

Particle size effect of carbon-supported platinum catalysts for the electrooxidation of methanol

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Particle size effect of carbon-supported platinum catalysts for the electrooxidation of methanol

T. Frelink, W. Visscher, J.A.R. van Veen

Eindhoven University of Technology, Laboratory for Inorganic Chemistry and Catalysis, P.O. Box 513, 5600 MB Eindhoven, Netherlands

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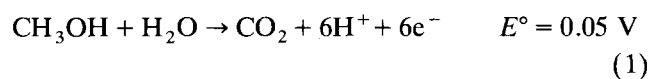
Abstract

The effect of the particle size of carbon-supported Pt catalysts on the electrooxidation of methanol was studied. Different methods were used to prepare Pt/C catalysts with particle sizes ranging between 1.2 and 10 nm. The possible interaction of Pt with carbon surface groups was also investigated by preparing catalysts on oxidized and non-oxidized carbon supports. The specific activity was found to decrease with decreasing particle size in the range 4.5–1.2 nm. Carbon-supported Pt particles appear to be more active than non-supported particles and the presence of an acidic group on the support slightly enhances this effect. The dependence of the activity on the particle size can be explained in terms of either its effect on the formation of an adsorbed hydroxy species or its effect on the number of methanol adsorption sites.

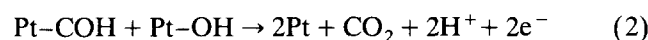
Keywords: Particle size; Carbon-supported platinum catalysts; Electrooxidation; Methanol

1. Introduction

The electrooxidation of methanol is a subject of intensive research in the context of the development of the direct methanol fuel cell. Though the reaction proceeds faster in alkaline than in acidic media, an acidic electrolyte is generally preferred for practical application since carbonate residues are not formed in this electrolyte. The choice of the electrocatalyst material is then confined to Pt, however, which has a low activity for the methanol electrooxidation:



It is generally accepted [1,2] that the crucial and rate-limiting step in this reaction is the oxidation of a methanol adsorbate by an adsorbed hydroxy species or activated water group. When it is assumed that $-\text{COH}$ is the methanol adsorbate, the rate-determining step is



The problem is generally recognized to be the lack of a suitable Pt surface-oxide species in the potential region 0–0.6 V [3], where methanol is adsorbed. The Pt oxide that is formed at and above +0.75 V blocks the surface and impedes the methanol oxidation. The electrooxidation of methanol begins at 0.45 V; therefore, adsorbed

hydroxy species or activated water groups must be the reaction partner. The rate of reaction (2) depends on coverage with θ_{COH} and θ_{OH} . Since $\theta_{\text{COH}} + \theta_{\text{OH}} \leq 1$, it implies that a high θ_{OH} or θ_{COH} will decrease the number of Pt sites that are available for the formation of an adsorbed methanol or hydroxy species, respectively, and the reaction rate will consequently be low. Hence it is obvious that the efficiency of the Pt catalyst would be improved if a well balanced co-adsorption of methanol and water could be realized at low potential.

The Pt electrocatalyst in fuel cells usually consists of Pt particles on a carbon support. The surface area of this electrocatalyst increases with smaller particles; however, it is known that by decreasing the particle size, the catalytic behaviour of the material can be altered [4,5]. Watanabe et al. [4] argued that the inter-particle distance can also affect the catalytic behaviour. In a later paper, however, Giordano et al. [6] could not find conclusive evidence for such an effect.

In their investigation of the interaction of oxygen with Pt particles sputtered on Teflon, Parmigiani et al. [7] found with XPS measurements that Pt is more easily oxidized when the particle size is decreased. This is confirmed by the electrochemical measurement of Pt oxide reduction by Takasu et al. [8], who observed a potential shift in the negative direction with a decrease in Pt particle size. This could imply that also the

oxidation occurs at lower potentials for smaller Pt particles. For electrocatalytic reactions such as the O₂ reduction, several workers observed a decrease in specific activity with smaller particles in the range 12–1 nm [9], which again could be related to the increased difficulty of reducing Pt–O species. Peuckert et al. [10] investigated oxygen reduction on highly dispersed platinum on carbon and concluded that there is a maximum in the activity expressed per unit weight of platinum for particle sizes between 3 and 5 nm. The results of Giordano et al. [6], however, revealed no clear evidence for such a maximum, but there was a sharp increase with smaller particles (< 5 nm).

Hence if in fact the onset of Pt oxidation is enhanced at smaller particles, one would expect Pt–OH species to be present on the catalyst surface at lower potentials. For the range of particle sizes where θ_{OH} does not become too high, one would therefore expect a positive effect on the activity of methanol oxidation. Such an effect has indeed been reported: Attwood et al. [11], employing Pt/C catalysts prepared in a variety of ways, found an optimum in the specific activity at a specific surface area of 140 m² g⁻¹, corresponding to a Pt particle size of about 3 nm. However, different preparation methods and different carbon supports were used, so the metal-support interaction could also have been changed. Indeed, in a recent paper [12] it was pointed out that carbon surface groups influence the electronic nature of the supported platinum. Enyo et al. [13] observed for small Pt clusters (Pt₉ and Pt₁₅), deposited on carbon, that the activity decreases for the smaller Pt clusters (these Pt aggregates, derived from platinum–carbonyl cluster anions below 1 nm in size, still exhibit a higher activity than smooth Pt). Watanabe et al. [14] prepared Pt catalysts with different particles sizes on several carbon supports, using the same preparation method. The surface area of these catalysts ranged from 70 to 201 m² g⁻¹, thus covering approximately the same range as those of Attwood et al. [11]. Surprisingly, however, they did not find a particle size effect; the specific activity for the methanol oxidation appeared to be the same for all Pt particle sizes. They also concluded that there was no intercrystallite distance effect. In contrast, Yahikozawa et al. [15], who prepared catalysts by chemical vapour deposition, found a decrease in activity with smaller particles (1.5–2.3 nm).

Considering all these results, it is not yet clear to what extent the performance of carbon-supported Pt for methanol oxidation is influenced by the particle size and by the nature of carbon surface groups. In this paper results are presented for the oxidation of methanol at Pt/C catalysts with different particle sizes. The catalysts were obtained not only by different preparation methods, but also by variation of a single preparation method. Further, to investigate possible

interaction with the carbon support, colloidal Pt was deposited on carbon as well as on oxidized carbon.

2. Experimental

2.1. Catalyst preparation

Carbon black (Vulcan XC-72, Cabot International) with a specific surface area (BET) of 340 m² g⁻¹ was used as a support for all catalysts.

The following carbon-supported Pt catalysts were prepared by ion exchange, impregnation or colloidal precipitation; the Pt loading was 3.5 – 5.5 wt%. Furthermore, some of the catalysts were modified by potential cycling, as described below.

Ion-exchanged catalyst

Carbon was oxidized with HNO₃ and then ion exchanged [16] with Pt(NH₃)₄(OH)₂ (Johnson Matthey). The ion-exchanged catalyst was reduced in H₂ at 200°C for 2 h.

Impregnated catalyst

Carbon was impregnated with H₂PtCl₆ (Drijfhout) in water by refluxing for 2 h, then reduced with formaldehyde. After a further 1 h of reflux, the catalyst was filtered, extensively washed in order to remove chloride ions and dried at 125°C.

Colloidal catalyst

Two preparation methods were employed. (a) Colloidal Pt was prepared by the method of Turkevich and co-workers [17], in which an aqueous H₂PtCl₆ solution is reduced with sodium citrate under reflux until a black Pt sol is formed. This sol is then added to the carbon suspended in water. After filtration, extensive washing with hot water and drying at 125°C, the Pt/C catalyst is obtained. The carbon was used either as received or in the oxidized form.

Colloidal Pt on a carbon support (carbon as received or oxidized) was prepared for us by Bönemann et al. [18] PtCl₂ is suspended in THF and reduced with (N(octyl)₄BEt₃H), where the ammonium salt functions as a stabilizer for the colloidal metal particles.

Impregnated-sintered catalyst

Sintered Pt/C was prepared by impregnating carbon with aqueous H₂PtCl₆ solution, followed by filtration, washing and drying at 125°C. The catalyst was thereafter reduced with H₂ at 700°C for 2 h.

Ageing of catalyst

Potential cycling can modify the particle size of Pt/C [19]; therefore, repeated potential cycling was applied as well on Pt/C catalysts.

2.2. Electrode preparation

Pt/C electrodes were prepared by pressing a mixture of the catalyst and a PTFE (Fluon GP1; DPI) suspension on a Pt or Au gauze. The electrode was dried at 125°C and then sintered in an argon atmosphere at 325°C for 2 hrs. The total amount of catalyst used was always ca. 10 mg on a gauze of ca. 2 cm² geometric area. The final PTFE content was 20 wt.%.

2.3. Catalyst characterization

The Pt particle size of the catalysts was determined by transmission electron microscopy on a Jeol JEM 2000FX microscope.

The Pt/C electrodes were characterized by cyclic voltammetry using a computer-controlled Autolab (Eco Chemie) potentiostat. Cyclic voltammetric scans were

obtained in 0.5 M H₂SO₄ between -0.65 and +0.6 V versus an Hg/Hg₂SO₄ electrode (+0.68 V vs. RHE), against which all potentials are given. Platinum specific surface areas were determined from the hydrogen desorption area in the anodic voltammogram, assuming that 1 cm² of smooth Pt required 210 μC [20].

2.4. Methanol oxidation

The activity for methanol oxidation was measured in 0.1 M CH₃OH + 0.5 M H₂SO₄ by applying a sweep at a scan rate of 5 mV s⁻¹, starting at open circuit potential. It was established that the results did not change significantly at lower scan rates. The activities per real unit surface area were obtained from the forward scan of the second sweep. All activity measurements were done at least in duplicate with a freshly prepared electrode for each new measurement.

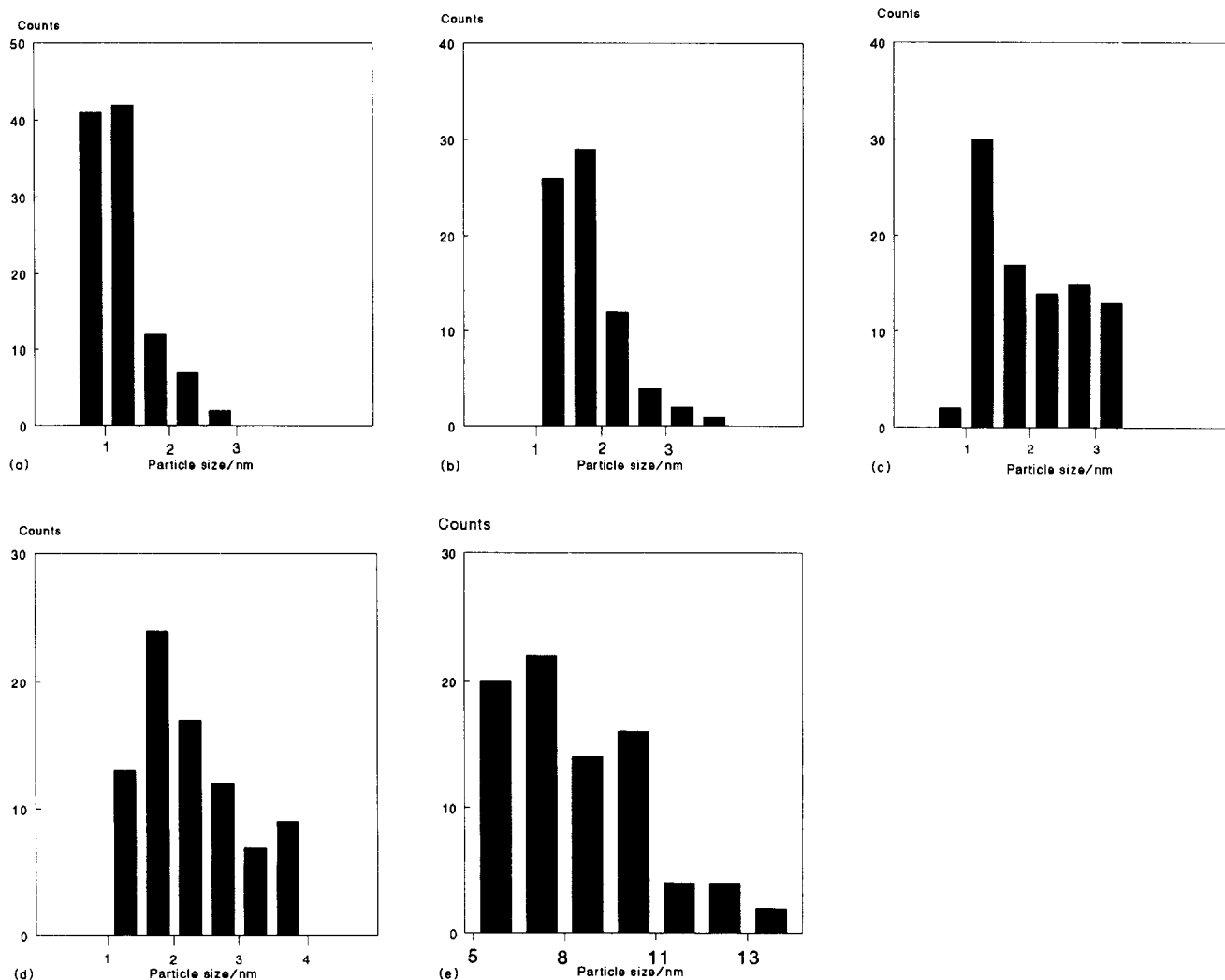


Fig. 1. Histograms obtained by TEM for the Pt/C catalysts. (a) Ion-exchanged catalyst; (b) impregnated catalyst; (c) colloidal "Turkevich" catalyst; (d) colloidal "Bönnemann" catalyst; (e) sintered catalyst.

3. Results

3.1. TEM characterization

Fig. 1 shows the histograms of the particle size distribution for all catalysts. The mean particle sizes are summarized in Table 1; they range from 1.2 to ca. 10 nm. The smallest Pt particles were obtained by the ion-exchange method on an oxidized carbon support. The Pt loading for the catalysts is also given in Table 1.

3.2. Electrochemical characterization

The cyclic voltammograms of the catalysts in 0.5 M H_2SO_4 are given in Fig. 2. The voltammogram of the Turkevich catalyst and the sintered Pt/C catalyst show the well known hydrogen adsorption/desorption characteristics for Pt; two cathodic adsorption peaks and three anodic desorption peaks, usually assigned to weakly, intermediate and strongly bonded hydrogen, respectively. The result that there are only two adsorption peaks while there are three desorption peaks is also found for polycrystalline Pt [21]. The shape of the hydrogen area for the colloidal catalysts is comparable, except that the ratio of weakly/strongly bonded adsorbed hydrogen is higher for the "Bönnemass" catalyst than for the "Turkevich" catalyst. For the ion-exchanged and impregnated catalysts (Fig. 2(a) and (b)), it appears that the strongly bonded hydrogen peak is totally absent and only two desorption peaks and one adsorption peak are seen.

Comparing the oxide reduction peaks for the catalysts clearly shows that the peak potential shifts to

Table 1

Mean particle size as measured by TEM

Catalyst/support	Pt loading/%	Particle size nm
Ion-exchanged/oxidized C	3.5	1.20 ± 0.4
Impregnated/C	4.4	1.70 ± 0.5
Colloidal "Turkevich"/C	5.5	2.50 ± 0.9
Colloidal "Bönnemann"/C	3.7	2.10 ± 1
Sintered impregnated/C	4.0	7.80 ± 2.5

higher values on going from ion-exchanged catalysts (Fig. 2(a)) to impregnated (Fig. 2(b)) to colloidal (Fig. 2(c)). In Fig. 3, the peak potential for the oxide reduction is plotted as a function of the (mean) particle size of the catalysts; this shows that the peak potential increases with increasing particle size in the range up to ca. 4.5 nm, to the value of smooth and platinized Pt. In the voltammogram in Fig. 2(d) ("Bönnemass" catalyst), two oxide reduction peaks seem to be present, which could point to a mixture of smaller and larger particles.

The effect of repeated potential cycling is shown in Fig. 4 for an impregnated catalyst. Both the oxide peak potential and the onset of oxidation are shifted to higher potentials with increasing number of potential cycles. Transmission electron micrographs taken after 60 cycles show an increase in particle size; this is shown in Table 2.

3.3. Oxidation of methanol

In Fig. 5, the cyclic voltammograms (second scan) of all catalysts in 0.1 M $CH_3OH + 0.5 M H_2SO_4$ are presented. The catalysts show different specific activi-

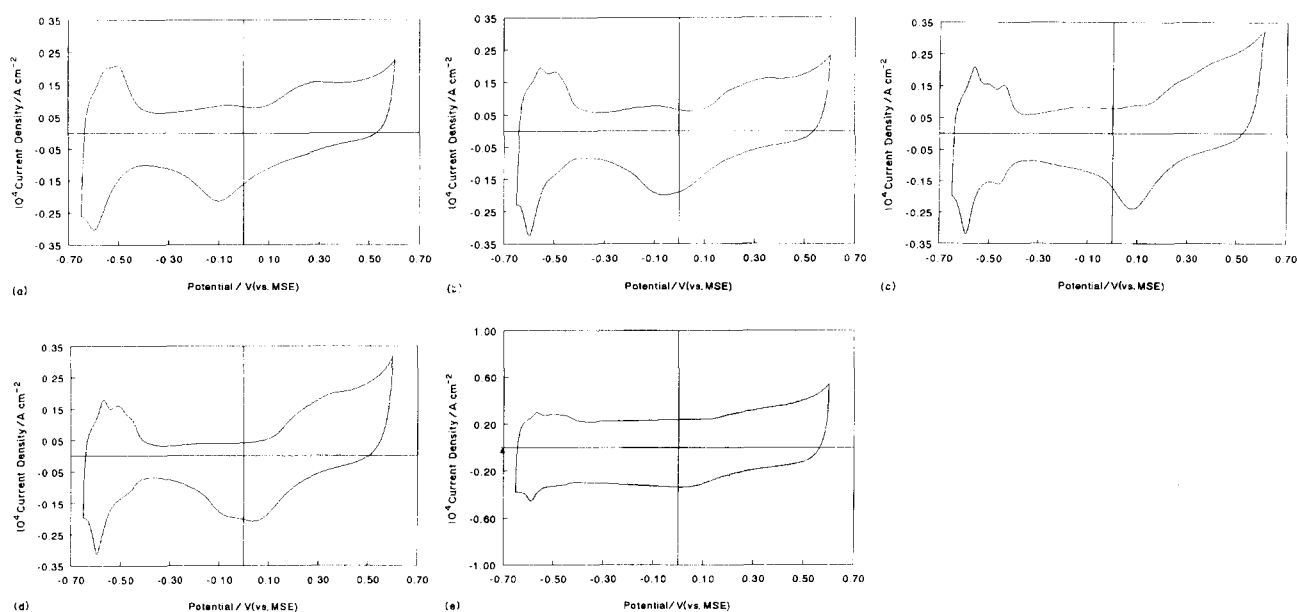


Fig. 2. Cyclic voltammograms of catalysts in Fig. 1 in 0.5 M H_2SO_4 . Scan rate, 10 mV s^{-1} .

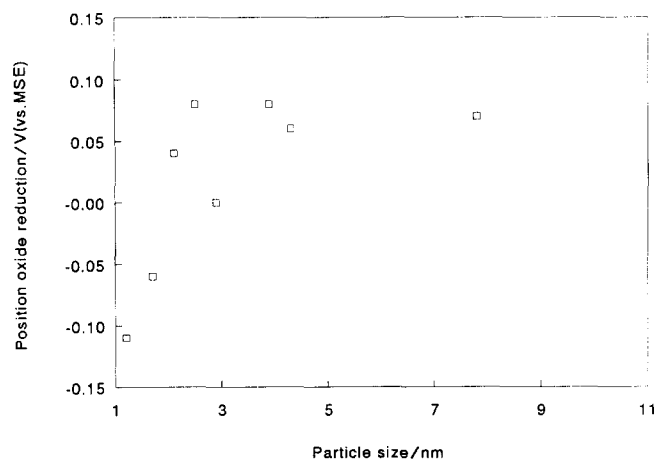


Fig. 3. Peak potential for the oxide reduction for the different catalysts in relation to their particle size.

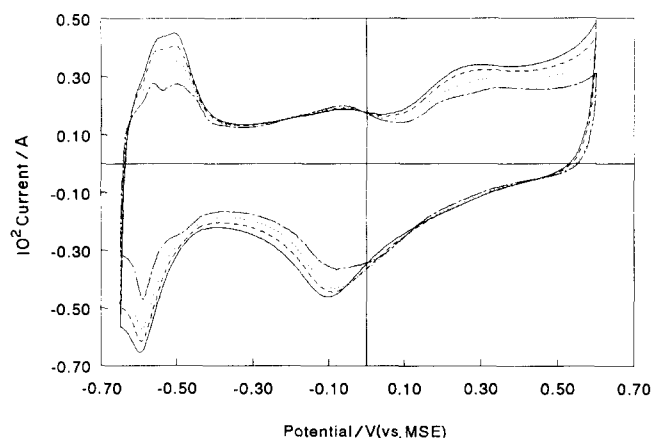


Fig. 4. Effect of repeated potential cycling in 0.5 M H_2SO_4 on the impregnated Pt/C catalyst. (—) Scan 6; (---) scan 12; (····) scan 19; (●●●) scan 62. Scan rate, 10 mV s^{-1} .

Table 2

Mean particle size after repeated potential scanning, as measured by TEM

Catalyst/support	Particle size nm
Impregnated/C	2.90 ± 1.4
Colloidal "Turkevich"/C	4.30 ± 1.9
Colloidal "Bönnemann"/C	3.90 ± 1.4

Table 3

Specific activity for methanol oxidation at -0.05 V vs. MSE in 0.5 M $\text{H}_2\text{SO}_4 + 0.1 \text{ M CH}_3\text{OH}$ at 23°C

Catalyst/support	Activity/ mA cm^{-2}	Activity after particle size growth mA cm^{-2}
Ion-exchanged/oxidized C	0.032	0.071
Impregnated/C	0.055	0.071
Colloidal "Turkevich"/C	0.080	0.110
Colloidal "Bönnemann"/C	0.060	0.086
Colloidal "Turkevich"/ oxidized C	0.085	—
Colloidal "Bönnemann/ oxidized C	0.073	—

ties for the methanol oxidation. The position of the peak potentials changes: there is a small difference in the forward scan between the different catalysts, but in the backward scan a larger shift is noted; this is, of course, related to the position of the oxide reduction potential. In Table 3 the specific activities of all catalysts for the methanol oxidation at a potential of -0.05 V vs. MSE are summarized. These data were taken from the forward scan of the cyclic voltammograms in Fig. 5.

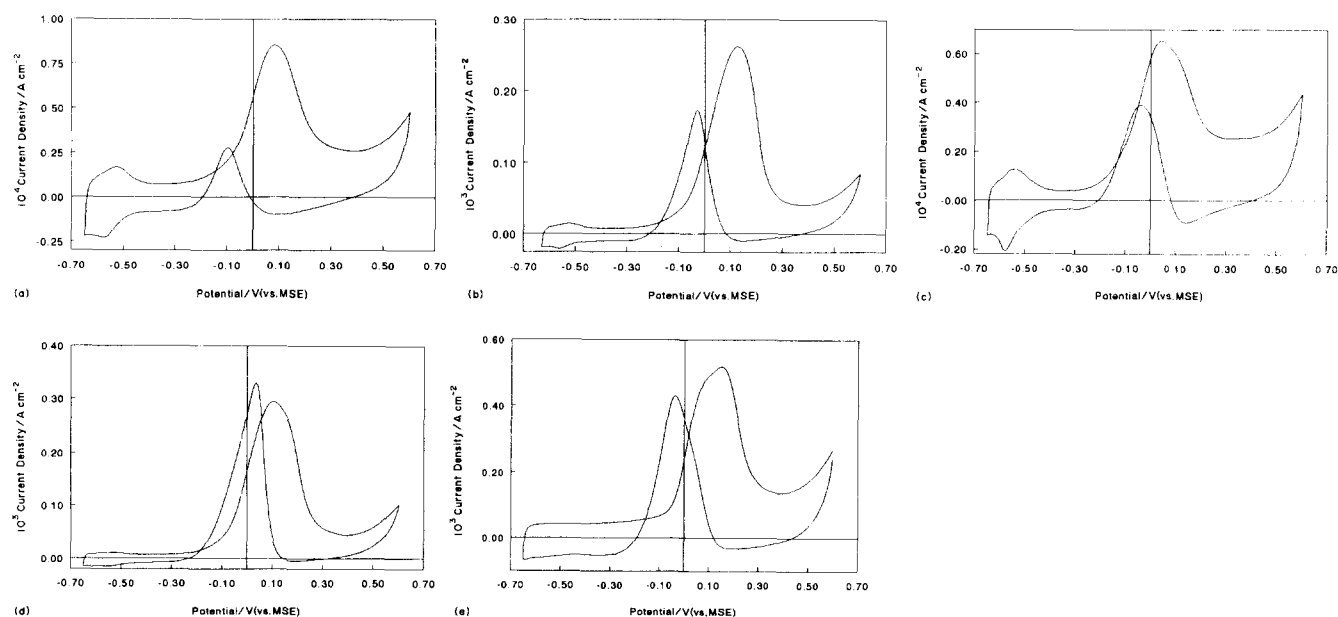


Fig. 5. Cyclic voltammograms (second scan) of the different catalysts in Fig. 1 in $\text{M CH}_3\text{OH} + 0.5 \text{ M H}_2\text{SO}_4$. Scan rate 5 mV s^{-1} .

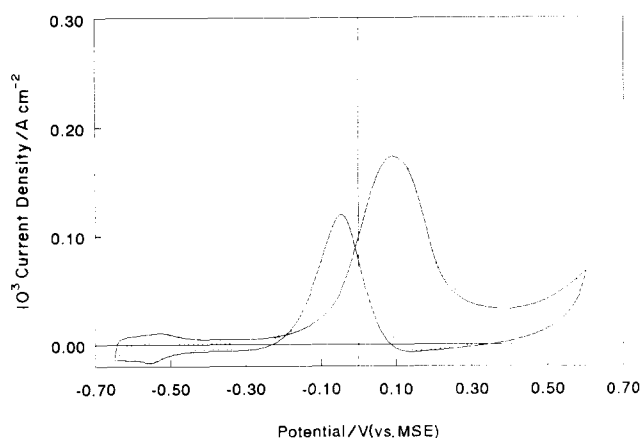


Fig. 6. Effect of scanning on the methanol oxidation for the impregnated catalyst. (—) After five scans in 0.5 M H_2SO_4 ; (·····) after 50 scans in 0.5 M H_2SO_4 . Scan rate, 5 mV s^{-1} in 0.1 M $\text{CH}_3\text{OH} + 0.5 \text{ M H}_2\text{SO}_4$.

Fig. 6 shows the effect of repeated potential cycling of the catalyst in 0.5 M H_2SO_4 on the methanol oxidation. In all cases this led to an increase in specific activity; in Table 3 the activities at -0.05 V vs. MSE are given.

3.4. Carbon support effect

The possible synergistic effect of the carbon support was studied by comparing the activity of the two colloidal catalysts on oxidized and non-oxidized carbon. TEM measurements revealed no change in particle size for the oxidized and non-oxidized carbon systems; the electrochemical characterization of the hydrogen area also does not reveal significant differences (Fig. 7). The specific activity for the methanol oxidation was higher for the oxidized catalyst, as shown in Fig. 8 for

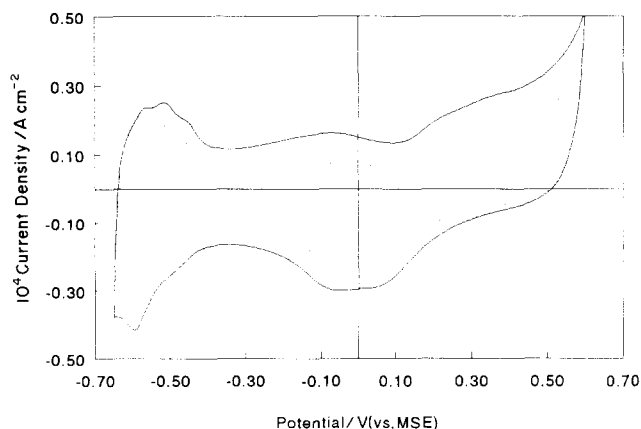


Fig. 7. Voltammogram of a non-oxidized (·····) and an oxidized (—) carbon support for the colloidal “Bönnemann” catalyst in 0.5 M H_2SO_4 . Scan rate, 10 mV s^{-1} .

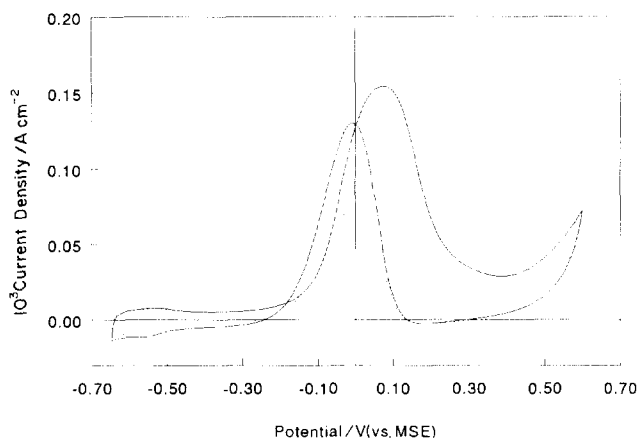


Fig. 8. Cyclic voltammetric curves of methanol oxidation for the catalysts in Fig. 7. Scan rate, 5 mV s^{-1} in 0.1 M $\text{CH}_3\text{OH} + 0.5 \text{ M H}_2\text{SO}_4$.

the “Bönnemann” preparation. Similar results were obtained with the “Turkevich” preparation.

4. Discussion

Repeated oxidation and reduction of the carbon-supported Pt catalyst causes a growth of the Pt particles (compare Tables 1 and 2). This is in agreement with Kinoshita et al. [19]. The accompanying shift to higher potentials for the Pt oxide reduction with increasing particle size is in agreement with results of Takasu et al. [8]. Also, the onset of oxidation is shifted to higher potentials (cf. Fig. 4). This is indicative of a lower Pt–O affinity for larger Pt particles and implies that the ability to activate water, i.e. to break H–O–H bonding with the formation of a Pt–OH species, proceeds at a lower potential for smaller particles. Hence we assume that the smaller sized ion-exchanged catalyst will contain more Pt–OH groups at a given potential than a colloidal catalyst, which in turn should contain more Pt–OH groups than smooth Pt. In view of reaction (2), we therefore expect an increase in specific activity for the methanol oxidation with a decrease in particle size. However, this is not observed, as can be deduced from Fig. 9, in which the specific activities (per real unit surface area) are presented for all of the Pt/C catalysts. The activity for platinized Pt (electrodeposited from H_2PtCl_6 at 10 mA cm^{-2} for 5 min) and smooth Pt (polycrystalline) are also included. For particle sizes in the range 10–4.5 nm, the activity is constant, whereas for particles in the range 4.5–1.2 nm the activity decreases with smaller sizes.

At first sight, these results appear to imply that the oxygen affinity of very small particles is so high that the catalyst surface is largely covered with Pt–OH, thus leaving insufficient sites for methanol adsorbates. Ow-

ing to the small amount of methanol adsorbates, the activity of the small Pt particles is low. The implication then is that water activation is already optimal for large platinum particles, contrary to the general view set out in the Introduction.

There is, however, an alternative possible interpretation: when the particle size decreases, the number of methanol adsorption sites decreases. It can be deduced from Fig. 2 that the ratio of the amount of weakly bonded H to strongly bonded H increases with decreasing particle size. At platinized Pt electrodes we observed that when the amount of strongly adsorbed hydrogen sites increases, the methanol oxidation activity also increases [22]. Beden et al. [23] also reported that methanol preferentially adsorbs on the sites that can strongly bind hydrogen. Hence the relative decrease in strongly bonded H features can be seen as indicative of a decrease in the preferred methanol adsorption sites. From this viewpoint, then, the change in methanol adsorption characteristics dominates over the increased water activation. At present we cannot distinguish between the two explanations.

In Fig. 10, the activity for the methanol oxidation expressed per unit weight of Pt is plotted vs. the Pt particle size; the results might indicate a slight maximum at ca. 1.8 nm. Such a maximum occurs due to the mixed influence of decreasing specific surface area and increasing specific activity with increasing particle size. With our catalysts, no substantial differences were found in the intercrystalline distances. The variation in this distance within one catalyst is at least comparable to the variation between the different catalysts.

The observed difference in specific activity between smooth and platinized Pt is difficult to explain. In the cyclic voltammetric curves in 0.5 M H₂SO₄, no difference was observed for the oxide-formation or oxide-reduction potential. The difference in methanol oxida-

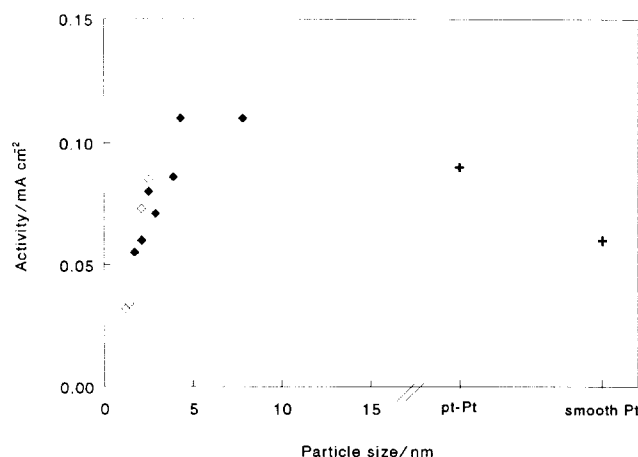


Fig. 9. Specific activity for the methanol oxidation of all of the Pt/C catalysts, platinized Pt and smooth Pt at -0.05 V vs. MSE. (\blacklozenge) Pt/C catalysts; (\diamond) Pt/C_{ox} catalysts; (+) smooth Pt and platinized Pt.

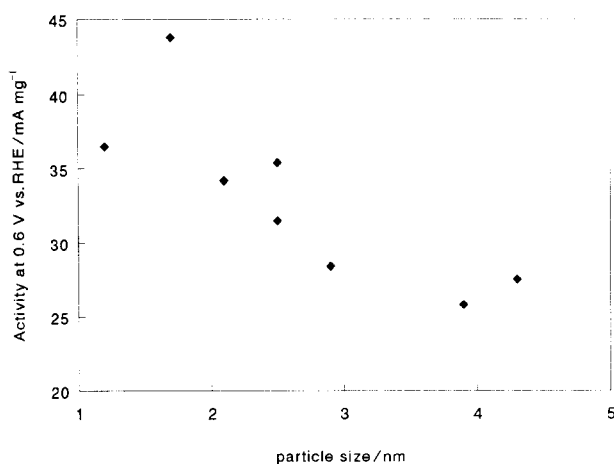


Fig. 10. Specific activity per unit weight of catalyst for the Pt/C catalysts in Fig. 9.

tion activity for these two catalysts thus may not be attributed to a different oxygen binding of the platinum. Furthermore, as there is almost no difference between the H_w/H_s ratios for the two systems, it may be assumed that the adsorption sites for methanol also do not differ substantially. At present it is therefore not clear why platinized platinum has a higher activity for the methanol oxidation.

It is seen in Fig. 9 that upon introduction of a carbon support, a further increase in methanol oxidation activity occurs. This suggests a metal support interaction, i.e. a ligand effect due to the carbon support. Using an oxidized carbon support, instead of a non-oxidized support, increases the activity even further, which confirms the presence of a metal–support interaction.

The results presented here differ from those of Attwood et al. [11], who observed a maximum in specific activity vs. platinum area. Estimation of the particle size from the specific surface area reveals that the sizes used by Attwood et al. are in the same range (1.5–4 nm) as those considered here. One can therefore conclude that the different preparation methods used by Attwood et al. should have a considerable influence on the behaviour of the Pt catalyst. The results of Watanabe et al. [14] and Enyo et al. [13] cannot be compared with our results since we do not know whether their catalysts give a shift in oxide reduction potential with change in particle size.

5. Conclusions

The Pt particle size clearly affects the methanol oxidation activity. For particle sizes in the range 1.2–4.5 nm a decrease in size results in a decrease in methanol oxidation activity; for sizes larger than ca. 4.5 nm the

methanol oxidation activity remains almost constant. Furthermore, a close relationship between particle size and the oxide reduction potential for particles in the range 1.2–4.5 nm is observed. This would imply that a higher coverage of OH species can be obtained on Pt if the particle size is decreased to values below 4.5 nm. However, the expected increase in the specific activity of Pt/C for the methanol oxidation is not observed. Apparently the OH/methanolic species coverage ratio has become unfavourable. This may be due to (1) a surface coverage of OH_{ads} that is too high and results in a decrease in COH_{ads} or (2) a decrease in the number preferred adsorption sites for methanol with a decrease in Pt particle size. For particle sizes > 5 nm the specific activity reaches a limiting value which is about twice that of smooth Pt.

Finally, it is found that a metal–support interaction exists for Pt/C catalysts; Pt on oxidized carbon shows a higher activity due to the introduction for an acidic group.

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