Characterization of graphite-supported platinum catalysts by electrochemical methods and XPS

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Characterization of Graphite-supported Platinum Catalysts by Electrochemical Methods and XPS

F. A. de Bruijn, G. B. Marin,* J. W. Niemantsverdriet, W. H. M. Visscher and J. A. R. van Veen
Schuit Institute of Catalysis, Eindhoven University of Technology, PO Box 513, NL-5600 MB Eindhoven, Netherlands

X-ray photoelectron spectroscopy and cyclic voltammetry have been used to characterize 4.9 wt.% platinum-on-graphite catalysts used for the oxidation with molecular oxygen of methyl α -D-glucoside in aqueous solution. Cyclic voltammetry indicates that a surface oxidic layer is formed on the platinum particles upon exposure to ambient air. This oxidation could not be confirmed by XPS, however. The oxidation of methyl α -D-glucoside in the liquid phase is accompanied by growth of the platinum particles. Open-circuit potential measurements indicated an increasing oxygen coverage of the platinum surface during reaction.

INTRODUCTION

Carbon- and graphite-supported platinum catalysts are frequently used for the liquid phase oxidation of organic molecules, in particular within the context of fuel cells. Owing to growth of metal particles,¹ deposition of carbonaceous species² or oxidation of the metal,³ the catalyst can deactivate during reaction. In order to get insight to this deactivation and hence to improve the catalyst, techniques are required to characterize alterations of the active material.

Both XPS and cyclic voltammetry yield distinct information on the exposed surface area of the platinum particles and thus on particle growth. Carbonaceous deposits on the platinum/graphite catalyst surface cannot be observed with XPS but can be derived from cyclic voltammetry. However, the simultaneous oxidation of the graphite support makes quantification of these deposits difficult. Oxidized platinum can be discerned clearly from metallic platinum by both XPS and cyclic voltammetry.

XPS and cyclic voltammetry are commonly used to characterize catalyst surfaces before and after reaction. *In situ* information on the state of the platinum surface during reaction can be obtained from the open-circuit potential of the catalyst; in contrast to cyclic voltammetry, no potential is applied on the catalyst electrode so that the surface is not influenced by the measurement itself.

Since x-ray photoelectron spectroscopy is performed under high-vacuum conditions, samples have to be dried to maintain the vacuum. Cyclic voltammetry is performed in the liquid phase and the analysis of wet catalysts is thus possible.

The surface sensitivity in x-ray photoelectron spectroscopy is mainly determined by the mean free path of the analysed electrons, in this case of the Pt 4f electrons, with a kinetic energy of 1410 eV when using an Al K α x-ray source. The corresponding mean free path is about 1.5 nm, implying that in many cases a major part of the atoms that contribute to the measured XPS signal are not exposed at the surface. Surface sensitivity

is, however, guaranteed for highly dispersed catalysts because a major part of all platinum atoms are exposed as the surface. Cyclic voltammetry is able to detect fractions of a monolayer of oxygen or of organic adsorbates and is thus highly surface-sensitive.

Measuring the catalyst electric potential gives the opportunity to monitor the surface state of platinum during reaction without disturbance. Indeed, the extent of coverage with hydrogen and oxygen adatoms has a dominant influence on the open-circuit potential of a platinum surface in solution. In alkaline medium (1N NaOH), hydrogen coverage occurs at potentials between 0 V at monolayer coverage and 0.4 V at low coverage *vs.* the reversible hydrogen electrode (RHE).⁴ Coverage with oxygen-like species occurs at potentials between 0.5 V/RHE at low coverage with OH_{ad} and 1.2 V/RHE at monolayer coverage with O_{ad}.^{5,6} In many liquid phase reactions, organic reactants are believed to be chemisorbed on the catalyst surface. Chemisorption of these organic molecules is often accompanied by dehydrogenation and partial destruction of the molecule. This dehydrogenation produces H_{ad} atoms on a bare platinum surface, thus lowering its potential. This effect has been measured by many authors (see e.g. Ref. 7). A shift in the potential during reaction thus indicates an alteration in the surface state of this electrode.

The aim of this study is to compare the possibilities of x-ray photoelectron spectroscopy and electrochemical methods for the characterization of platinum/graphite catalysts used for liquid phase oxidation reactions. For this purpose a method has been developed for the manufacturing of electrodes from platinum/graphite catalysts that enables direct analysis of catalysts after reaction.

EXPERIMENTAL

Graphite-supported catalyst

A catalyst comprising 4.9 wt.% platinum supported on graphite was used in this study. The preparation procedure was described by Richard and Gallezot.⁸ The particle diameter as determined by TEM was 1.85 nm.

* Author to whom correspondence should be addressed.

The fraction of exposed platinum atoms as determined by CO chemisorption amounted to 0.7 assuming a 1:1 stoichiometry.⁹ The Brunauer-Emmett-Teller (BET) surface area of the graphite support amounted to 117 m² g⁻¹.

Sample treatment

Four platinum/graphite catalysts from the same batch were examined in this study. Two samples were exposed to the gas phase and two samples were exposed to the liquid phase.

The samples exposed to the gas phase were reduced with a 10%–20% hydrogen-in-nitrogen gas mixture at a temperature of 473 K for 2 h. This reduced catalyst was carefully transported in a nitrogen-saturated box to the x-ray photoelectron spectrometer. After analysis the reduced catalyst was exposed to air at room temperature for more than 200 h and analysed again.

The samples exposed to the liquid phase were reduced for 1 h with molecular hydrogen in a neutral aqueous solution at a temperature of 363 K, after which 0.2 M methyl α -D-glucoside was added. After this treatment one catalyst was analysed and the other was subsequently used for the liquid phase oxidation of methyl α -D-glucoside in a continuously stirred tank reactor in the presence of molecular oxygen. Following filtration, all catalysts were dried at a pressure of 5 kPa at 313 K for 16 h, except the samples on which the amount of oxidized platinum was determined by cyclic voltammetry.

X-ray photoelectron spectroscopy

The XP spectra were collected on a VG Escalab 200 spectrometer using monochromated Al K α radiation as an excitation source and equipped with a hemispherical analyser and a five-channel detector. The catalyst powder was pressed in an indium foil and mounted on a tantalum sample holder. In the case of catalysts that had been used in the liquid phase, no special care was taken to prevent air contact. The analysis was based on the binding energy of the Pt 4f level. The C 1s signal was set at a value of 284.4 eV and used as an internal reference.

Cyclic voltammetry

The cyclic voltammetric analysis was performed with the catalyst as working electrode. The most frequently used method¹⁰ to prepare electrodes of carbon-supported platinum catalysts consists of mixing dry catalysts with a Teflon suspension, followed either by hot pressing at temperatures of about 400 K or by cold pressing and then thermal baking at temperatures above 573 K. These thermal treatments are required for long-term stability of the electrodes. However, this procedure cannot be applied in the case of catalysts used for reactions since it alters the state of the platinum. Because long-term stability is not an essential requirement for the analysis of the electrodes, a method is developed for preparation of electrodes without any thermal treatment. Dry or wet catalyst samples can be

used for the preparation; a glassy carbon electrode is used as a physical support.

An amount of 20 mg of dry or 40 mg of wet catalyst was suspended in 2 ml 1:1000 diluted polytetrafluoroethylene suspension (DMI Fluon GPI 60% dispersion) and agitated in an ultrasonic bath for 15 min. This suspension was then filtered on a 0.45 μ m Schleicher & Schüll membrane filter. The resulting residue was a sticking paste which was mounted on a glassy carbon electrode with a geometrical surface area of 0.24 cm². The cyclic voltammograms of this catalyst electrode showed that it was stable for several hours at a temperature of 298 K and pH 14. Wet catalysts were used for detection of platinum oxides, dried catalysts for determination of the surface area.

Platinum foil was used as auxiliary electrode and Hg/HgO as reference electrode. The potential was varied using a Potentiostat Wenking POS 73. All reported potentials are referred to the reversible hydrogen electrode. All cyclic voltammetry measurements were performed in oxygen-free solutions of 1N NaOH (Merck analytical grade) at a temperature of 298 K. Deionized and doubly distilled water was used.

Determination of platinum surface area. The surface area of platinum is determined from the charge associated with the anodic oxidation of hydrogen atoms between 0 and 0.4 V. The fraction of exposed platinum was determined by varying the potential between 0.12 and 1.52 V at a scan rate of 1 mV s⁻¹. The charge associated with the reduction of platinum oxide can be used as an alternative to determine the surface area. Prior to this analysis the working electrode was treated by repetitive oxidation and reduction cycles between the same potentials as during analysis for 15 min at a scan rate of 10 mV s⁻¹ in order to guarantee that this surface area loss of active centres is permanent and not caused by removable carbonaceous species on the surface: these would certainly be oxidized at potentials of 1.5 V.

Detection of platinum oxides. Platinum oxides can be reduced cathodically at potentials lower than 0.8 V. Different platinum oxides can be discerned in cyclic voltammetry by the potentials at which reduction occurs. Surface oxides can be reduced at $\sim$ 0.75 V whereas the reduction of bulk oxides requires a potential of $\sim$ 0.4 V.¹¹ In order to detect the presence of platinum oxides, the potential was varied between 1.06 and 0.12 V at a scan rate of 1 mV s⁻¹. The starting potential is near the open-circuit potential of the catalyst after reaction. Electrochemical oxidation of platinum only occurs significantly above this potential. Two successive scans were performed. After the first cathodic scan the catalyst is in the reduced state and comparable to a catalyst reduced by gas phase hydrogen. The difference between the first and second cathodic scans was taken as the reducible amount of platinum oxide.

Open-circuit potential measurements

Open-circuit potential measurements were performed on a platinized platinum electrode. This electrode had a

geometric surface area of 6 cm² and a real surface area of 2440 cm², as determined by the electrochemical oxidation of adsorbed hydrogen. This corresponds to a platinum particle diameter of 15–20 nm.^{12,13} A platinized platinum foil was used instead of the catalyst electrode because it was more suitable for the open-circuit potential measurements¹⁴ in the electrochemical cell used in the present study. The use of a platinized platinum foil is the best compromise between a good measurement of the open-circuit potential and a platinum surface area similar to that of platinum supported on graphite. The chemisorption of oxygen is, however, stronger on the small particles of the catalyst than on the relatively large particles of the platinized platinum electrode.¹⁵ An Hg/HgO electrode was used as reference electrode. All potentials are again referred to the reversible hydrogen electrode.

Open-circuit potentials were first measured in nitrogen-, hydrogen- and oxygen-saturated solutions of 0.1 M NaClO₄ of pH 12 at a temperature of 323 K. The potentials established were considered to correspond to a clean platinum surface, to a monolayer coverage of the platinum with hydrogen adatoms or to a monolayer coverage with oxygen adatoms.

The influence of reactant adsorption was measured in a nitrogen-saturated solution of 0.1 M NaClO₄ and 0.1 M methyl α -D-glucoside solution of pH 12 at 323 K. This solution was subsequently saturated with oxygen and the open-circuit potential was followed during the proceeding reaction.

RESULTS AND DISCUSSION

X-ray photoelectron spectroscopy

In order to see whether surface oxides on platinum/graphite can be detected by XPS, a reduced and an air-exposed platinum/graphite sample were investigated. XP spectra of all catalyst samples examined are given in Fig. 1. Binding energies of the Pt 4f level of the analysed platinum/graphite catalysts are given in Table 1 together with Pt 4f/C 1s peak area ratios.

As can be seen in Fig. 1, the XP spectra of the air-exposed catalyst and both the gas and liquid-phase-reduced catalysts differ only slightly if at all. The measured binding energy of 71.3 eV is almost equal to that of platinum bulk metal, 71.0 eV,^{16–18} indicating that a major part of the platinum particles are in the metallic state. The spectra contain no features that can be attributed to oxidized platinum.

Table 1. Binding energies of the Pt 4f level and Pt 4f/C 1s peak area ratios in various 4.9 wt.% platinum/graphite catalyst samples

Pt/graphite catalyst	Pt 4f _{7/2} (eV)	Pt 4f _{5/2} (eV)	Peak area ratio Pt/C (a.u.)
Reduced	71.3	74.6	3.4
Air-exposed	71.5	74.6	3.4
Reduced in liquid phase	71.4	74.4	3.4
After liquid phase oxidation	71.4	74.6	2.0

Figure 1. (A) XP spectrum of the platinum 4f level of a 4.9 wt.% platinum/graphite catalyst after reduction with 10%–20% molecular hydrogen at 473 K for 2 h (B) As A, followed by exposure to ambient air for 200 h. (C) After liquid phase reduction with molecular hydrogen at 363 K pH 7, for 1 h followed by addition of 0.2 M methyl α -D-glucoside. (D) As C followed by oxidation of methyl α -D-glucoside with molecular oxygen at 323 K, pH 9, for 20 h.

As can be seen from Fig. 1 and Table 1, the only difference between the XP spectrum of the catalyst used for the liquid phase oxidation and the XP spectra of the other catalysts lies in the Pt 4f/C 1s peak area ratio of the measured XPS signal. The binding energies of the Pt 4f level are about the same. The full width at half-maximum of the Pt 4f_{7/2} peak is 0.4 eV broader in the spectrum of the freshly reduced sample than for the catalyst after reaction. This might be the result of a narrower particle size distribution in the catalyst after reaction, the smaller particles having disappeared. The decreased Pt 4f/C 1s peak area ratio supports this hypothesis. There is no consensus in the literature concerning the stability of platinum oxides during XPS measurements. Hammond and Winograd¹⁸ and Katrib¹⁹ observed a decomposition of platinum oxides and platinum chloride complexes under x-ray fluxes, even in the case of a monochromated x-ray flux,¹⁸ while Peuckert *et al.*²⁰ did not observe any instability of platinum oxides. Peuckert *et al.*²⁰ analysed partially oxidized platinum foils, while Hammond and Winograd¹⁸ and Katrib¹⁹ used powders in their studies. The possibility that the stability depends on the platinum particle size should not be excluded.

In contrast to the present study, Parmigiani *et al.*²¹ found an extended oxidation of platinum after exposure to air in highly dispersed platinum/silica and platinum/Teflon catalysts with comparable dispersion to the catalyst in the present study. The reason for this contradiction could be, as suggested by Parmigiani *et al.*,²¹ that the influence of exposure to air is strongly dependent on the catalyst support. Another possibility is that platinum oxides dispersed on silica are more stable towards x-ray-flux-induced decomposition in high vacuum than platinum particles dispersed on a graphite support.

The obtained XP spectra do not give evidence of any platinum oxidation during the liquid phase oxidation

reaction or during exposure to air. The only difference between platinum/graphite catalysts before and after liquid phase reaction is that the Pt 4f/C 1s peak area ratio decreased by a factor of 1.7, indicating that platinum particle growth has taken place during reaction.

Open-circuit potential

The measured potentials for uncovered, hydrogen-covered and oxygen-covered platinum surfaces are given in Table 2. After adsorption of methyl α -D-glucoside on a bare platinum surface—which means devoid of hydrogen adatoms, oxygen adatoms or organic adsorbates—the potential decreased to 0.30 V within a few minutes, indicating that dehydrogenation takes place during adsorption. The measured potential of a platinized platinum surface during liquid phase oxidation of methyl α -D-glucoside is given in Fig. 2. The potential at $t = 0$ refers to the potential stabilized within a few minutes after saturation of the reaction mixture with oxygen.

Comparing Fig. 2 with Table 2 leads to the conclusion that at the beginning of the oxidation reaction the platinum surface is covered by both adsorbed reactant and oxygen. During reaction, however, the potential

Figure 2. Open-circuit potentials of platinized platinum during the oxidation of 0.1 M methyl α -D-glucoside at 323 K, pH 12, in 0.1 M NaClO₄ with molecular oxygen.

shifts towards values that correspond to oxygen-covered platinum. Reactant molecules are thus displaced by oxygen adatoms.

Cyclic voltammetry

Platinum surface area. The cyclic voltammograms of the catalysts for determination of the surface area are given in Fig. 3 together with the cyclic voltammogram of the graphite support before ion exchange with platinum ions. Figure 3A shows the cyclic voltammogram obtained on a freshly reduced platinum catalyst used to determine the surface area. Clearly, all features typical for platinum, such as the deposition and oxidation of hydrogen atoms and the adsorption and reduction of oxygen atoms, are present. These features are super-

Table 2. Open-circuit potentials of platinized platinum at 323 K, pH 12, 0.1 M NaClO₄ for various surface states

Surface state of platinized Pt	Open-circuit potential (V/RHE)
Bare	0.53
Hydrogen-covered	0
Oxygen-covered	1.12

Figure 3. (A) Cyclic voltammogram of a freshly reduced 4.9 wt.% platinum/graphite catalyst; scan rate 1 mV s⁻¹ (B) Cyclic voltammogram of graphite support before ion exchange with platinum ions; scan rate 1 mV s⁻¹. (C) Cyclic voltammogram of a 4.9 wt.% platinum/graphite catalyst after reduction in liquid phase at $T = 363$ K, pH 7, for 1 h with molecular hydrogen followed by addition of 0.2 M methyl α -D-glucoside. (D) As C followed by oxidation of methyl α -D-glucoside with molecular oxygen at $T = 323$ K, pH 9, for 20 h.

posed on the cyclic voltammogram of the graphite support shown in Fig. 3B.

The fraction of exposed platinum atoms on the catalyst reduced in the liquid phase can be deduced from Fig. 3C. The effect of reaction on the fraction of exposed platinum atoms follows from comparison of Fig. 3C and 3D. Clearly the fraction of exposed platinum atoms has strongly decreased after reaction. The cyclic voltammogram of the used catalyst strongly resembles the cyclic voltammogram of the graphite support, Fig. 3B.

Platinum oxides. Cyclic voltammograms of the catalysts for determination of platinum oxides are given in Fig. 4. Figure 4A shows the cyclic voltammogram of the catalyst after exposure to ambient air resulting from two successive scans. The presence after the first scan of a cathodic reduction peak with a shape and a surface area similar to the reduction peak shown in Fig. 3A points to the existence of oxidized platinum after exposure to ambient air. The reduction potential in the air-exposed catalyst indicates the presence of a surface oxide rather than a bulk oxide. The ratio of oxygen to platinum surface atoms amounts to 0.75. The electrochemical observation of platinum oxide after exposure to air is in contradiction with the XPS observation indicating that no appreciable amount of platinum oxide is present after exposure to air. This contradiction strengthens the idea of the instability of platinum surface oxides during XPS measurements.

The cyclic voltammograms of the catalyst after reduction in the liquid phase and after reaction, shown in Figs 4B and 4C, are similar. This similarity and the coincidence of the two successive scans suggest that no modification of the platinum occurs during reaction. During transportation of wet catalysts from the reactor to the electrochemical cell no oxidation of platinum has taken place.

The small measured net reduction area in platinum/graphite catalysts before and after the liquid phase oxidation is in contradiction with open-circuit potential measurements which indicate that the platinum surface is completely covered with adsorbed oxygen. This adsorbed oxygen is removed by reducing reactant still present after filtration.

CONCLUSIONS

In order to characterize graphite-supported platinum catalysts in terms of the oxidation state and the fraction of exposed platinum atoms, a combination of techniques is required.

XPS does not allow us to establish the presence of oxidic platinum or surface oxygen atoms on the investigated catalyst. Cyclic voltammetry does, however, show that a surface oxidic layer is formed upon exposure to ambient air. It was also shown that the developed method for preparation of catalyst electrodes allows *ex situ* characterization of catalysts. Open-circuit potential measurements on platinized platinum can be performed *in situ* and can provide information on the nature and amount of adsorbed species during reaction. A specially designed electrochemical cell is required to apply this technique on powder catalysts, however.

The fraction of exposed platinum atoms can also be obtained from cyclic voltammetry measurements. The sensitivity of the technique is limited for catalysts with high-surface-area supports as investigated in the present work. In that respect XPS presents advantages since it allows the determination of the fraction of exposed platinum atoms based on the ratio of the Pt/C signal.

Figure 4. (A) Cyclic voltammogram of a 4.9 wt.% platinum/graphite catalyst after exposure to ambient air. Dashed curve is first cathodic scan; solid curve is second scan. (B) Cyclic voltammogram of a 4.9 wt.% platinum/graphite catalyst after reduction in liquid phase at $T = 363$ K, pH 7, for 1 h with molecular hydrogen followed by addition of 0.2 M methyl α -D-glucoside. Dashed curve is first cathodic scan; solid curve is second scan. (C) As B followed by oxidation of methyl α -D-glucoside with molecular oxygen at $T = 323$ K, pH 9, for 20 h. Dashed curve is first cathodic scan; solid curve is second scan.

REFERENCES

1. A. Honji, T. Mori and Y. Hishinuma, *J. Electrochem. Soc.* **135**, 355–359 (1988).
2. I. T. Bae, X. Xing, C. C. Lin and E. Yeager, *J. Electroanal. Chem.* **284**, 335–349 (1990).
3. J. B. Goodenough, A. Hamnett, B. J. Kennedy and S. A. Weeks, *Electrochim. Acta* **32**, 1233–1238 (1987).
4. K. Kinoshita, D. R. Ferrier and P. Stonehart, *Electrochim. Acta* **23**, 45–54 (1978).
5. M. Peuckert, *Electrochim. Acta* **29**, 1315–1320 (1984).
6. V. S. Bagotzky and M. R. Tarasevich, *J. Electroanal. Chem.* **101**, 1–17 (1979).
7. O. A. Petry, B. I. Podlovchenko, A. N. Frumkin and H. Lal, *J. Electroanal. Chem.* **10**, 253–269 (1965).
8. D. Richard and P. Gallezot, in *Scientific Basis for the Preparation of Catalysts IV*, ed. by B. Delmon, P. Grange, P. A. Jacobs and G. Poncelet, pp. 71–79. Elsevier, Amsterdam (1987).
9. J. J. F. Scholten, A. P. Pijpers and A. M. L. Hustings, *Catal. Rev. Sci. Eng.* **27**, 151–206 (1985).
10. K. Kordesch, S. Jahangir and M. Schautz, *Electrochim. Acta* **29**, 1589–1596 (1984).
11. P. A. Attwood, B.D. McNicol and R. T. Short, *J. Catal.* **67**, 287–295 (1981).
12. M. M. P. Janssen and J. Moolhuysen, *Electrochim. Acta* **21**, 861–871 (1976).
13. T. D. Gladysheva, E. I. Shkol'nikov, Y. M. Vol'fkovich and B. I. Podlovchenko, *Elektrokhimiya* **18**, 435–442 (1982).
14. R. DiCosimo and G. M. Whitesides, *J. Phys. Chem.* **93**, 768–775 (1989).
15. M. Peuckert, T. Yoneda, R. A. Dalla Betta and M. Boudart, *J. Electrochem. Soc.* **133**, 944–947 (1986).
16. D. Briggs and M. P. Seah, *Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy*. Wiley, Chichester (1983).
17. M. Hara, K. Asami and K. Hashimoto, *Electrochim. Acta* **28**, 1073–1081 (1983).
18. J. S. Hammond and N. Winograd, *J. Electroanal. Chem.* **78**, 55–69 (1977).
19. A. Katrib, *J. Electron Spectrosc. Relat. Phenom.* **18**, 275–278 (1980).
20. M. Peuckert, F. P. Coenen and H.P. Bonzel, *Electrochim. Acta* **29**, 1305–1314 (1984).
21. F. Parmigiani, E. Kay, P. S. Bagus and C. J. Nelin, *J. Electron. Spectrosc. Relat. Phenom.* **50**, 39–46 (1990).