as 35 mV/decade were obtained at high temperatures (80 °C) and interpreted through a main reaction path involving reactions 1, 2, and 6, the latter one being the rate determining step (rds). Higher Tafel slopes (80−110 mV/decade) such as those measured at 0 °C were a result of a change to a different rds, related to the $NH_{3,ad}$ oxidation to $NH_{2,ad}$.

This mechanism was later supported by differential electrochemical mass spectrometry (DEMS) experiments.[4] These studies confirm that oxygenated nitrogen species, such as NO, N_2O, nitrite, and nitrate, are formed only at high potentials for which adsorbed oxygen is present. Adsorbed oxygen would be able to oxidize the poison and clean the surface at these high potentials. De Vooys et al.[5] have also studied the activity for ammonia oxidation and the intermediates formed during ammonia anodic oxidation on platinum, palladium, rhodium, ruthenium, iridium, copper, silver, and gold polycrystalline surfaces. They reported that only the 5d metals platinum and iridium show a steady-state activity toward the selective formation of nitrogen.

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TABLE 1: Crystallographic Description of the Electrode Surfaces Used in This Work

zone	Miller indices	terrace-step notation
[0$\bar{1}$1]	(39,1,1)	20(100) × (111)
	(19,1,1)	10(100) × (111)
	(11,1,1)	6(100) × (111)
	(7,1,1)	4(100) × (111)
	(5,1,1)	3(100) × (111)
	(3,1,1)	2(100) × (111)
	(2,1,1)	3(111) × (100)
	(5,3,3)	4(111) × (100)
	(7,5,5)	6(111) × (100)
	(5,4,4)	9(111) × (100)
	(15,13,13)	14(111) × (100)
	(11,10,10)	21(111) × (100)
[001]	(15,1,0)	15(100) × (110)
	(9,1,0)	9(100) × (110)
	(6,1,0)	6(100) × (110)
	(4,1,0)	4(100) × (110)
	(3,1,0)	3(100) × (110)
	(2,1,0)	2(100) × (110)
	(3,2,0)	3(110) × (100)
	(5,4,0)	5(110) × (100)

These previous studies had been always carried out with polycrystalline surfaces. The first studies about the oxidation of ammonia on platinum single crystals were recently published by our group.[6] In this paper, we reported how sensitive this reaction is toward Pt(100) sites, where its oxidation almost exclusively takes place. More recently, platinum nanoparticles with a preferential structure of (100) have been synthesized and the ammonia oxidation has been employed to evaluate the amount of (100) sites[7,8] because of its sensitivity toward this type of geometry. The aim of the present work would be to explore systematically the reactivity of Pt(100) sites in ammonia oxidation, and both two-dimensional domains and one-dimensional domains will be considered. The first ones through the terrace width in a series of surfaces with terrace-step notations, Pt(S)[n(100) × (111)] and Pt(S)[n(100) × (110)], that would also show the role of the symmetry of the step. On the other hand, one-dimensional arrays of (100) step sites separated by terraces of (111) or (110) symmetry, Pt(S)[n(111) × (100)] and Pt(S)[n(110) × (100)], respectively, will be used to point out the influence of the symmetry of the neighbor terrace atoms on the reactivity of the surface toward the oxidation of ammonia, which is an example of a particularly structure sensitive process.

Experimental Section

Platinum single crystals were oriented, cut, and polished from small single crystal beads (2.5 mm diameter) by the procedure described previously.[9] The different electrodes used, including Miller indices, terrace-step notation, and crystallographic zone, are shown in Table 1. The electrodes were flame-annealed, cooled in a H_2 + Ar atmosphere, and protected with water in equilibrium with this gaseous mixture in the usual way.[10] It has been shown that this treatment leads to well-defined surfaces.[11] A single crystal platinum bead, obtained by melting and slow cooling of a Pt wire, was used as a well-defined polycrystalline surface having a uniform distribution of all surface sites.

Electrochemical experiments were carried out in a conventional three-electrode cell with a large Pt counter electrode. As reference, a Reversible Hydrogen Electrode (RHE) electrode placed in a separate vessel was used. Ammonia solutions (10^{-3} M) were obtained by the addition of $(NH_4)_2SO_4$ to a 0.1 M NaOH solution. Both reagents were of p.a. quality (Merck). It is known that sulfate specific adsorption does not take place on platinum at such high pH values. Solutions were prepared
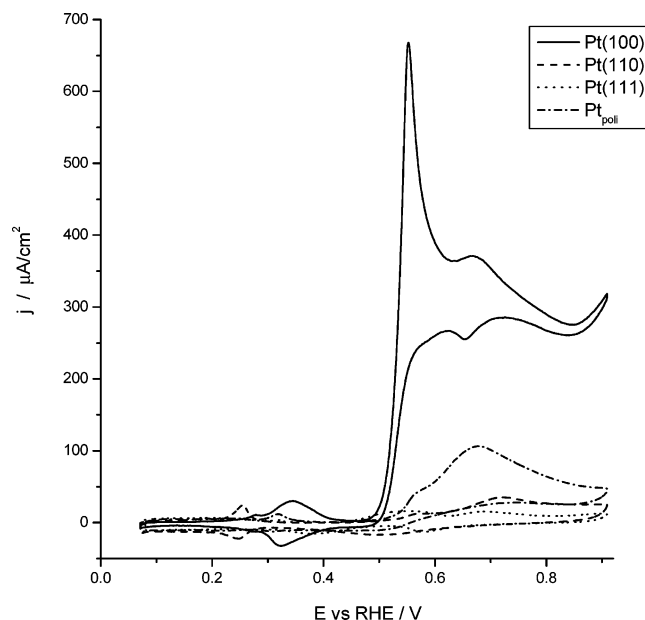

Figure 1. Voltammetric profiles of Pt(100), Pt(110), Pt(111), and polyoriented Pt single crystal in 0.1 M NaOH and 10^{-3} M NH_3. Scan rate 10 mV·s^{-1}.

using Millipore Milli-Q water. Oxygen was eliminated by bubbling Ar (Air Liquide N50) for 20 min. The Ar atmosphere was maintained inside the cell during the experiments. To maintain a constant concentration of the solution, the gas was previously bubbled through a solution of the same composition as that in the electrochemical cell. All the voltammograms presented are the first cycle after the flame-annealing and cooling treatment, when the surface is not poisoned at the beginning of the cycle.

Results

The selectivity of ammonia oxidation toward Pt(100) sites is clearly reflected in Figure 1 that shows the corresponding voltammograms on the three platinum basal planes and on the polyoriented single crystal platinum bead in 0.1 M NaOH and 10^{-3} M NH_3. The polyoriented single crystal shows a well-marked peak at 0.67 V and a shoulder in its ascending branch at about 0.55 V. Concerning basal planes, Pt(111) and Pt(110) show a very small reactivity, whereas in the case of Pt(100) a very sharp peak with a high current density is observed at comparatively lower potentials. These results reflect clearly that ammonia oxidation is a structure sensitive process.

In the case of Pt(100), the main peak of the ammonia oxidation takes place at 0.55 V. This potential is similar to the well-marked shoulder observed on the polyoriented platinum single crystal. In this way, it seems fairly straightforward to assume that this shoulder is related to the presence of long (100) domains on the polyoriented platinum single crystal, as they are indeed observed as small facets in the middle of a square array of larger (111) facets. As a result of these observations, the oxidation of ammonia on stepped surfaces containing (100) sites will be described in the following.

Two-Dimensional (100) Domains. The effect of the Pt(100) terrace width was studied with stepped surfaces having both (111) and (110) monatomic steps in order to point out long range order effects, as well as the modification of its reactivity due to the symmetry of the step. Figure 2 shows the characteristic voltammograms for several Pt(S)[n(100) × (111)] stepped surfaces and also for Pt(100) in a 0.1 M NaOH solution
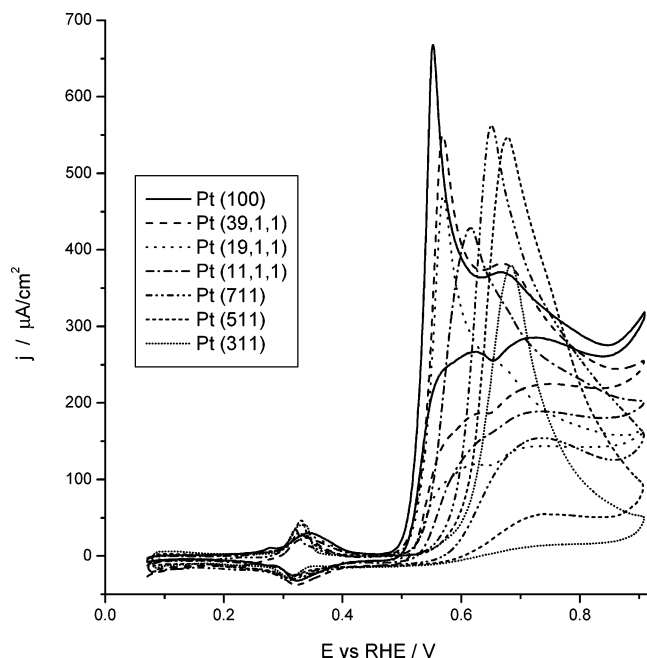
Figure 2. Voltammetric profiles of Pt(111), Pt(39,1,1), Pt(19,1,1), Pt(11,1,1), Pt(711), Pt(511), and Pt(311) in 0.1 M NaOH and 10^{-3} M NH$_3$. Scan rate 10 mV·s^{-1}.
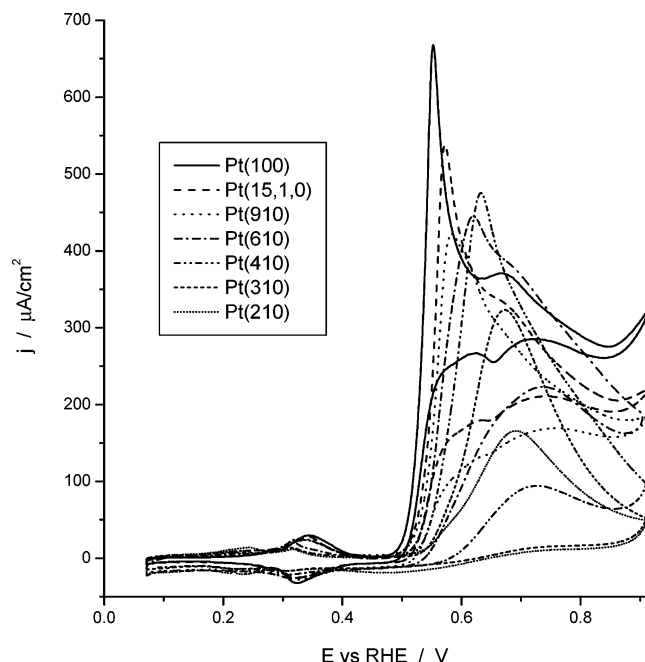

Figure 3. Voltammetric profiles of Pt(100), Pt(15,1,0), Pt(910), Pt(610), Pt(410), Pt(310), and Pt(210) in 0.1 M NaOH and 10^{-3} M NH$_3$. Scan rate 10 mV·s^{-1}.

containing 10^{-3} M NH$_3$. These stepped surfaces have Pt($2n -$ 1,1,1) Miller indices, where n is the number of atoms in the terrace (terrace width). In a preliminary study,[6] it was remarked that the effect of narrowing the terrace had important effects on the final reactivity, because the intensity of the main oxidation peak of ammonia oxidation diminishes and its potential shifts toward more positive values. In the results shown in Figure 2, it is observed that this trend is partially broken at surfaces having intermediate terrace lengths, such as Pt(511) and Pt(711). In these cases, an increase in the current density with respect to longer (100) terraces such as Pt(39,1,1), Pt(19,1,1), or Pt(11,1,1) electrodes is unexpectedly attained. However, the potential of the main peak regularly increases when narrowing terrace width.

In the case of Pt(100) (see also Figure 1 for the sake of clarity), Pt(19,1,1), Pt(11,1,1), Pt(711), and another peak at 0.66 V can also be observed in the descending branch of the main peak. In the negative-going scan, these four electrodes show a reduction peak at 0.65 V, which is likely related to the species generated in that previously described. This redox couple is also sensitive to the terrace width, and its intensity progressively decreases in such a way that is negligible on Pt(511) and Pt(311) electrodes. In these latter cases, only a bell-shaped main oxidation peak at 0.68 V is observed.

The DEMS studies carried out up to now[4] show that nitrogen is the main product at 0.70 V and nitrogen oxides at potentials higher than 0.80 V on polycrystalline platinum. In this way, the second couple of peaks could be attributed to the formation of these oxides but at a lower potential in the case of (100) sites or maybe to the oxidation to NO$_2^-$ or NO$_3^-$ that cannot be studied with DEMS. These peaks are also observed in the case of Pt(S)[n(100) × (110)] stepped surfaces, as will be presented below and at the same potential. This fact suggests that this redox couple cannot be related to the oxidation of intermediate species at (111) geometry sites.

A similar result is shown in Figure 3, where the voltammograms have been recorded for Pt(S)[n(100) × (110)] stepped surfaces, having Pt(n,1,0) Miller indices, under the same

conditions as in the previous series. In this case, it is also possible to observe how intermediate terrace-length surfaces such as Pt(610) and Pt(410) have higher current densities than Pt(910), in a parallel way as it has been previously mentioned for Pt(S)[n(100) × (111)] electrodes. In the present series of surfaces, Pt(610) appears to have an intermediate behavior between long and short terraces. As in the previous series, a second peak can be also observed at 0.66 V, in the descending branch of the main peak, and it also has a counterpart in the same position as in the previous series. This suggests that this reaction seems to be a nonsensitive reaction to the symmetry of the steps, thus reinforcing the conclusion that this redox process takes place on (100) terrace sites.

All of these results are summarized in Figure 4 that shows the plot of current density values measured at 10 mV·s^{-1} versus the step density for both the Pt(S)[n(100) × (111)] and Pt(S)[n(100) × (110)] series. In this figure, two different trends can be appreciated, one for long (100) terraces and the other for short ones. A transition at intermediate terraces is also observed in both cases.

The voltammograms presented in Figures 2 and 3 show how such a small molecule as ammonia is so sensitive to the width of (100) terraces. This fact is also confirmed with the measurements of the Tafel slope, which changes from 28 mV/decade on Pt(100) to 94 mV/decade on Pt(311). On Pt(210), the log j/E plot shows two slopes, the first one is 40 mV/decade at low potentials and the second is 128 mV/decade at more positive potential values. This suggests that the reaction kinetics could play a significant role in the observed voltammetric behavior. As it has been described, the 35 mV/decade slope was observed on platinum black electrodes at high temperatures and was related to the consideration of recombination reaction 6 as the rds after reactions 1 and 2:

$$2NH_{2,ad} \rightarrow N_2H_{4,ads} \qquad (6)$$

Hydrazine will be oxidized very fast at these relatively high potentials.[2] In relation to the formation of the NH$_{2,ad}$ intermediates, the potential of zero total charge of Pt(100) electrodes,

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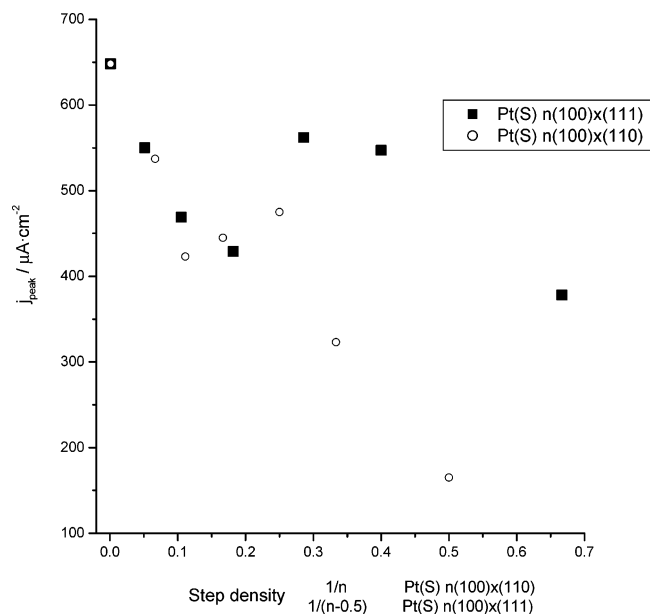*J. Phys. Chem. B, Vol. 109, No. 26, 2005* **12917**

Figure 4. Correlation between the current density of the main ammonia oxidation peak and Pt(111) and Pt(110) step density on Pt(100) terraces for Pt(S)[n(100) × (111)] and Pt(S)[n(100) × (110)] surfaces. Solution 0.1 M NaOH and 10^{-3} M NH$_3$. Scan rate 10 mV·s^{-1}.

0.43 V versus RHE at pH 12,[12] is lower than that required to oxidize ammonia. In this way, the general reaction scheme proposed by Gerischer and Mauerer that involves adsorbed OH species[1] can be maintained. Under the present conditions, this mechanism would take place on large (100) terraces. As the number of step sites increases, the current density diminishes because the concentration of active intermediates on the terraces decreases, due to their disappearance by stronger adsorption on step sites. Finally, a transition is produced at higher potentials and a new, more oxidized intermediate species becomes the predominant one. Higher Tafel slopes reflect that the active intermediate NH$_{2,ad}$ could be retained on the step sites and thus not be able to dimerize and form hydrazine but oxidize further to NH$_{ad}$. This would be equivalent to the behavior observed by Gerischer et al.[1] at low temperatures, in which the mobility of the intermediate NH$_{2,ad}$ would be limited. In the same way as the terrace width diminishes, the mobility of the NH$_{2,ad}$ species would be restricted by the increasing density of steps. At the present stage, it appears to be clear that careful kinetic studies on selected well-defined surfaces are necessary to understand the reactivity of the different surface sites to the postulated intermediates. Systematic kinetic studies are part of an ongoing project in our laboratory in which surface spectroscopy would also be incorporated in an attempt to characterize possible intermediates.

Interesting situations are also observed with intermediate terraces: the 4-atom (100) terrace-length electrode with monatomic (111) steps, Pt(711), shows a higher current density of the main peak than the equivalent 20-atom one of the same series, Pt(39,1,1). In the same way, a 9-atom terrace separated by (110) monatomic steps, Pt(910), shows a higher current density than that of longer terraces. This plot likely reflects a change in the relevant steps of the reaction mechanism: at higher potentials, the intermediates controlling the rate determining step of the reaction can change and thus relatively small (100) terraces with (111) or (110) steps become more active toward ammonia oxidation concerning current density.

Although for Pt(S)[n(100) × (111)] and Pt(S)[n(100) × (110)] the results are very similar, it is interesting to point out the
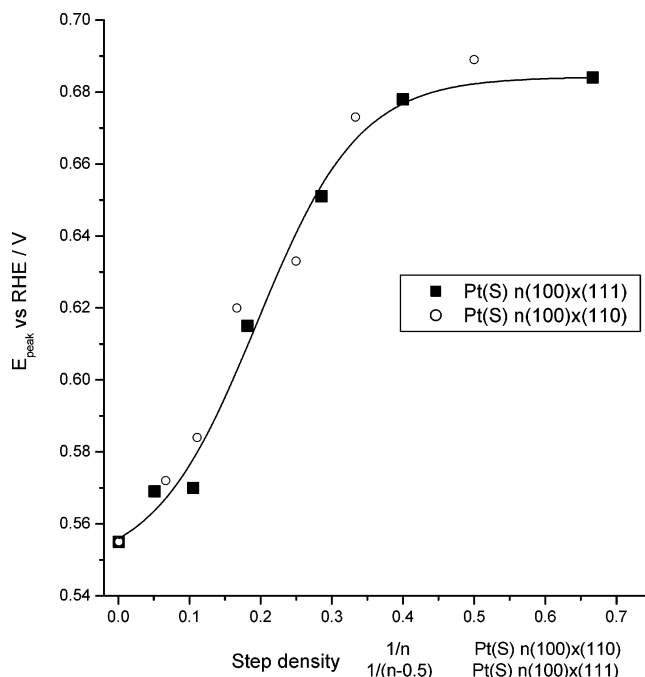

Figure 5. Correlation between the potential of the main ammonia oxidation peak and Pt(111) and Pt(110) step density on Pt(100) terraces for Pt(S)[n(100) × (111)] and Pt(S)[n(100) × (110)] surfaces. Solution 0.1 M NaOH and 10^{-3} M NH$_3$. Scan rate 10 mV·s^{-1}.

difference between the effects of (111) and (110) steps on (100) terraces. It is clearly visible that the shape of the voltammograms and the current densities of the peaks are different for the same "n" values (terrace length). The most remarkable difference is observed in the limiting case of two-atom-length (100) terraces, respectively the Pt(311) and Pt(210) electrodes, where the current density on the Pt(311) electrode doubles that measured on the Pt(210) electrode. This points out a higher ability of the (110) step sites to retain the possible intermediates of the reaction adsorbed, with respect to the (111) step sites. Moreover, we have assumed that there are two different trends, for long and short terraces, with the short ones showing a higher current density in the presence of (111) steps as it happens also for the intermediate surfaces. On the other hand, for long (100) terraces, the effect seems to be independent of the step geometry, as would be expected if the reaction is mainly carried out on the wide (100) domains. In this case, the low density of step sites would not have the possibility to show significant differences in ammonia oxidation.

Although the (110) and (111) steps cause different effects concerning current densities, if we pay attention to the main peak potential, we can see a clear unique trend, as is shown in Figure 5, where the potential of the main peak is presented versus the step density for both Pt(S)[n(100) × (111)] and Pt(S)[n(100) × (110)] electrodes. In this case, the trend is uniform and there are no differences for long, intermediate, or short terraces, irrespective of the symmetry of the step. This result is compatible with the previous assumption of a change of the intermediate reactive species from NH$_{2,ads}$ to NH$_{ads}$ as the potential increases.

One-Dimensional Domains. For a better understanding of the role of (100) sites in the ammonia electrochemical oxidation on platinum in alkaline solution, it seems interesting to compare the previous results with those given by stepped platinum surfaces having (111) or (110) terraces regularly separated by (100) monatomic steps. First of all, the series having (111) terraces will be studied. Figure 6 shows the voltammetric
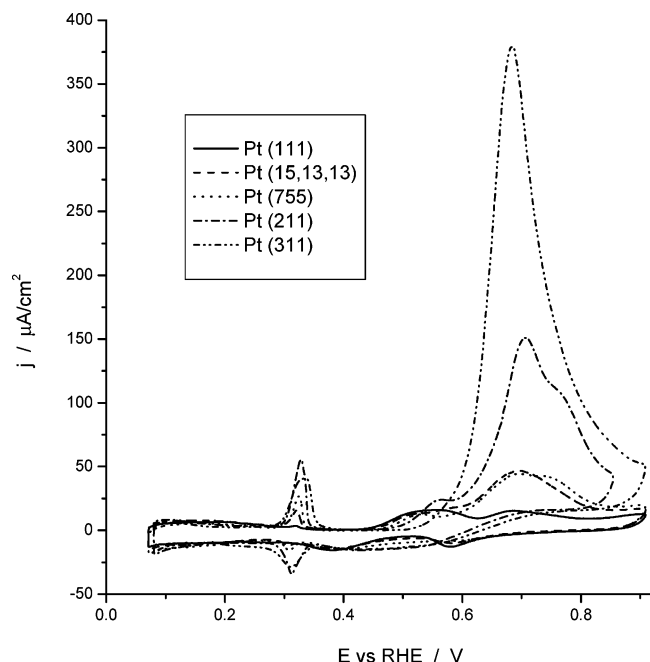
Figure 6. Voltammetric profiles of Pt(111), Pt(15,13,13), Pt(755), Pt(211), and Pt(311) in 0.1 M NaOH and 10^{-3} M NH$_3$. Scan rate 10 mV·s^{-1}.

Figure 7. Voltammetric profiles of Pt(110), Pt(540), Pt(320), and Pt(210) in 0.1 M NaOH and 10^{-3} M NH$_3$. Scan rate 10 mV·s^{-1}.

profiles of Pt(S)[n(111) × (100)] stepped surfaces, having Pt(n + 1,n − 1,n − 1) Miller indices. The oxidation process takes place at much higher potentials than on the wide (100) terraces discussed previously, so the reaction would likely be carried out by more oxidized intermediates. It is clear that the current density becomes higher when the (100) step density increases. Although the voltammetric profiles look quite complicated, three different contributions could be distinguished. At approximately 0.52 V, there is a small shoulder, likely due to the oxidation of ammonia on wide (111) terraces because it is more important on the Pt(111) basal plane. The other two are more easily observed in surfaces with short (111) terraces and (100) steps at 0.70 and 0.75 V as Pt(211) and Pt(533) (three and four terrace atoms, respectively). The peak at about 0.70 V is related to (100) sites, whereas the one at 0.75 V could reflect a two-step kinetics. In this way, the reaction could start on Pt(100) sites and the intermediates would diffuse to (111) sites where further reaction on these sites at slightly higher potentials might take place. As will be shown below, this behavior does not occur on surfaces with (110) terraces with (100) steps, so this second step could also be a structure sensitive reaction that only takes place on (111) sites. In the particular case of Pt(311), which corresponds to the turning point of the [0$\bar{1}$1] zone (the terraces are only one atom wide), this behavior is not observed and there is only one contribution, agreeing with the trend shown before in surfaces with (100) terraces and (111) steps. In the case of long (111) terraces, as Pt(15,13,13), there is only one peak at about 0.70 V, related to the NH$_3$ oxidation at the step sites.

Concerning (110) terraces with (100) monatomic steps, Figure 7 shows the effect of increasing the density of (100) steps in the series Pt(S)[n(110) × (100)], having Pt(n,n − 1,0) Miller indices. The effect of the increase in the step density makes the main oxidation peak shift toward less positive values and the current density get higher, as is expected for this reaction, extremely sensitive to the density of (100) sites on the surface.

A relevant description of these voltammetric results is summarized in Figures 8 and 9 that report current densities and main peak potentials for both series of surfaces. It should be
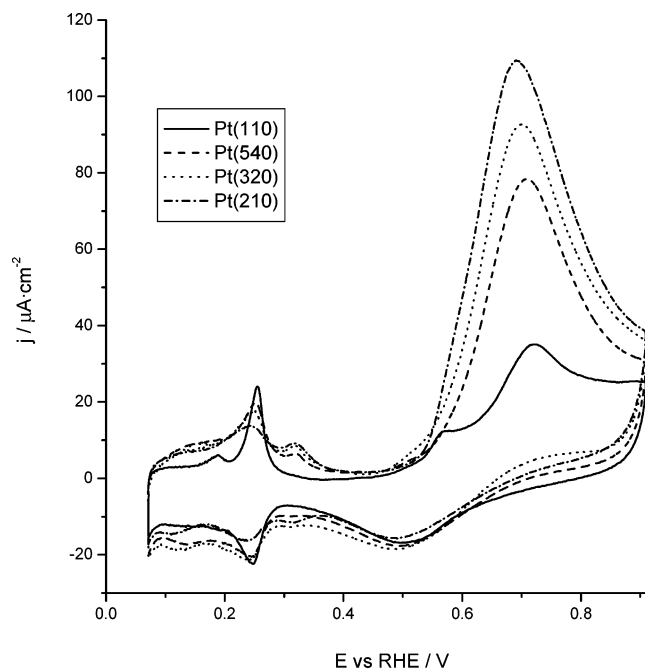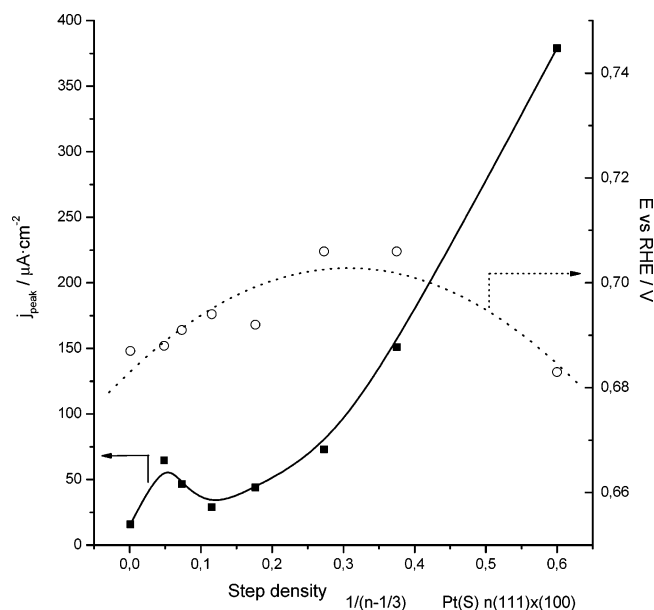

Figure 8. Evolution of the current density of the main ammonia oxidation peak (solid line) and the potential of the main ammonia oxidation peak (dotted line) vs the step density for Pt(S)[n(111) × (100)] electrode surfaces. Solution 0.1 M NaOH and 10^{-3} M NH$_3$. Scan rate 10 mV·s^{-1}.

stressed that the currents are quite small on surfaces having a low density of (100) steps and small differences in the thermal treatment could cause some modifications in the reported values. This could also be considered as an example of the limitations of the work with single crystals under meniscus configuration to perform kinetic studies at limiting electrode activity: small surface disorder or faceting may lead to apparent irregular behavior.

In the case of the Pt(S)[n(111) × (100)] series, Figure 8, the main peak potentials appear to be constant, although the lowest value corresponds to the surface having the highest density of (100) steps. Currents also increase as the step density increases, steeply at the highest step densities, thus suggesting that the
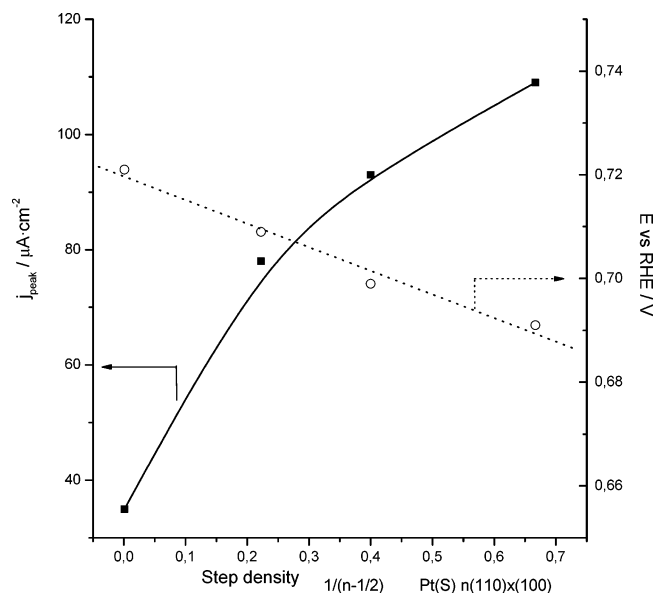
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Figure 9. Evolution of the current density of the main ammonia oxidation peak (solid line) and the potential of the main ammonia oxidation peak (dotted line) vs the step density for Pt(S)[$n(110) \times (100)$] electrode surfaces. Solution 0.1 M NaOH and 10^{-3} M NH$_3$. Scan rate 10 mV·s^{-1}.

reaction takes place mainly on this type of sites. In this way, ammonia oxidation around 0.7 V is faster on one-dimensional (100) arrays than on terraces with (111) symmetry. The same is observed in the other series, Pt(S)[$n(110) \times (100)$], Figure 9. In this case, the main peak potential decreases linearly with the step density. At the same time, current densities increase as the density of the (100) steps on the surface increases. There is however a main difference with respect to the previous series, because the current density increase is not so steep and the highest current densities are about one-third of those measured on the surfaces having (111) sites. It appears that the combination of (111) × (100) sites is more effective that that of (110) × (100) sites for ammonia oxidation. These results also support the idea that the reaction kinetics is very complex and that detailed studies are necessary to understand the particular behavior of the surface sites on the final reactivity.

Conclusions

The oxidation of ammonia on platinum is a clear structure sensitive process that takes place almost exclusively on Pt(100) sites. It appears that the ammonia molecules are also able to discriminate the width of the (100) terraces and the density of steps with (100) symmetry, showing how the potential and the current density of the main oxidation peak change for the different stepped surfaces. A special sensitivity to the size of (100) terraces has been pointed out. This result is quite surprising considering the small size of the ammonia molecule (N−H = 0.102 nm, H−H = 0.163 nm) and its umbrella geometry. In addition, the reaction may involve contributions either from adsorbed OH species or from OH$^-$ in solution, since the potential of zero total charge (pztc) of the electrodes is lower than the potential range at which the reaction takes place at an appreciable rate.

Two different trends have been reported for two-dimensional (100) domains (terraces). The same behavior is observed for wide terraces, irrespective of the presence of (111) or (110)

steps, whereas on short terraces higher current densities are obtained in the case of surfaces having (111) steps. It appears that the (100) × (111) junction is more effective than the (100) × (110) one for ammonia oxidation. A similar result is observed in the case of one-dimensional (100) domains (steps), where the combination of $n(110) \times (100)$ sites inhibits the reaction rate more effectively than that of $n(111) \times (100)$ sites. This fact points out the role of the surface in the adsorption of the active intermediate species that may appear in this complex electrocatalytic reaction involving at least three electrons and three N−H bond breakings per ammonia molecule.

Interestingly, the Tafel slopes measured on large terraces, and especially the Pt(100) basal plane, are comparable to the behavior reported at high temperature on platinum black electrodes. This suggests that the surface long range order can play as a parameter in the reaction kinetics, diminishing the activation energy of the reaction. This point is likely related to the mobility of intermediate adsorbed species and would require more investigation. In particular, a systematic study of the reaction at different temperatures on different single crystal electrodes will be carried out in our laboratory. A remarkable result has been reported for intermediate terraces that show higher oxidation currents than some surfaces with longer (100) terraces. All of these differences are likely due to the different surface stabilities of the intermediates that can appear it this complex reaction. The geometry of the surface may affect the different stabilities of the intermediates that can appear in the reaction. This shows how reaction kinetics is affected by the surface structure, not only by the site symmetry but also by its neighborhood. Despite the fact that these conclusions can be easily suggested from voltammetric data, more work should be done in relation to the elucidation of the reaction mechanism on the different electrodes to clarify the details of this specially structure sensitive reaction.

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