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Influence of surface morphology on methanol oxidation at a glassy carbon-supported Pt catalyst

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Abstract: Platinum supported on glassy carbon (GC) was used as a model system for studying the influence of the surface morphology of a Pt catalyst on methanol oxidation in alkaline and acidic solutions. Platinum was deposited by the potential step method on GC samples from H_2SO_4 + H_2PtCl_6 solution under the same conditions with loadings from 10 to 80 μg cm^{-2}. AFM and STM images of the GC/Pt electrodes showed that the Pt was deposited in the form of 3D agglomerates composed of spherical particles. Longer deposition times resulted in increased growth of Pt forms and a decrease in the specific area of the Pt. The real surface area of Pt increased with loading but the changes were almost negligible at higher loadings. Nevertheless, both the specific and mass activity of platinum supported on glassy carbon for methanol oxidation in acidic and in alkaline solutions exhibit a volcanic dependence with respect to the platinum loading. The increase in the activity can be explained by the increasing the particle size with the loading and thus an increase in the contiguous Pt sites available for adsorption and decomposition of methanol. However, the decrease in the activity of the catalyst with further increase of loading and particle size after reaching the maximum is related to the decrease of active sites available for methanol adsorption and their accessibility as a result of more close proximity and pronounced coalescence of the Pt particles.

Keywords: glassy carbon; methanol oxidation; electrochemical Pt deposition; surface morphology.

INTRODUCTION

Methanol is one of the most extensively investigated small organic molecules, both from a fundamental and practical point of view. Considered as a poten-

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tial fuel for fuel cells, studies of its oxidation on Pt and supported Pt catalysts have intensified during the last decades. The overall reaction:

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \quad (1)$$

occurs in several steps[1–3] but the two main processes are adsorption followed by dehydrogenation of methanol and oxidation of CO_{ad}.[1] Oxidation of CO_{ad} commences when oxygen-containing species are produced in the interaction of water with platinum.[1] Studies of this reaction at Pt poly and single crystal electrodes showed that the adsorption of methanol as well as its oxidation exhibit strong surface sensitivity, which is reflected in the amount and rate of surface coverage by CO_{ad}.[1,4,5] Ren *et al.*[6] examined methanol oxidation at smooth, mildly rough (roughness factor ≈ 50) and highly rough (roughness factor ≈ 200) Pt electrodes prepared by electrochemical treatment and found a difference in the potential of the peak current which indicated an effect of the surface roughness. Raman spectroscopy showed that CO oxidation becomes slower on a highly rough surface, *i.e.*, a surface with more defects, such as edges, kinks and step sites, than on a less rough surface. Beden *et al.*[3,7] studied the electroadsorption and oxidation of methanol on smooth and rough polycrystalline, single crystalline and preferentially oriented Pt electrodes using electromodulated infrared spectroscopy (EMIRS). They found that poisoning by CO was reduced on electrodispersed Pt (roughness factor ≈ 20) in comparison to smooth Pt, indicating that the structure of the surface plays an important role in diminishing the phenomena of CO_{ad} poisoning.

Chemical or electrochemical deposition of platinum on a substrate with a high surface area results in a Pt catalyst with a roughness which depends on the Pt particle size, *i.e.*, on the Pt loading. Mikhaylova *et al.*[8] deposited Pt on glassy carbon by cyclic voltammetry with loadings from 10 to 540 $\mu g\ cm^{-2}$ and obtained electrodes with a roughness factor < 20. The catalytic effect on methanol oxidation in acid increased with increasing loading up to 60 $\mu g\ cm^{-2}$ (roughness factor ≈ 6) and remained unchanged with further growth of the deposit. At higher loadings, the specific activities were close to that of smooth platinum, which was explained by the similar coverage of Pt with organic particles on those surfaces with a roughness factor from 6 to 20 and on smooth Pt. They concluded that the catalytic effect is connected with the change in the bond strength of methanol adsorbates with Pt particles, caused by the structural properties of the deposits. Umeda *et al.*[9] used porous-microelectrodes prepared by the chemical deposition of Pt on carbon black for methanol electro-oxidation. The activity of the catalyst first increased and then decreased with loading. As the potential of Pt oxide formation also shifted anodically with increasing loading, their results showed that the peak potential of methanol oxidation strongly depends on the formation of Pt oxide. Hence, they concluded that the maximum activity is determined by the properties of the Pt surface. Tang *et al.*[10] investigated the effect of loading of Pt deposited on a graphite electrode and on graphitic nanofibers by cyclic voltammetry. The mass activity for methanol oxidation on Pt on nanofibers increased up to a loading of 180 μg cm^{-2} and then decreased for higher loadings. They explained such results by the accumulation of Pt and a decrease of the valuable Pt surface for methanol oxidation. However, for the same range of loadings, the mass activity for methanol oxidation on Pt deposited on a graphite electrode only increased. According to the authors, the particle size and dispersion of Pt deposits are important factors determining the activity of a catalyst. Duarte *et al.*[11] used the potential step method to deposit Pt on glassy carbon, graphite fibers and graphite cloth. Pt on glassy carbon exhibited the highest activity for methanol oxidation. On these electrodes, a pronounced increase of the Pt surface area with loading up to 30 μg cm^{-2} was observed, while loadings higher than 50 μg cm^{-2} had a small effect on the surface area of Pt. The increase of activity with increasing mass specific surface area was explained by the reduction of the particle size. The effect of particle size on the activity for methanol oxidation was pointed out also by Frelink *et al.*[12] These authors used different methods as well as variations of a single method to prepare Pt catalysts supported on carbon black with loading of 3.5 to 5.5 % of platinum with a particle size in the range 1.2 to 7.8 nm. They found a decrease of the activity for methanol oxidation activity with decreasing particle size from 4.5 to 1.2 nm but for particles larger than 4.5 nm, the activity remained almost constant. According to the authors, the dependence of the activity on the size of the Pt particles could be explained either by the particle size effect on the formation of adsorbed hydroxyl species or its effect on the number of methanol adsorption sites. Yahikozawa and coworkers[13] studied methanol oxidation on a Pt catalyst vacuum evaporated on glassy carbon with a particle size of 3.8 and 5.3 nm. The decrease of the activity for methanol oxidation with decreasing particle size was related to the existence of some oxide layer on the surface closely related to the exposed crystal planes. Examining methanol oxidation on carbon black supported Pt catalyst with 10 and 60 wt. % of platinum and particles of 2.0 and 8.8 nm respectively, Park *et al.*[14] also observed a particle size dependent electrocatalytic effect. The decrease of the activity on decreasing the particle size to below 4 nm, was explained by a decrease of contiguous Pt sites ("ensemble effect") needed for dehydrogenation of methanol to form CO. Scheijan *et al.*[15] also attributed the decrease of activity with decreasing particle size to a decrease in the number of Pt ensemble sites available for adsorption and decomposition of methanol. However, they examined this reaction using Pt catalysts with particles ranging from 10–20 and 10–120 nm and also a full monolayer of Pt and concluded that the shape and the morphology rather than size of the particles played predominant roles in the reaction kinetics.

Despite the differences in the hitherto reported results, all the authors suggested that the change of activity of the catalyst is mainly based on the particle size.

In this work, the influence of surface morphology of platinum deposited on glassy carbon support by the potential step method on methanol oxidation was studied.

EXPERIMENTAL

Platinum was deposited on two glassy carbon (GC) (Sigradur–Sigri, Elektrographite, GmbH, Germany) disc electrodes with different geometric area (A_{GC}): 0.21 (GC_I) and 0.39 cm^2 (GC_{II}).

The GC electrode surfaces were refreshed before each deposition of platinum, by abrasion with emery paper of decreasing grain size followed by polishing with alumina of 1, 0.3 and 0.05 μm particle size. The final cleaning of the electrodes was performed in high purity water (Millipore 18 MΩ cm) in an ultrasonic bath.

Before each deposition of platinum, a cyclic voltammogram of the GC electrode was recorded in 0.10 M NaOH solution or in 0.50 M H_2SO_4 (potential range –0.20 V to 1.4 V, sweep rate 50 mV s^{-1}), to ensure that the GC surface was clean and free of Pt from the previous experiment.

Platinum was electrodeposited on glassy carbon by the potential step method in deoxygenated 0.50 M H_2SO_4 + 6.0 mM H_2PtCl_6. A potential perturbation from 0.06 V to 0.36 V was applied after 0.5 s at the initial potential. Platinum was deposited under the same conditions in each experiment but with loadings (W_{Pt}) from 10 to 80 μg cm^{-2}. The amount of platinum deposited was estimated from the charge calculated by integrating the I–t transient. After deposition, the electrode was thoroughly rinsed with high-purity water and transferred to the cell containing 0.10 M NaOH or 0.50 M H_2SO_4. The real surface area of platinum deposited, A_{Pt} (cm_R^2), was estimated from the hydrogen adsorption/desorption region of the basic voltammogram (integrated part of the CV was in the potential range from 0.06 V to 0.45 V with a correction for a double layer charging). The specific catalyst area S_{Pt} (m^2 g^{-1}) was calculated from the equation: $S_{Pt} = 100A_{Pt}/(A_{GC}W_{Pt})$.[16]

The electrocatalytic activity of the GC/Pt electrodes for methanol oxidation was studied in 0.10 M NaOH + 0.50 M CH_3OH and in 0.50 M H_2SO_4 + 0.50 M CH_3OH solutions. Methanol was added to the solution while holding the electrode potential at 0.06 V. The potential was cycled between 0.06 V and 1.3 V with sweep rates of 50 and 1.0 mV s^{-1}.

The employed reagents were of p.a. purity, and the solutions were prepared with high purity water (18 MΩ cm). The electrolytes were purged with purified nitrogen prior to each experiment.

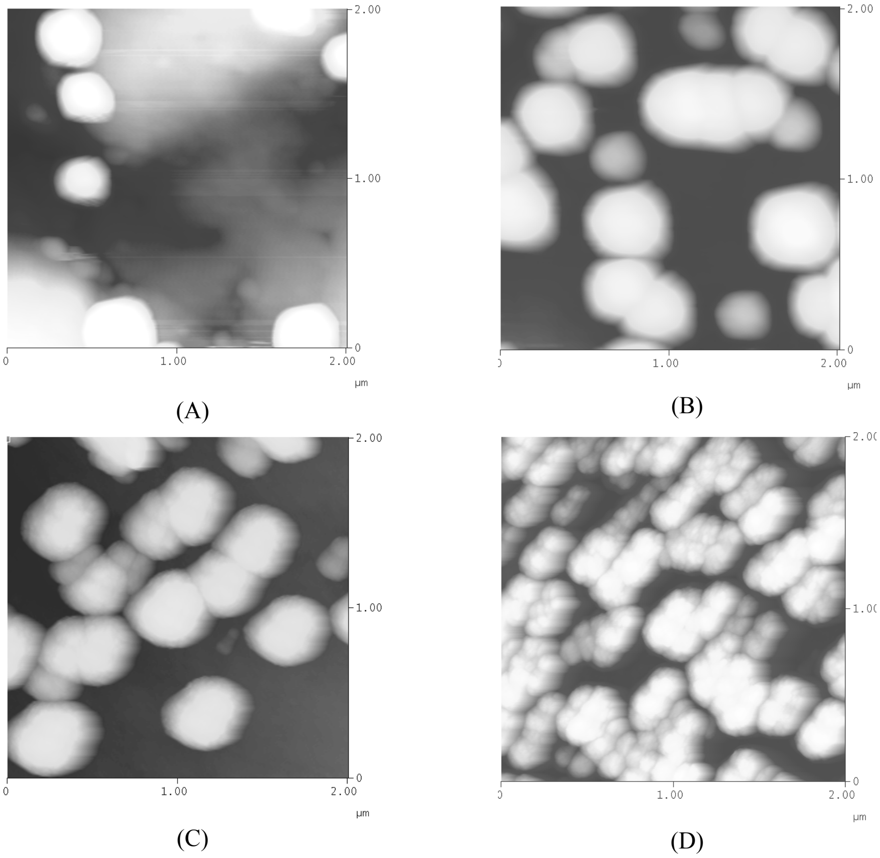
All electrochemical experiments were performed at room temperature in a standard three-electrode/three-compartment glass cell. The counter electrode was a Pt wire while a bridged saturated calomel electrode (SCE) was used as the reference electrode. However, all potentials are given *versus* the reversible hydrogen electrode (RHE). The electronic equipment in all of the experiments consisted of a PAR Model 273 potentiostat and Philips Model 8033 X–Y recorder.

GC_{II}/Pt electrodes with different loadings were characterized at room temperature in air by atomic force (AFM) and scanning tunneling microscopy (STM) techniques. The structural characterization was performed with a NanoScope III A (Veeco, USA) microscope. The AFM observations were performed in the contact mode using NanoProbes silicon nitride cantilevers with a force constant 0.06 N m^{-1}. The STM images were obtained in the height mode using a Pt–Ir tip (set-point current, i_t: from 1 to 2 nA; bias voltage, V_b: –300 mV).

RESULTS

AFM and STM

The AFM and STM techniques were used for the characterization of GC/Pt electrodes with different loadings. The AFM images (Fig. 1) reveal the topography of the glassy carbon electrodes with platinum deposited on the surface in the form of large 3D agglomerates of lateral size ranging from 100 to 700 nm. Increasing the loading leads to an increase in the number and predominant size of the agglomerates, their closer proximity and pronounced coalescence. Agglomerates composed of Pt particles were also observed in STM images by Duarte *et al.*[11] and Gloaguen *et al.*[16] Their formation can be explained by nucleation and growth of the Pt electrodeposits. According to Gloaguen *et al.,*[16] at very beginning of the electrodeposition process ($t < 0.3$ s), a large number of nano-sized

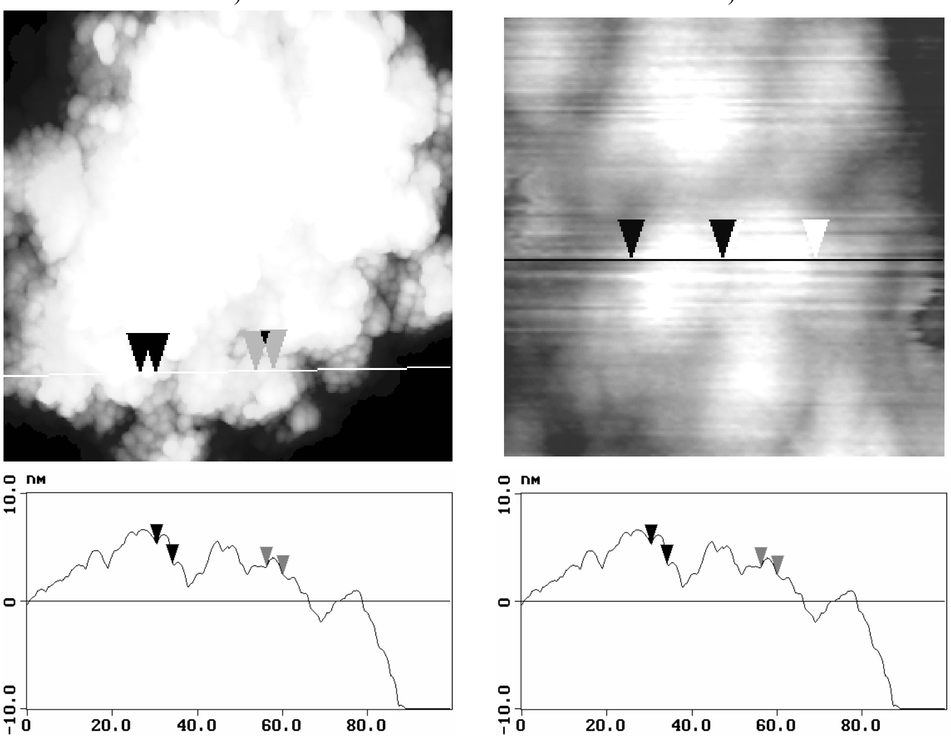


(A) (B) (C) (D)

Fig. 1. AFM Images (2.00×2.00 µm^2) of the GC/Pt, with low loadings of 11.9 (A), 28.9 (B), 49.8 (C) and 72.3 µg cm^{-2} (D).

particles is formed and they might be mobile and assemble in Pt agglomerates. The number as well as the size of the particles increases during deposition. The first process is predominant at short times of deposition, while the other prevails at longer times.

The STM images of the Pt agglomerates (Fig. 2) show that they consisted of spherical nanoparticles of platinum. The size distributions of the particles for the examined loadings, ascertained from the STM images,[17] are given in Table I. Increasing the Pt loading led to an increase of the particle size, their distribution and density. The Pt particles were rather loose at the lowest loading, becoming closely packed at the highest one.


A)

B)

Fig. 2. STM Images (125×125 nm^2) of the GC/Pt with a low loading of 11.9 μg cm^{-2} (A) and a high loading of 49.8 μg cm^{-2} (B).

TABLE I. Pt particle size for GC$_{\mathrm{II}}$/Pt electrodes with different Pt loadings

Loading, W_{Pt} / μg cm^{-2}	11.9	21.1	28.9	49.8	72.3
Particle size, d / nm	4.4±0.7	8.9±1.6	10.6±2.3	36.1±5.3	52.4±11.1

Electrochemical characterization

Platinum was deposited on two samples of glassy carbon (GC_I and GC_{II}) under the same conditions with loading ranging from 10–80 μg cm^{-2}. Typical cyclic voltammograms of a GC_I/Pt electrode in 0.10 M NaOH and of a GC_{II}/Pt in 0.50 M H_2SO_4 are shown in Figs. 3A and 3B, respectively. They resemble the corresponding voltammograms for smooth platinum with well defined hydrogen adsorption/desorption region (from 0.06 V to 0.40 V), separated in sulfuric acid (Fig. 3B) from the region of surface oxide formation at higher potentials by a double layer charging/discharging region. In alkaline solution (Fig. 3A) the hydrogen desorption is followed by reversible OH^- adsorption (0.40 V < E < 0.75 V) and irreversible oxide formation at potentials higher than 0.75 V. The potentials of all the anodic and cathodic peaks remained the same regardless of the loading. The ratio between the peak heights for strongly (h_{Ps}) and weakly (h_{Pw}) bound hydrogen, remained almost constant for all the examined electrodes (inserts in Fig. 3).

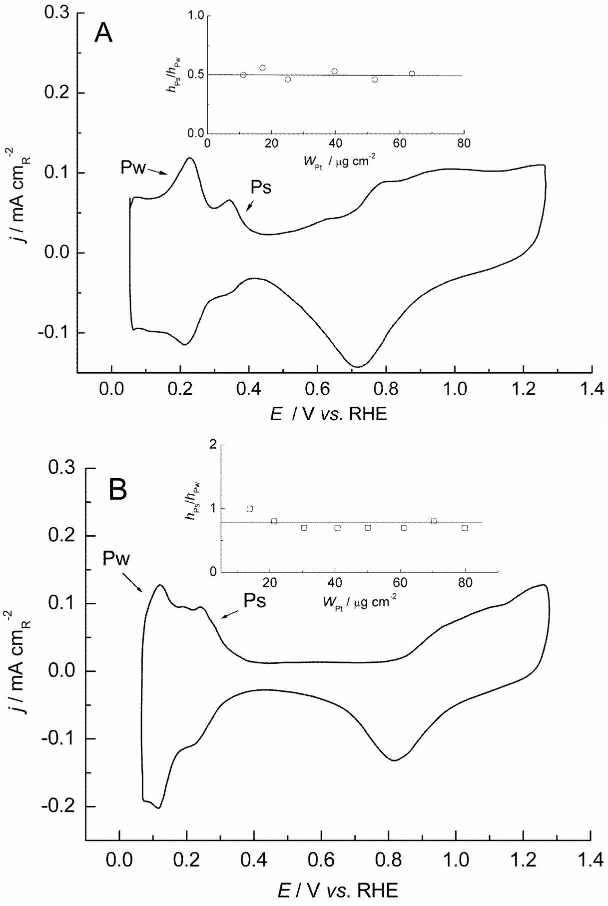


Fig. 3. Cyclic voltammograms of GC/Pt electrodes in 0.10 M NaOH (A) and 0.50 M H_2SO_4 (B), sweep rate 50 mV s^{-1}. Insets: the dependence of the ratio of the peak heights, h_{Ps}/h_{Pw}, on the loading for all the GC/Pt electrodes.

The real surface area of the platinum catalysts (A_{Pt}), determined from the hydrogen adsorption/desorption charge, is plotted *versus* the loading in Fig. 4. The Pt real surface area initially increased with loading but at higher loadings remained nearly constant. A similar dependence of the Pt surface area with loading was found by Duarte *et al.*[11] The difference in the surface areas of the Pt particles deposited on the $\mathrm{GC_I}$ and $\mathrm{GC_{II}}$ supports arises from the different geometric area of the glassy carbon substrates and the non-homogeneity of this material and is in accordance with literature data.[18]

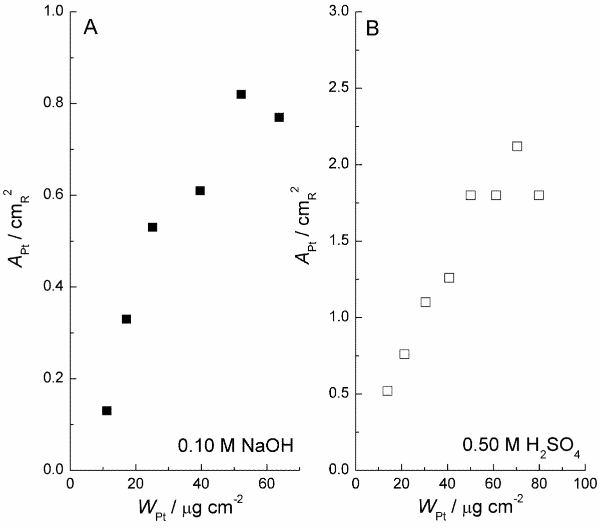


Fig. 4. The dependence of the real surface area (A_{Pt}) on the loading of Pt deposited on the smaller $\mathrm{GC_I}$ (A) and larger $\mathrm{GC_{II}}$ (B) substrate.

The dependence of the specific catalyst area (S_{Pt}) on the loading is depicted in Fig. 5. The specific catalyst area generally decreases with the loading. This trend is more pronounced at the higher loadings (Figs. 5A and 5B), which is in accordance with reported data.[8,9,11,19] However, for the electrode with the support of smaller geometric area examined in alkaline solution (Fig. 5A), the dependence attained a maximum at ≈ 25 μg cm^{-2}, was followed by decrease in S_{Pt}. An initial increase in S_{Pt} at low loadings was shown by Mikhaylova *et al.*[8] and considered as deviations from the regularity attributed to inaccuracies in the determination of the real surface area, A_{Pt}, of small deposits. Although this possibility cannot be neglected, based on the presented results, we are of the opinion that this initial increase in S_{Pt} of the studied GC/Pt electrodes might be related to the conditions of the Pt electrodeposition. In the region of small loadings, *i.e.*, short deposition times, the Pt agglomerates were smaller, well separated and their number increased with the amount of Pt, resulting in the increase of the specific surface. Longer times of deposition favor the growth of Pt crystals relative to nuclei formation. Consequently, the deposition of Pt at higher loadings results in the increased growth of the Pt forms, their higher concentration and closer proximity at the same geometric surface and in a decrease of the specific area of Pt because the ratio of the surface to bulk atoms decreases. This might be the reason why the dependence of the specific area on the loading exhibited a maximum.

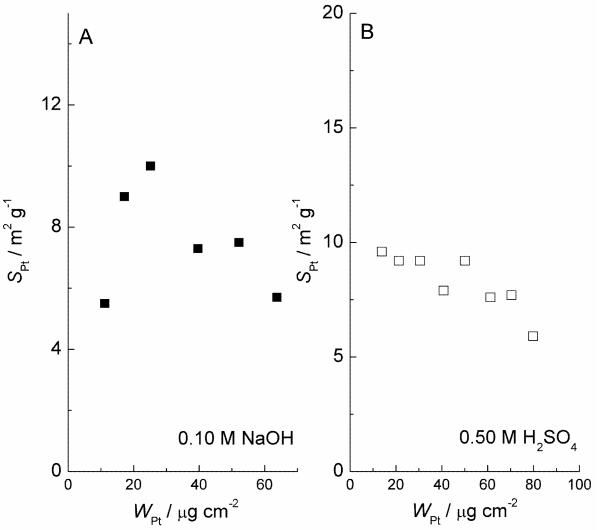


Fig. 5. The dependence of the specific catalyst area (S_{Pt}) upon the loading of Pt deposited on the smaller GC_I (A) and larger GC_{II} (B) substrate.

Methanol oxidation

The influence of the loading, *i.e.*, surface morphology, of the GC/Pt electrodes on their electrocatalytic activity for methanol oxidation was studied in 0.10 M NaOH and in 0.50 M H_2SO_4.

Methanol oxidation under potentiodynamic conditions at GC/Pt electrodes with a loading of ≈ 30 μg cm^{-2} in 0.10 M NaOH and 0.50 M H_2SO_4 is shown in Figs. 6A and 6B, respectively. Methanol oxidation commences at the onset of OH anion adsorption (Fig. 3A) and proceeds on the surface covered by reversible OH_{ad} species. The maximum of the current is attained at potentials ($E \approx 0.85$ V) where the rate of methanol dehydrogenation and the rate of oxidation of the dehydrogenated product by OH_{ad} species are in balance.[20]

The coverage of the GC_{II}/Pt electrode with adsorbed organic species, calculated from the hydrogen adsorption/desorption region in the presence and in the absence of methanol, given as the covered area is depicted in Fig. 7. As can be seen, the coverage initially increases with increasing loading, reaches a maximum and then decreases at higher Pt loadings. It should be mentioned here that such a dependence was not obtained for the GC_I/Pt electrode with a smaller geometric surface used in alkaline solution because of the scattered data for the calculated area. This might be explained by the possibility that OH adsorption, to a certain extent, overlaps with H adsorption in alkaline solutions.[21]

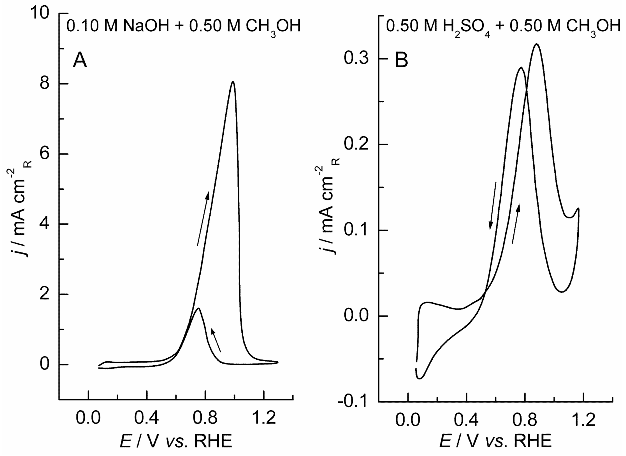


Fig. 6. Cyclic voltammograms of the GC/Pt electrodes in 0.10 M NaOH + 0.50 M CH_3OH (A) and 0.50 M H_2SO_4 + 0.50 M CH_3OH (B); sweep rate 50 mV s^{-1}.

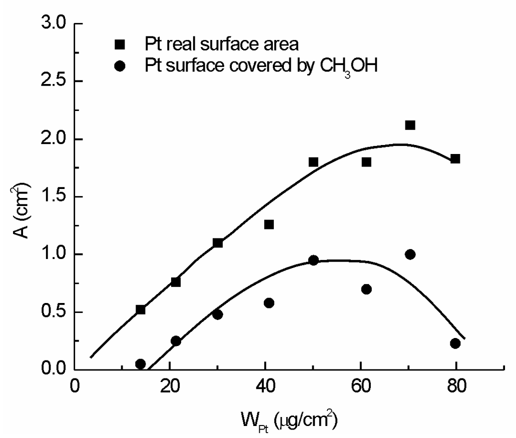


Fig. 7. The dependence of Pt surface area covered by adsorbed organic particles in 0.50 M H_2SO_4 + 0.50 M CH_3OH on the loading. The real Pt surface area, A_{Pt}, is given for comparison.

The electrocatalytic activity of the GC/Pt electrodes for methanol oxidation was considered under potentiostatic conditions, as the activities observed under potentiodynamic measurements are transient in nature. Tafel plots, recorded using linear sweep voltammetry at 1.0 mV s^{-1}, are presented in Fig. 8. Well defined straight lines with the Tafel slopes of approximately 100 mV dec^{-1} in NaOH (Fig. 8A) and 80 mV dec^{-1} in H_2SO_4 (Fig. 8B) were obtained at all loadings. However, a decrease of activity of the GC/Pt electrode with higher Pt loadings was clearly observed in both cases.

The dependences of the specific and mass activity (at 0.62 V) on the loading of the GC/Pt electrodes are shown in Figs. 9 and 10, respectively. Inspection of these figures revealed that the activity increased, reached a maximum and then decreased as the loading increased. A maximum activity for this reaction in acid solution at supported platinum catalysts *versus* the specific catalyst area was also described by Umeda *et al.*[9] and Attwood *et al.*[18] The results of Frelink *et al.*[12]

for the same reaction showed a slight maximum of the specific activity with particle size but when the mass activity of the same electrode was plotted *versus* the particle size such a maximum was not found. Comparing their results with those of Attwood and coworkers,[18] the authors concluded that the preparation method could have a considerable influence on the behavior of the Pt catalysts. It should be mentioned that all these authors used different methods for the chemical deposition of Pt. On the other hand, the activity of Pt electrodeposited on GC either increased with loading[8] or showed a maximum at much higher loadings if the Pt was deposited on nanofibers.[10]

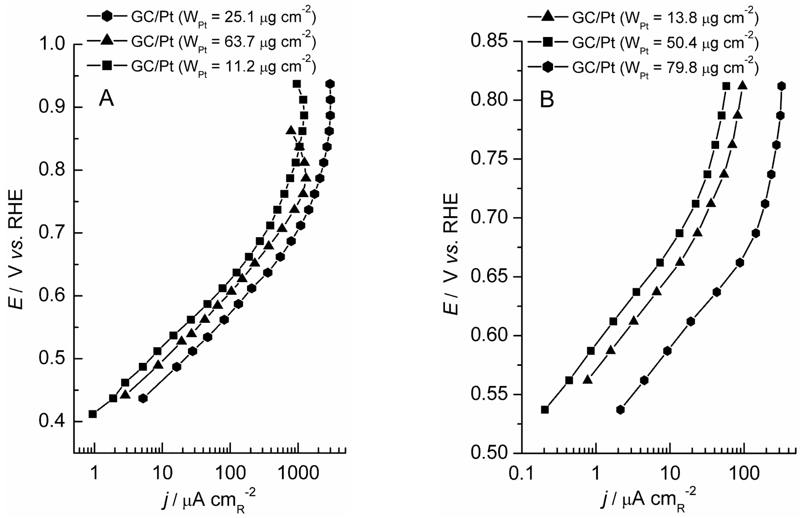


Fig. 8. Tafel plots for the oxidation of 0.50 M CH_3OH on the GC/Pt electrodes in 0.10 M NaOH (A) and 0.50 M H_2SO_4 (B).

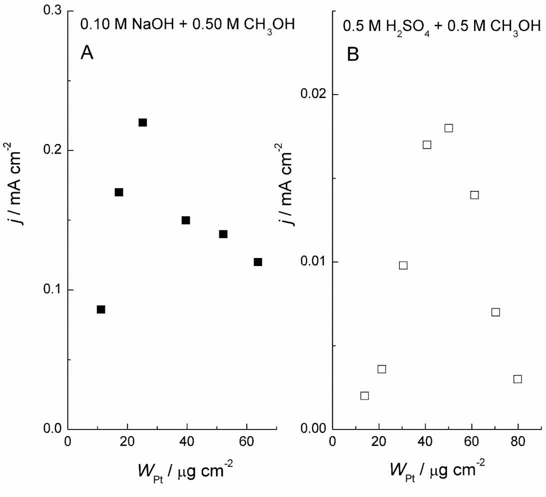


Fig. 9. The specific activity for methanol oxidation *versus* loading of the GC/Pt electrodes in 0.10 M NaOH (A) and 0.50 M H_2SO_4 (B).

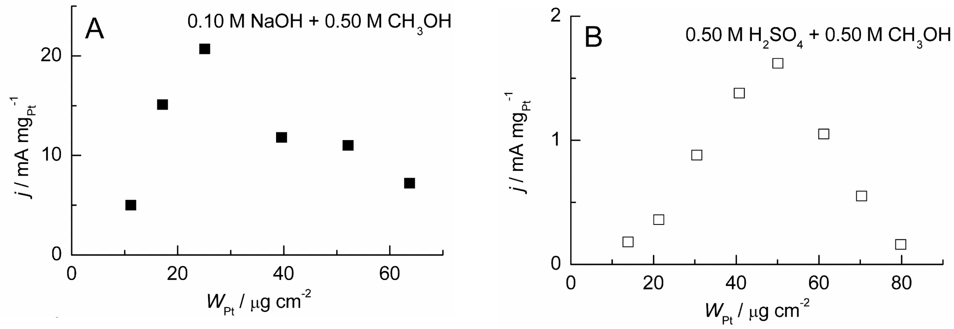


Fig. 10. The mass activity for methanol oxidation *versus* loading of the GC/Pt electrodes in 0.10 M NaOH (A) and 0.50 M H_2SO_4 (B).

DISCUSSION

The activity of the GC/Pt electrodes depended generally on the Pt loading in both solutions (Figs. 8–10), increasing at lower loadings, reaching a maximum at ≈ 30 and ≈ 50 μg Pt cm^{-2} in alkaline and acidic solutions, respectively, and then decreasing rapidly with further increase of the loading.

Activity of GC/Pt catalysts in methanol oxidation has mostly been related to the particle size effect and discussed in the numerous papers.[9–25] Basically, the particle size effect assumes that the activity of the electrode is determined by the number of contiguous sites available for methanol adsorption.[14] In this sense, the higher the number of correspondingly arranged sites is, the higher is the activity. Accordingly, the increase of activity up to the maximum value (Figs. 8–10) could be attributed to the increase of the Pt particle size. However, further increase of loading leading to a decrease of the activity of the catalyst, being not in accordance with the particle size effect, clearly indicates to the importance of the surface morphology.

AFM and STM images of GC/Pt electrodes obtained under conditions of lower loadings (Figs. 1A, 1B and 2A) show that the Pt was deposited in the form of randomly distributed, mostly well separated agglomerates consisting of small, rather loose particles. This surface morphology remains unaffected significantly by increasing of particle size with loading (Fig. 1B). In the range of lower loadings, the real surface area increases (Fig. 4) as well as the specific catalyst area of Pt deposited on the smaller support (Fig. 5A), while the specific catalyst area of Pt on the larger support remains almost unchanged, probably due to the non-homogeneity of the glassy carbon with different geometric areas. The maximum activity for methanol oxidation in both solutions (Figs. 8–10) was exhibited by electrodes with a high value of the real surface area and the maximum value of the specific catalyst area (Figs. 4 and 5), suggesting clearly that the corresponding surface morphology provides the high number of contiguous sites available for the reaction. On the other hand, it suggests also that particle size effect, operative under the conditions of lower loadings should be related to the surface morphology.

It should be noted that any significant changes concerning the hydrogen adsorption/desorption or Pt oxide formation/reduction on the basic voltammograms, as well as the peak position on the cyclic voltammograms for methanol oxidation, usually observed with a change of particle size,[9,12,13,20,21] were not detected (Figs. 3 and 6). Most likely this was caused by the rather wide particle size distribution in each loading and the overlapping of the same particle sizes in two loadings (Table 1).

Increasing of Pt loading altered the surface morphology leading to the deposition of predominantly larger agglomerates with increased particle size, their higher density, closer proximity and even coalescence (Figs. 1C, 1D and 2B). Simultaneously, the real surface area remained almost constant due to the saturation of the substrate with Pt. Consequently, the specific catalyst area decreased due to the diminishing ratio of surface to bulk atoms. Such a change of the parameters cannot explain the decrease of the catalytic activity. However, the surface morphology under conditions of high loadings, which indicates the existence of different defects caused by the close proximity and coalescence of agglomerates and particles, could help in the solution of this problem.

The presence of defect sites related to steps and grain boundaries which interconnect nanoparticles into complex structure was postulated by Millard *et al.*[26] and Cheristiouk *et al.*[27] As the number of defects increases with the enhancement of Pt loading, due to the increase of particle coalescence, the ratio between facets, *i.e.*, flat surface domains, and defects increases in favor of defects, leading to a diminishing of the Pt contiguous sites available for methanol adsorption. This view is supported by the fact that the coverage of GC_{II}/Pt electrode with adsorbed organic species increased parallel with increasing real surface area up to a loading corresponding to the maximum activity and then decreased (Fig. 7), while the real surface area remained practically constant.

CONCLUSIONS

The activities of GC/Pt electrodes in the oxidation of methanol in both acidic and alkaline solutions exhibit an volcano dependence with respect to the platinum loading.

The activity increases in the range of lower loadings following the particle size effect as the Pt particles are distributed in mostly well separated agglomerates, which provides for a high number of contiguous sites for methanol adsorption. The activity decreased in the range of high loadings when different defects were formed due to the close proximity and coalescence of the Pt particles. Decreasing of the ratio between the flat surface domains and the defects in favor of the defects with increasing Pt loading leads to a diminishing number of contiguous sites for methanol adsorption.

Finally, it could be concluded that the activity of the catalyst cannot be explained exclusively by particle size effect without relating this effect to surface morphology.

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ИЗВОД

УТИЦАЈ ПОВРШИНСКЕ МОРФОЛОГИЈЕ НА ОКСИДАЦИЈУ МЕТАНОЛА НА ПЛАТИНСКИМ КАТАЛИЗАТОРИМА СА ПОДЛОГОМ ОД СТАКЛАСТОГ УГЉЕНИКА

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Платина исталожена на стакласти угљеник (GC) коришћена је као модел систем за испитивање утицаја морфологије површине Pt катализатора за реакцију оксидације метанола у алкалним и киселим растворима. Платина је таложена потенциостатском пулсном методом на GC подлогу из $H_2SO_4 + H_2PtCl_6$ раствора под истим условима у количини од 10 то 80 μg cm^{-2}. АФМ и СТМ слике GC/Pt електрода показују да је Pt исталожена у облику 3D агломерата који се састоје од сферних честица. Дуже време таложења доводи до повећаног раста Pt форми и смањења специфичне површине наталожене платине. Реална површина исталожене платине расте са повећањем количине исталожене платине достижући плато. Без обзира на ово, специфична и масена активност платине исталожене на стакласти угљеник за оксидацију метанола како у киселим тако и у алкалним растворима показује вулканску зависност од количине исталожене платине. Повећање активности се може објаснити преко повећања величине честица са количином исталожене платине, односно преко повећања суседних Pt места доступних за адсорбцију и декомпозицију метанола. Међутим, смањење каталитичке активности са даљим повећањем количине исталожене платине и величине њених честица након постигнутог максимума је повезано са смањењем броја активних места доступних за адсорпцију метанола и резултат је смањења растојања и израженог стапања Pt честица.

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