

ADSORPTION OF METHANOL AT POLYCRYSTALLINE Pt AND LOW INDEX Pt
SINGLE CRYSTALS: A VOLTAMMETRIC STUDY OF IRREVERSIBLE
ADSORPTION ON Pt(100)

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Abstract

The oxidative adsorption of 0.1 M methanol in 1 M HClO₄ on Pt(111), (110), (100) and Pt(poly) electrodes was studied by cyclic voltammetry. Freshly prepared single crystals were immersed in methanol-containing solution at 0.05 V vs. r.h.e. The voltammetric profiles of the very first positive-going potential scan exhibit a well defined anodic current peak around 0.40 V only for the Pt(100) face. The peak current (*i_p*) and potential (*E_p*) were evaluated as function of the potential sweep rate. The adsorption process was assigned to an irreversible surface reaction of methanol with Pt (100) leading to the formation of oxidative adsorbed intermediates. The interpretation of the experimental data indicates that the second electron transfer, i.e. the second deprotonation reaction of CH₃OH, was the rate-determining step.

Keywords: Pt single crystals, methanol, oxidative adsorption, cyclic voltammetry.

Introduction

The electrooxidation of methanol on Pt in acid solution to CO₂ and partially oxidized products (HCHO, HCOOH and HCOOCH₃) is accompanied with the formation of strongly adsorbed intermediates. These species poison the catalyst surface and are being regarded as the main reason for the rather low reaction rate for methanol oxidation. However, the direct electrochemical methanol oxidation is an attractive option for fuel cell application [1]. The numerous papers concerning this electrochemical reaction has been summarized in several review articles [2-4]. A

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structural effect for methanol oxidation has been observed on low index platinum single crystals [5-11].

The adsorption process involves several dehydrogenation reactions according to the general reaction scheme first proposed by Bagotzky et al [12]:



Spectroscopic methods have been used in order to elucidate the structure of adsorbed intermediates formed in reactions (1)-(4). Adsorbed CO [12,13] as well as COH, HCOH and H₂COH species [11,14] have been detected on polycrystalline Pt. *In situ* FTIR and EMIRS spectra on Pt(100), Pt(110) and Pt(111) reveal terminally bonded (on-top) CO as the major component of such an adlayer, although bridge bonded CO is also formed on Pt(111) and Pt(100) [7-11]. For the latter face, interconversion between CO-species occurs in the 0.25-0.50 V potential range vs. r.h.e [11]. On Pt(111) and Pt(110), beside the detection of (CO)_{ad}, other hydrogenated adsorbed species such as HCO and COH have been observed by EMIRS [8,9] and FTIRS [11], respectively.

In spite of a great number of spectroscopic data concerning the nature of adsorbed intermediates, kinetic aspects of the adsorption reaction of methanol on an unpoisoned Pt surface (i.e. not covered with organic intermediates), are still rather unclear. The reaction of methanol on an unpoisoned polycrystalline Pt electrode has been first studied by Stonehart by means of cyclic voltammetry using a flow cell technique [15]. The experimental procedure used by this author consisted of the following steps: 1) after potential cycling of the Pt electrode between 0.05 and 1.60 V vs. NHE in 1 M HClO₄, the potential was held constant at 0.05 V; 2) the electrolyte was exchanged against 0.01 M methanol solution at 0.05 V; and 3) a positive-going potential scan starting at 0.05 V up to 1.60 V was recorded in this solution. Under these conditions, a broad anodic current peak has been observed at about 0.35 V vs. nhe in the very first positive-going potential scan which was not apparent in the second and following scans in the methanol-containing solution [15]. A combination of cyclic voltammetry and on-line mass spectrometry has recently shown that no volatile and gaseous reaction products are detected parallel to this voltammetric peak [11,16]. This fact provides evidence that the peak is associated to the formation of adsorbed species and confirms the occurrence of

dehydrogenation reactions of methanol on the Pt(poly) surface of those types given in equations (1)-(4). Moreover, these results demonstrate that for polycrystalline Pt the rate of the oxidative adsorption of methanol is very slow at $E_{ad} = 0.05$ V since the surface is largely covered by adsorbed hydrogen at this potential.

The purpose of the present work is to investigate the *oxidative adsorption of methanol* on low index Pt single crystal surfaces by means of cyclic voltammetry using the experimental concept previously designed by Stonehart in [15], but adapted to the single crystal configuration. In this way, the adsorption process on an unpoisoned Pt surfaces can be studied under potentiodynamic conditions and new kinetic data can be calculated.

Experimental

Pt(poly) (real area = 0.71 cm^2) and Pt single crystals (real area = 0.48 cm^2) were prepared at Forschungszentrum Jülich and polished with an orientation accuracy of $\pm 0.1^\circ$ [17]. Two electrochemical cells were used for the experiments, one containing pure base electrolyte (1 M HClO_4), and the second containing a 0.1 M $\text{CH}_3\text{OH}/1 \text{ M HClO}_4$ solution. In both cells, an annealed Pt wire was used as counter electrode and the potentials were measured against the reversible hydrogen electrode (rhe) in the same electrolyte solution. At the beginning of each set of experiments, the working electrode was annealed in a gas/oxygen flame and cooled in a $\text{H}_2 + \text{Ar}$ stream according to the method proposed by Clavilier et al. for single crystals [18]. Then the electrode was transferred into the first electrochemical cell protected by a droplet of water in equilibrium with the cooling gases, and contacted the electrolyte solution at $E = 0.05$ V vs. rhe using the hanging meniscus method. Subsequently, a potential scan was started in the positive direction at $dE/dt = 0.050 \text{ V}\cdot\text{s}^{-1}$ and the quality of the surface was checked. The voltammetric profiles corresponding to the first and second potential cycles for the Pt(100), (110) and (111) faces in the potential range of hydrogen adsorption/desorption are shown in Fig. 1. A slight difference between both cycles is observed in the positive-going scan. These profiles starting from 0.05 V are comparable with literature data [10,18-20].

After checking the cleanliness of the single crystals, the adsorption reaction of methanol at unpoisoned Pt surfaces was studied. For this purpose the working electrode was annealed and treated again as described before, and contacted at 0.05 V with a 0.1 M $\text{CH}_3\text{OH}/1 \text{ M HClO}_4$ solution in the second electrochemical cell. Two potential cycles starting from 0.05 V up to 0.55-0.60 V were

performed avoiding the oxidation of the adsorbed species formed at lower potentials [6]. Methanol (p. a.) and perchloric acid (suprapur) were obtained from Merck. All experiments were carried out at room temperature.

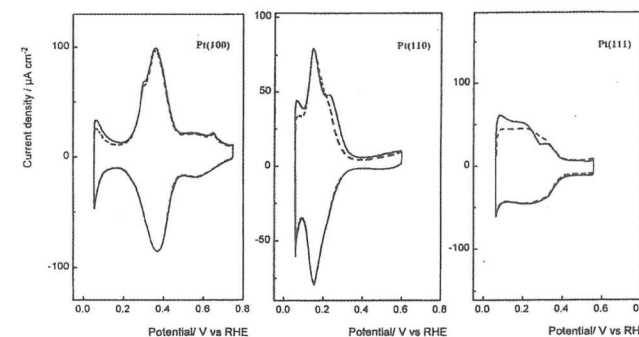


Figure 1. Cyclic voltammograms of Pt single crystals at $v = 0.050 \text{ V s}^{-1}$ in 1 M HClO_4 . The electrodes were flame annealed, cooled in a $\text{H}_2 + \text{Ar}$ mixture and contacted the solution at 0.05 V. (—) first cycle; (---) second cycle.

Results and Discussion

The oxidative adsorption of methanol was first studied on polycrystalline Pt using the hanging meniscus configuration, in order to check the experimental procedure by comparison with previous results in the literature. Fig. 2a shows the first and second cycle for Pt(poly) at $v = dE/dt = 0.05 \text{ Vs}^{-1}$ in 1 M HClO_4 , whereas in Fig. 2b the corresponding voltammetric profile in 0.1 M $\text{CH}_3\text{OH}/1 \text{ M HClO}_4$ is given. Similar features as those previously described by Stonehart [15] were observed during the first positive-going potential scan: a broad anodic current is apparent at about 0.35 V followed by an exponential increase in the current [16]. However, in Fig. 2b two peaks at 0.33 and 0.38 V can be seen, in contrast to only one at 0.35 V shown in references [15] and [16]. This result is explained in terms of the differences in the experimental procedure: in the present paper the electrode was annealed before each experiment and the anodic potential limit was adjusted at 0.55 V in order to compare results with those obtained on Pt single crystals. During the second potential scan (Fig. 2b, dashed line), the hydrogen adsorption region is partially blocked by the presence of adsorbed intermediates formed during the first potential cycle.

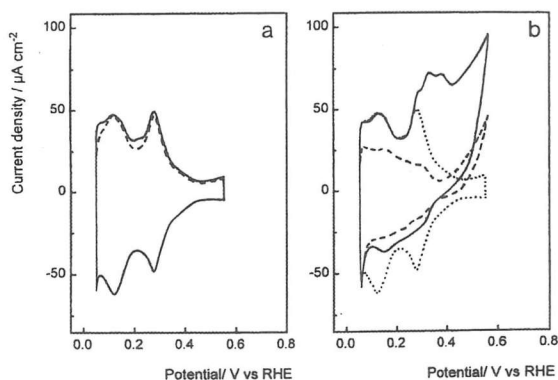


Figure 2. Cyclic voltammograms of polycrystalline Pt at $v = 0.050 \text{ V s}^{-1}$ (same experimental procedure as in Fig. 1). a) 1 M HClO_4 . (—) first cycle; (---) second cycle. b) 0.1 M $\text{CH}_3\text{OH} + 1 \text{ M HClO}_4$. (—) first cycle; (---) second cycle; (.....) supporting electrolyte.

Figs. 3a-c show the first (solid line) and second (dashed line) potential cycles between 0.05 and 0.60 V for the experiments carried out with Pt(100), Pt(110) and Pt(111) at 0.05 Vs^{-1} in 0.1 M $\text{CH}_3\text{OH}/1 \text{ M HClO}_4$ following the procedure described in the experimental section.

A well defined anodic peak is observed only for the (100) face at 0.38 V (Fig. 3a). The peak potential (E_p) coincides with the second peak observed at Pt(poly) for the same experiment.

At Pt(110) (Fig. 3b), the current in the methanol-containing solution is somewhat lower than in pure electrolyte up to potentials of 0.28 V. This fact indicates that methanol reacts to a certain extent at the starting potential. In the range between 0.28 and 0.40 V, an anodic current is recorded during the first cycle but no peak is apparent. This contribution may correspond to the superposition of the dissociative adsorption and the bulk oxidation of methanol, and could be responsible for the first peak at 0.33 V observed at the polycrystalline surface.

Finally, on Pt(111) the difference in the voltammetric profiles between 1 M HClO_4 and 0.1 M $\text{CH}_3\text{OH}/1 \text{ M HClO}_4$ in the hydrogen adsorption/desorption region, is the least pronounced of all surfaces, in agreement with previously reported data [8].

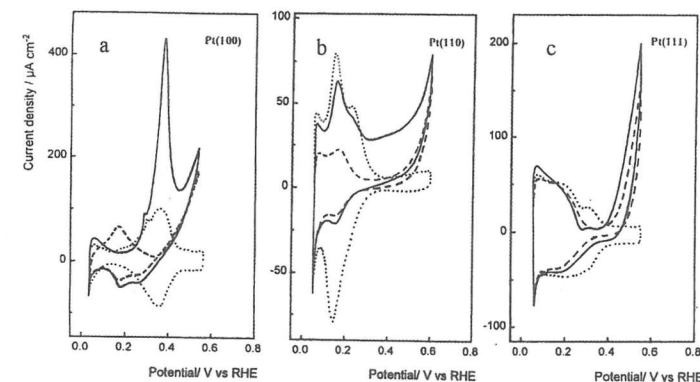


Figure 3. Cyclic voltammogram of Pt single crystals at $v = 0.050 \text{ V s}^{-1}$ in 0.1 M $\text{CH}_3\text{OH} + 1 \text{ M HClO}_4$ (same experimental procedure as in Fig. 1). (—) first cycle; (---) second cycle; (.....) supporting electrolyte. a) Pt(100); b) Pt(110); c) Pt(111).

The inhibitory effect of adsorbed hydrogen for methanol reaction is clearly shown for Pt(100) (Fig. 3a). Methanol does not react at 0.05 V. However, as hydrogen desorption commences at $E > 0.20 \text{ V}$ (see Fig. 1 and dotted line in Fig. 3a), a peak appears at 0.38 V associated to the oxidative methanol adsorption. This anodic current peak is superimposed with the hydrogen desorption peak at the same potential, which is visible in the methanol-free solution. In the second cycle the hydrogen region is partially blocked by the presence of adsorbed intermediates formed during the first potential sweep. It is interesting to note that the anodic peak related to hydrogen desorption appears at 0.18 V during the second positive-going potential scan (Fig. 3a dashed line), whereas for the unpoisoned surface this contribution is centered about 0.37 V (Fig 3a dotted line). Therefore, it can be concluded that the presence of the adsorbates formed from methanol during the first cycle induces the hydrogen desorption to occur at lower potentials, i.e. the energy of the Pt-H bond is decreased by the presence of the coadsorbed layer. Comparable features were observed after the adsorption of formic acid on Pt(100) in 0.1 M HClO_4 [21].

The oxidative methanol adsorption at Pt (100) was then studied in more details at several scan rates in the range between 0.005 and 0.200 V s^{-1} . As example, Figs. 4a and 4b show the

potentiodynamic profiles in 0.1 M CH₃OH/1 M HClO₄ at 0.020 and 0.200 V s⁻¹. The values of the current at the peak (i_p) and the peak potential (E_p) were determined for each scan rate.

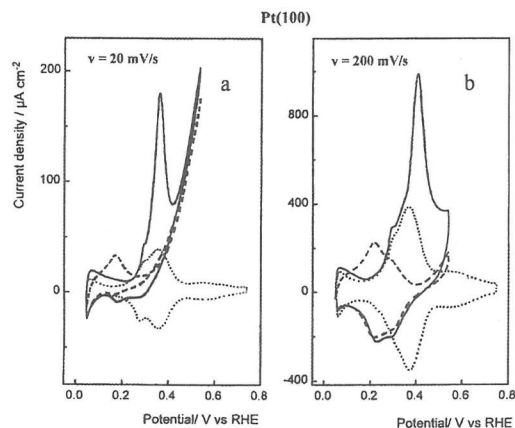
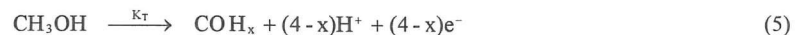


Figure 4. Cyclic voltammogram of Pt(100) in 0.1 M CH₃OH + 1 M HClO₄ (same experimental procedure as in Fig. 1). (—) first cycle; (---) second cycle; (····) supporting electrolyte. a) v = 0.020 V s⁻¹; b) v = 0.200 V s⁻¹.

The values for i_p were obtained after subtraction the current contribution for hydrogen desorption in the same potential range determined in pure electrolyte. The evaluation of the data comes to linear relationships between E_p vs. log v and i_p vs. v (see Figs. 5 and 6, respectively). These results are in agreement with an irreversible adsorption reaction. Assuming that the final adsorbed species are mainly CO and COH [11], the global reaction can be written as follows:



where x = 0 or 1 for CO and COH species, respectively. In this case a highly irreversible reaction is considered for which the net reaction rate is nearly equal to its forward rate.

The total current involved in the overall reaction (5) is given by:

$$i_p = AnFK_T C_{\text{CH}_3\text{OH}} (1 - \theta_T) e^{\frac{\alpha_a F}{RT} E} \quad (6)$$

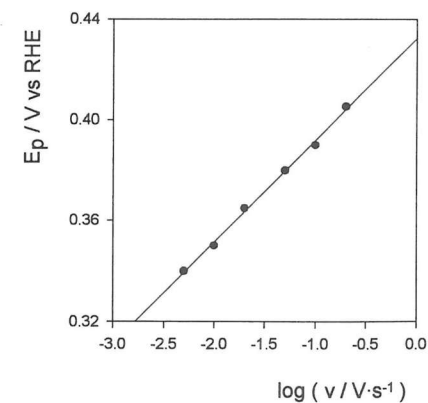


Figure 5. E_p vs. log v for the oxidative adsorption peak obtained on Pt(100) in a 0.1 M CH₃OH + 1 M HClO₄ solution.

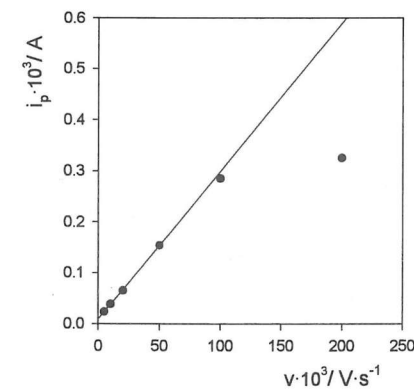


Figure 6. i_p vs. v for the oxidative adsorption peak obtained on Pt(100) in a 0.1 M CH₃OH + 1 M HClO₄ solution.

In this equation F , R , and T have their usual meaning, A denotes the electrode real area, n the number of electrons involved in (5), K_T the rate constant for the global process, C_{CH_3OH} the methanol concentration in the solution, θ_T the total coverage of the adsorbed species given in reactions (1)-(4), and α_a the transfer coefficient for the anodic reaction. From this equation and according to Srinivasan and Gileadi [22], the equations for E_p and i_p for the adsorption process are deduced:

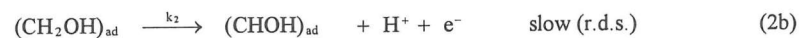
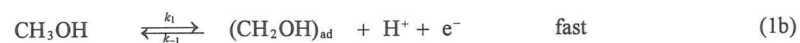
$$E_p = \frac{2.303RT}{\alpha_a F} \log \frac{k\alpha_a F}{nK_T C_{CH_3OH} RT} + \frac{2.303RT}{\alpha_a F} \log v \quad (7)$$

$$i_p = A \frac{1}{e} \frac{k\alpha_a F}{RT} v \quad (8)$$

where k is the charge required to form a monolayer of adsorbed intermediates. Therefore, linear relationships between E_p vs. $\log v$ and i_p vs. v should be expected for this surface irreversible process, as observed in Figs. 5 and 6.

The slope of the plot in Fig. 5 is 40 mV/decade and the origin 0.43 V. This Tafel slope can be explained assuming that the number of electrons transferred during the rate-determining step is 3 (i.e. for $\alpha_a = 1.5$), indicating the loss of three protons of the methanol molecule in this reaction step. This fact could explain that methanol does not adsorb on a Pt electrode covered by hydrogen: each methanol molecule reacts on ensembles with at least three neighboring Pt sites. This situation is not probable on a surface fully covered with adsorbed hydrogen. However, the simultaneous transfer of 3 electrons in the rate-determining step is rather improbable. Therefore the mechanism should be considered in more detail.

It is reasonable to assume that the adsorption proceeds through the steps proposed in reactions (1)-(4). With a Langmuir-type adsorption, the Tafel slope of 40 mV can be explained considering that the first electron transfer is reversible and the second electron transfer is the rate-determining step [23]. In this way, reactions (1) and (2) should be rewritten as:



For the rate-determining step (2b) we have:

$$i_2 = AFk_2 \theta_{CH_2OH} e^{\frac{\beta F}{RT} E} \quad (9)$$

where β is the symmetry factor. The preceding step (1b) is a monoelectronic step at quasi-equilibrium and the corresponding equation is:

$$\frac{\theta_{CH_2OH}}{1 - \theta_T} = K_1 C_{CH_3OH} e^{\frac{F}{RT} E} \quad (10)$$

where $K_1 = k_1 / k_{-1}$. Combining (9) and (10), the rate equation results as follows:

$$i = ni_2 = AnFK_1 k_2 C_{CH_3OH} (1 - \theta_T) e^{\frac{(1 + \beta)F}{RT} E} \quad (11)$$

Comparing (11) and (6), it can be established that $\alpha_a = 1 + \beta \approx 1.5$ if we use the value of $\beta \approx 0.5$. However, one should be careful to assume symmetry factor to be close to 0.5 which is only valid for simple electron transfer reactions [24]. For an adsorption process, as the oxidative methanol adsorption, the transfer coefficient could vary in a wide range. It is hard to come up with a satisfactory explanation and the theory for such rather complex electrochemical surface reactions is still lacking. However, there seems to be some good experimental evidence that this value is a good approximation, at least in a large number of experimental systems [23].

In a previous paper, Tripkovic et al. has considered the second electron transfer during adsorption to be the rate-determining step for the oxidation of methanol on Pt(100) in alkaline solution [25]. However, the Tafel slope obtained by these authors was 60 mV/decade, and therefore, a Temkin-type adsorption [23] was assumed to occur in this media [25]. It has to be kept in mind that all kinetic studies in the literature (as examples see [10] and [25]), refer to oxidation of methanol to stable reaction products. In this respect the adsorption of methanol is considered as a prior step during the overall oxidation process.

Using the slope from the plot in Fig. 6 ($2.9 \text{ mA s}^{-1} = 2.9 \text{ mF}$ which is the apparent maximum Langmuir adsorption pseudo-capacitance) [22], a value of $k = 0.290 \text{ mC cm}^{-2}$ is obtained

for the adsorption of a monolayer. Combining this value with the 0.43 V of the origin in Fig. 5, K_T is evaluated giving $\approx 1 \times 10^{-14} \text{ cm s}^{-1}$ which is in agreement with an irreversible surface reaction [23].

The charge involved in the adsorption process (Q_{ad}) can also be estimated from the potentiodynamic profiles at different scan rates, by integration the area under the peak during the first positive-going potential scan and subtraction of the area associated to hydrogen desorption in the same potential range obtained in 1 M HClO₄. These values are summarized in Table 1 for the scan rates in the linear region in Fig. 6.

Table 1.

Charge density involved in the adsorption of methanol (Q_{ad}) and the desorption of hydrogen (Q_H) as well as its ratio $n_{Pt} = Q_{ad}/Q_H$ on Pt (100) at different scan rates (v). The hydrogen (θ_H) and methanol (θ_{met}) coverage after adsorption are also given. For details see text.

$v / \text{V}\cdot\text{s}^{-1}$	$Q_{ad} / \text{mC}\cdot\text{cm}^{-2}$	$Q_H / \text{mC}\cdot\text{cm}^{-2}$	$n_{Pt} = Q_{ad} / Q_H$	θ_H	θ_{meth}
0.010	0.325	0.241	1.35	0.41	0.59
0.020	0.331	0.248	1.33	0.44	0.56
0.050	0.319	0.260	1.23	0.46	0.54
0.100	0.300	0.256	1.17	0.47	0.53

An average charge of $0.312 \pm 4\%$ mC cm⁻² was obtained. This value is in good agreement with the 0.290 mC cm⁻² given before (a difference of 8% is observed). The hydrogen desorption charge (Q_H), calculated from the cyclic voltammograms in the supporting electrolyte after double layer correction (assuming a constant charging current in the entire potential range), are shown in Table 1. An average of $0.251 \pm 6\%$ mC cm⁻² was estimated. Similar values were obtained for Pt(100) cooled in H₂ + Ar in 0.1 M [18] (0.255 mC cm⁻²) and 0.01 M HClO₄ [26] (0.258-0.262 mC cm⁻²) at $v = 0.050 \text{ V s}^{-1}$. Considering that each H-atom occupies one Pt-site, the ratio $n_{Pt} = Q_{ad}/Q_H$ represents the number of electrons involved in the adsorption process per Pt-site. This ratio varies between 1.17 and 1.35 (Table 1).

On the other hand, as the adsorbed species oxidize at $E > 0.60 \text{ V}$ (which is the positive potential limit in these experiments), the hydrogen coverage of the surface after adsorption (θ_H) is calculated from the charge density involved in the hydrogen desorption region during the second positive-going potential scan (see Figs. 3a, 4a and 4b dashed lines), determined by integration of the

curves after double layer correction, divided by Q_H at each scan rate. This coverage represents the free Pt-sites after methanol oxidative adsorption. The coverage related to the presence of adsorbed species from methanol (θ_{met}) can be considered as $\theta_{met} = 1 - \theta_H$. These values are also given in Table 1. A θ_{met} of $0.56 \pm 5\%$ is observed in agreement with the $0.57 \pm 3\%$ reported in 0.1 M HClO₄ [6].

Conclusions

Despite the amount of spectroscopic and voltammetric data on the reactivity of methanol on platinum, new information on the *adsorption process* can be obtained by cyclic voltammetry if an appropriate experimental procedure is designed. The voltammetric study on the *oxidative methanol adsorption* on low index Pt single crystals clearly demonstrates a structure sensitivity of this complex dehydrogenation reaction. The Pt(111) is less sensitive to methanol oxidation, whereas on Pt (110) the displacement of adsorbed hydrogen by adsorbing methanol occurs already at potentials around 0.05 V. On the Pt(100) face a well defined current peak is observed and the *oxidative methanol adsorption* takes place. The cyclic voltammetric study at different scan rates allows the assignment of this peak to an irreversible surface reaction. The second electronic transfer seems to be the rate-determining step during adsorption.

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