

# Thiol protected platinum black and palladium black catalysts in oxidation catalysis

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## Abstract

Platinum and palladium metals are common catalysts for formic acid wet oxidation, exhibiting high activity and good stability. However, in the presence of some reactive organic substances, even in low concentrations, they suffer severe deactivation. This paper demonstrates the feasibility of protecting metal catalysts from aggressive media by creating a tertiary structure over the active sites. The approach is based on the known principle of metal surface modification by self-assembled organic monolayer films. We have found that self-assembled monolayers (SAMs) fabricated from heterocyclic thiols containing nitrogen, e.g., 6-mercaptopurine (6MP), can protect platinum and palladium black catalysts for formic acid oxidation in the presence of iminobis[methylenephosphonic acid] (IDMPA). IDMPA was chosen as a model inhibitor because it displays strong chelating properties. Catalysts protected with 6MP demonstrate higher activity and stability and have significantly lower metal leaching (up to 15 times in case of palladium black) than their unprotected counterparts. The surface structure of the catalysts and their surface composition were characterized using X-ray photoelectron spectroscopy (XPS) and Scanning Tunneling Microscopy (STM). © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Platinum and palladium catalysts; Oxidation; Formic acid; Self-assembled monolayers; Thiols

## 1. Introduction

Heterogeneous catalytic processes on metals are governed by the subtle interplay of participating players: catalysts and substrates at the interface. A slight modification of the metal surface can dramatically change the surface chemistry and therefore the activity of the catalyst.

Recently, formation of self-assembled organic monolayer films has become an attractive approach for modification of metal surfaces [1]. Being strongly bonded to the metal surface, self-assembled molecules form highly ordered and densely packed monolayers. Such organized organic surface structures have been studied by many research groups, especially in the areas of adhesion [2,3], corrosion [4], microelectronics [5,6], electrochemistry [7], and analytical chemistry [8]. In this article, we demonstrate the idea of using self-assembled monolayers (SAMs) to protect metal catalysts from aggressive media

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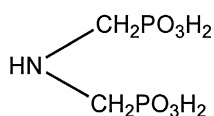
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by creating a tertiary structure over the active metal sites. Iminobis[methylenephosphonic acid] CAS [17231-34-6], (IDMPA) (Scheme 1), was chosen as a model inhibitor because of its strong chelating properties [9].

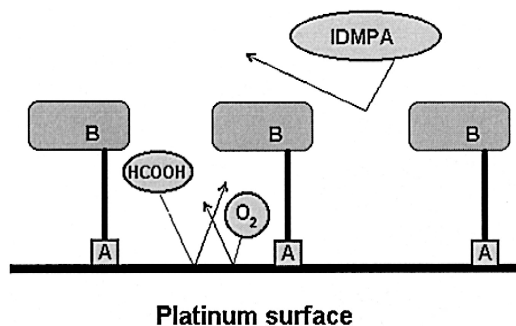
Formic acid oxidation has been utilized as a test reaction in heterogeneous oxidation catalysis [10,11]. Platinum and palladium metals are common catalysts for this reaction, and they exhibit high activity and good stability for formic acid destruction [12]. However, in the presence of some reactive organic substances, even in low concentrations, these noble metal catalysts suffer severe deactivation and dissolution into the reaction media (leaching) [13]. For our application, in contrast to the standard SAM preparation techniques [14], not all active sites should be covered in order to preserve sufficient catalytic activity. Conceptually, some active sites must be available for catalysis while others are required to provide the scaffold for construction of the tertiary structure responsible for discrimination and filtering of potential adsorbates and reactants at the molecular scale. Our approach can be illustrated by Scheme 2.

Formation of the monolayer is achieved through specific binding of site ‘‘A’’ with a noble metal. In this way, we can deposit a functionality ‘‘B’’ over the metal surface. The functionality ‘‘B’’ could be charged or uncharged. The extent of surface coverage can be controlled by the number ratio of A/Pt<sub>surface</sub> and/or bulkiness of functionality ‘‘B.’’

It is well known in the literature [15,16] that sulfur-containing molecules bind tightly with platinum through the sulfur atom. The sulfur atom is, therefore, a good anchor point (i.e., functionality ‘‘A’’ in Scheme 2) for binding to the platinum surface. An amine group is chosen



Scheme 1. Iminobis[methylenephosphonic acid].



Scheme 2. Tertiary structure on platinum surface rejects undesirable molecule of IDMPA and while allowing formic acid and oxygen to reach the Pt surface.

as the functionality ‘‘B’’, which upon protonation can create a cationic monolayer.

It has been demonstrated earlier that certain purines form SAMs on crystalline gold [17]. One could anticipate that these compounds might also form monolayers on other noble metals like Pt and Pd. In this article, we report our findings that SAMs fabricated from heterocyclic thiols containing nitrogen, e.g., 6-mercaptapurine (6MP), can effectively protect platinum and palladium black catalysts for formic acid oxidation in the presence of IDMPA.

## 2. Experimental

### 2.1. Screening catalyst procedure

Formic acid oxidation experiments were carried out at atmospheric pressure with an oxygen flow of 100 ml/min in a 250-ml four-neck glass round bottom flask equipped with reflux condenser, thermocouple, magnetic stir bar, and heating mantle. All reactions were run at 60°C. Oxygen was bubbled through the reaction mixture using a metal gas dispenser and controlled by a flow controller. The amounts of catalyst used were: 0.187 g for platinum-based catalysts and 0.101 g for palladium-based catalysts, respectively, and the total mass of the reaction mixture was 200 g. with a loading of 0.2 wt.%

of IDMPA. During the experiment, equal doses of formic acid (7.3 mmol) (pulses) were injected into the reaction with 40 min between pulses. After reaction, the catalyst was removed by filtration and the filtrate was analyzed for Pt or Pd by inductively coupled plasma mass spectrometry (ICP-MS). The amount of carbon dioxide generated from formic acid oxidation was monitored using an inline Rozenmount 880A carbon dioxide analyzer. Workbench 3.00.15 software (Strawberry Tree) was used for data acquisition.

## 2.2. Catalyst preparation

Platinum and palladium blacks were purchased from Strem Scientific and Aldrich, respectively. IDMPA was obtained from Sigma. Other chemicals were purchased from Aldrich and Acros. All chemicals were used as received without purification. Catalysts were prepared by dissolving organic adsorbates in 150–200 ml of suitable solvent (water for 6MP, hypoxanthine, and purine; hexane for 1-naphthalenethiol) in a round bottom flask equipped with condenser, magnetic stir bar, and thermocouple. Platinum or palladium black powders were added to the solution and stirred at 60°C for 7 h. Then, the flask was cooled down to room temperature and stirred for an additional 13 h. In the case of organic solvents, the treatment was carried out at room temperature. After these equilibrations, the slurry was filtered and washed at room temperature with deionized water (or with corresponding organic solvent). The nut cake was dried under vacuum at 60°C for 2 h. The catalysts were analyzed for sulfur, nitrogen, and carbon by elemental analysis and X-ray photoelectron spectroscopy (XPS).

## 2.3. Catalyst characterization

### 2.3.1. XPS

XPS measurements were performed using a Physical Electronics Quantum 2000 Scanning XPS Microprobe equipped with a variable tem-

perature sample stage. Most samples were studied at ambient temperature with the exception of the pure 6MP, IDMPA and purine standards as well as the IDMPA/Pt black samples which were cooled to  $-100^{\circ}\text{C}$ . This was necessary in order to assure the integrity of these materials and to reduce their vapor pressure to an acceptable level for the measurements. Data were acquired using monochromatic Al  $K\alpha$  radiation. The analysis area was typically an approximately 200  $\mu\text{m}$  diameter region irradiated using a 40-W focused X-ray beam. Only the analysis area was irradiated by the X-rays during data collection. This minimizes the propensity for radiation damage and modification of the sample.

### 2.3.2. Scanning Tunneling Microscopy (STM)

STM (Digital Instruments, Santa Barbara, CA) was used to characterize the self-assembly of 6MP on a 2000-Å Pt film that had been evaporated onto a glass plate substrate. The microscope was operated in air using a platinum/rhodium tip. Both constant current and constant height modes of operation were used.

### 2.3.3. ICP-MS

ICP-MS was utilized in the determination of platinum and palladium in the water phase.

### 2.3.4. Elemental analysis of catalyst

Elemental analyses for carbon, nitrogen, and hydrogen were obtained by combustion treatment of samples in oxygen following analysis of gases by GC equipped with TC detector (Control Equipment T40XA). Sulfur was analyzed using an oxygen flask combustion method followed by hydroperoxide treatment of the gases to yield sulfuric acid. This was titrated with barium perchlorate using dimethylsulfonazo (III) as an indicator.

### 2.3.5. UV-VIS

UV-VIS spectra were recorded on Beckman DU 640 spectrophotometer.

### 3. Results and discussions

#### 3.1. Effect of IDMPA on platinum black activity

Fig. 1 shows carbon dioxide concentration profiles of the effluent gas streams from five consecutive formic acid oxidation experiments (pulses) using platinum black (a) in the presence of 0.2 wt.% IDMPA in solution and (b) without IDMPA in the reaction mixture. In the case of ideal stable catalysts under our oxygen diffusion-limited conditions, the carbon dioxide profile should look like a truncated spike. The drop off curve should be close to vertical. Tailing of the carbon dioxide profile implies increasing deactivation of the catalyst which results in a longer reaction time. The differences between these curves can be characterized by a turnover-like parameter which was defined as amount of converted formic acid per gmol of catalyst (Fig. 2).

To help visualize the extent of tailing (i.e., deactivation), and to facilitate quantitative com-

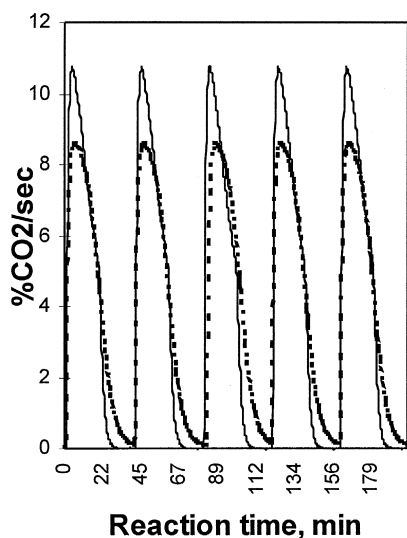


Fig. 1. Carbon dioxide concentration in the flow of oxygen plotted against reaction time in formic acid oxidation on platinum black without IDMPA (—) and with 0.2% of IDMPA (---).

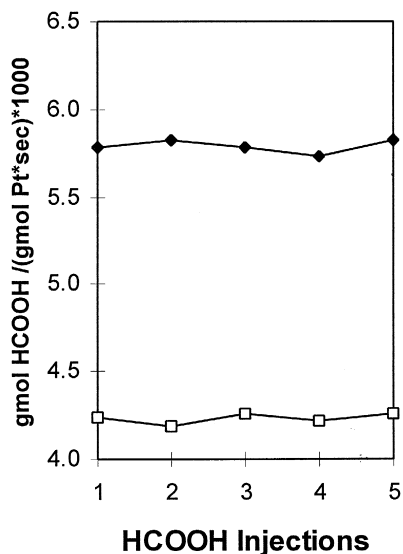


Fig. 2. The role of IDMPA in platinum black deactivation. In the presence of IDMPA (□), reaction takes longer time for 98% conversion of HCOOH than without IDMPA (◆).

parison, we developed a parameter  $K$  defined as:

$$K = \frac{d[\log(\%CO_2/s)]}{dt} \times 10^3.$$

We postulate that the parameter  $K$  is a measure of the effectiveness of the film to inhibit catalyst poisoning by IDMPA. A higher  $K$  value implies better protection. The time profile of the parameter  $K$  with progressive injections gives an indication of the stability of the tertiary structure on the catalyst surface. The metrics provided by  $K$  and by the turnover-like parameter are similar since both reflect the reaction rate to yield  $CO_2$ . The measurement of the parameter  $K$  is a well-defined procedure using the slope from the linear portion of the tailing expressed on a logarithmic scale. This eliminates some of the vagaries associated with precise determination of the formic acid consumed that is used in the calculation of the turnover-like parameter. Furthermore, comparison of Figs. 2 and 3a shows that  $K$  gives better resolution between the different reaction conditions.

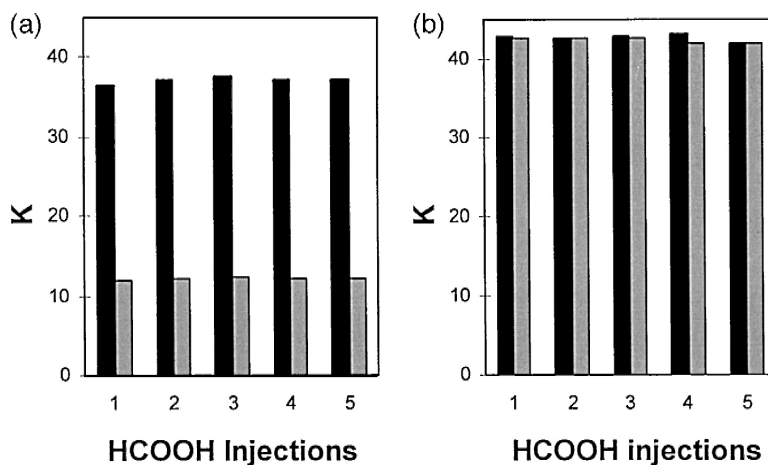


Fig. 3. Parameter  $K$  in formic acid spiking experiment on platinum black (a) and platinum black protected with 6MP (b) both without IDMPA (■) and in the presence of IDMPA (box with lighter shade).

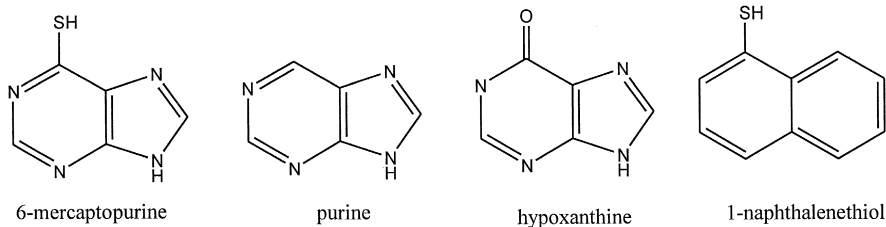
### 3.2. Platinum black protected with 6MP and other compounds

Clearly the presence of IDMPA suppressed the rate of formic acid oxidation on pure platinum black. Note that  $K$  dropped from  $\sim 38$  without IDMPA to  $\sim 12$  in the presence of the inhibitor (see Fig. 3a). We believe that chelating IDMPA forms a strong complex with surface platinum, thus blocking active sites and decreasing the reaction rate. On the contrary, the 6MP-treated platinum black is insensitive to the addition of IDMPA. The parameter  $K$  remains almost the same,  $\sim 42$  (Fig. 3b) for the reactions in the presence of and without the inhibitor.

It should be noted that addition of 6MP directly into the reaction zone in quantities equal

to the surface concentration of 6MP on platinum black totally suppressed formic acid oxidation.

Comparative studies were also conducted using other heterocyclic compounds with similar structure but different functional groups (Scheme 3). They also exhibit some protective properties, but to a lesser extent than 6MP (Fig. 4). Purine- and hypoxanthine-treated catalysts are less effective due to the fact that they do not have specific strong binding with platinum. They are only weakly adsorbed onto the platinum surface by  $\pi$ -binding, and therefore they are likely to be washed away or displaced from the surface under the reaction conditions. 1-Naphthalenethiol does not have any nitrogen that can be protonated at low pH and as a result, we believe it does not generate a protective charge barrier.



Scheme 3. Heterocyclic compounds used for protection.

### 3.3. Platinum black activity vs. amount of 6MP

Platinum black catalysts with different loadings of 6MP were also studied in the formic acid oxidation experiment. The amount of 6MP on the catalyst was determined by analyzing the sample for sulfur content. As the sulfur content increases from 0 to ca. 0.3 wt.%, the protection of the catalyst increases (Fig. 5). Beyond 0.3 wt.% S, inhibition of the catalytic reaction is seen. It also correlates with previously reported data that formic acid cannot be oxidized on a Pt/S electrode at the saturation adsorption coverage of sulfur [18].

Interestingly, even very low dosages of 6MP significantly changes the activity of platinum black in the presence of IDMPA. With only 0.07 wt.% of sulfur, which is equivalent to 0.33 wt.% of 6MP loading, the parameter  $K$  increases by almost three times as compared to reactions using non-protected platinum.

### 3.4. Palladium black

Palladium black is almost as active a catalyst in formic acid oxidation as platinum. Neverthe-

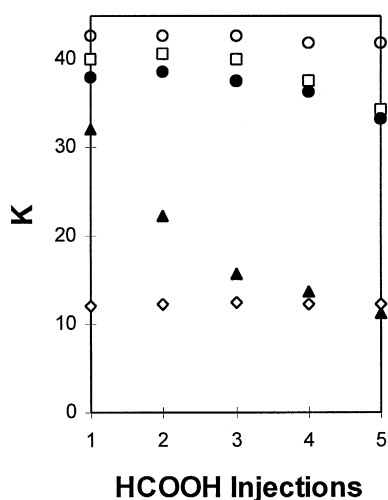


Fig. 4. The effect of different protective layers on platinum black activity in formic acid oxidation: 6MP (○), hypoxanthine (□), purine (●), 1-naphthalenethiol (▲), and without protection — pure platinum black (◇).

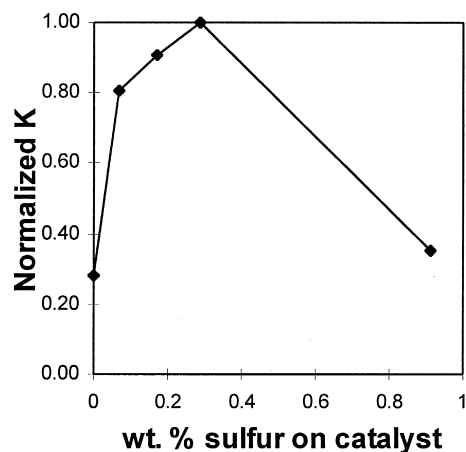


Fig. 5. Normalized parameter  $K$  of platinum black catalysts protected with 6MP vs. amount of sulfur on platinum surface in formic acid oxidation in the presence of IDMPA.

less, because of its less “noble” character, Pd is much more susceptible to over-oxidation and, therefore, to dissolution into reaction media (leaching). The presence of a strong chelating agent like IDMPA further promotes metal dissolution.

Using unprotected palladium black catalyst results in almost 20.5% of the metal being lost by dissolution into reaction media after 3 h. With 6MP-protected palladium black the leaching was much lower, about 1.3%. In the case of platinum black catalysts, no leaching of Pt was observed.

Data shown in Fig. 6 illustrates the advantage of protection of palladium black with 6MP in terms of activity.

### 3.5. Kinetics of impregnation of 6MP on platinum black

The rate of formation of SAMs on metals is governed by many factors: temperature, solvent, pH, concentration and nature of adsorbate [14]. Fig. 7 shows the time-resolved UV spectra of the 6MP solution during the impregnation process. Almost all the 6MP were gone from solution in less than 10 min. When either 6-methylthiopurine (*S*-methyl-6-mercapto-purine) or purine (non-thiol) were used, the uptake was

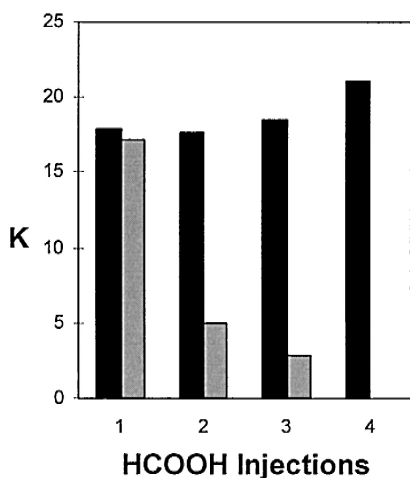


Fig. 6. The effect of protection palladium black with 6MP in formic acid oxidation in the presence of IDMPA, pure palladium black (■) and palladium black with 6MP (■).

much lower ( $\sim 30\%$  after 4 h) as monitored by UV–VIS spectroscopy. This is expected because they both lack the specific binding interaction with platinum.

Fast adsorption of 6MP on platinum black nevertheless does not imply rapid self-assembly onto the metal surface. Platinum black treated with 6MP for only 10 min (just to adsorb 6MP) demonstrated exceedingly low activity. Appar-

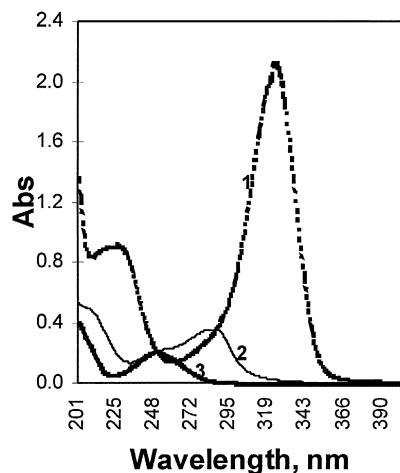


Fig. 7. Demonstrates the rate of 6MP disappearance during the impregnation process (1) 6MP spectrum before platinum black addition, (2) 10 min after addition of platinum black, and (3) 2 h after addition.

ently, rapid adsorption is the first step in a relatively long process of self-assembling where randomly oriented molecules of 6MP slowly line up to form an ordered and organized configuration. Similar conclusions have been demonstrated in the literature for adsorption 6MP on polycrystalline gold [17].

### 3.6. Deactivation of catalysts

Protection of platinum catalyst by 6MP lasts for more than six pulses before the activity begins to decrease. A possible mechanism of catalyst deactivation is oxidation of the Pt–S bond in the thiol monolayer to the corresponding sulfite or sulfate. The oxidized moiety is less effectively bound to the metal, thus it can then be rinsed from the surface with water resulting in the loss of protective layer. This mechanism of loss of the monolayer was previously observed on gold [19].

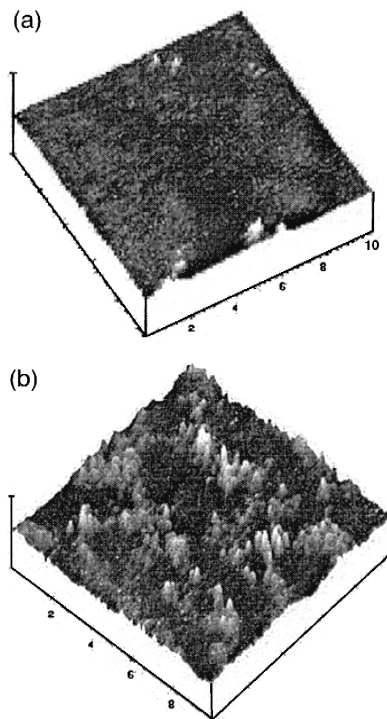


Fig. 8. STM pictures demonstrate the difference between non-treated platinum film on glass (a) and after treatment with 6MP (b). The scan size is  $10 \times 10$  nm.

### 3.7. STM images of 6MP on Pt surface

To examine changes that occur to the surface of Pt caused by 6MP, two samples of Pt coated onto glass were examined using STM. One sample was placed in water at 60°C and allowed to remain in contact for 20 h. The second sample was placed in water with 6MP added and allowed to react for 20 h. After 20 h, the samples were removed from the water, washed and allowed to cool slowly under a stream of dry nitrogen. STM images of these two samples are shown in Fig. 8.

Fig. 8a shows a 10-nm square portion of the surface for the control that was exposed to water at 60°C for 20 h. This surface is typical of a Pt on glass. The comparison between the control and the 6MP sample (Fig. 8b) shows gross changes in the STM images. This may reflect massive changes in the topography of the Pt on glass surface caused by 6MP. Alternatively, it may manifest other effects associated with the molecules adsorbing on the surface of the Pt.

### 3.8. XPS

#### 3.8.1. XPS of fresh platinum black

The composition of the original platinum black was determined by XPS which showed

that 50–60% of the surface was Pt. In general agreement with literature [20], the fresh platinum black was partially covered with residual carbon and oxygen. The maximum intensity of the Pt4f<sub>(7/2, 5/2)</sub> signal was determined to be at 70.8 eV, appropriate for bulk Pt metal. Curve fitting using an asymmetric doublet either unconstrained or constrained using the atomic spin orbit splitting with the relative intensity of the two components in the theoretical *j*-multiplet ratio could not account for the observed spectral envelope. Addition of another Pt doublet, with a Gaussian–Lorentzian functional shape and allowed to vary independently, suggested the presence of approximately 10% of the Pt in the form of Pt(IV). Analysis of the carbon signal revealed that it was predominantly graphitic material with some hydrocarbon and a minor oxidized component. The oxygen signal was consistent with the metal oxide and an oxidized carbonaceous material being present. No other signals were detected in the survey spectra.

#### 3.8.2. XPS of platinum black after impregnation of 6MP

After 10 min of exposure of platinum black to 6MP, changes were apparent in the spectrum of the Pt surface as measured by XPS. Photo-

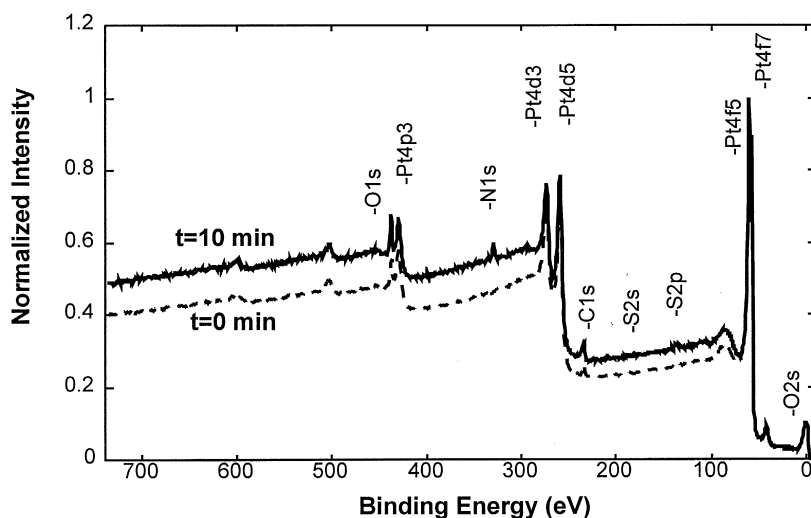


Fig. 9. Platinum surface survey spectra before ( $t = 0$  min) and after 10 min of 6MP treatment shows an adsorption of thiol onto platinum.



electron peaks appeared in the broad survey spectrum which were assigned to N1s and S2p signals (Fig. 9). The two spectra shown in Fig. 9 were normalized to coincide at the extremes of the counts. The increased inelastic background is evident in the spectrum of the 10 min exposed material that is a manifestation of the overlayer coverage scattering the electrons emanating from the Pt atoms in the substrate.

High resolution multiplex data of S2p regions revealed two peaks at binding energies of  $\sim 163$  and  $\sim 168$  eV. The first line represents an alkyl sulfide or thiol ( $S^{2-}$ ) moiety while the latter is appropriate for either a sulfite or sulfate ( $S^{6+}$ ) environment [20]. The atom ratio between the oxidized and reduced species was found to be 3:1 after 10 min of 6MP impregnation and gradually decreased to 2:1 on samples that had been equilibrated for 23 h.

For the 6MP crystals, the photoelectron spectra in S2p region also revealed two signals at the same positions, but with the sulfide as the predominant species (ratio  $S^{2-}/S^{6+}$  10:1). These data indicate that the thiol group from 6MP is being oxidized during the equilibration or adsorption process.

The nitrogen/sulfur atom ratio for both samples Pt + 6MP and 6MP crystals was similar (ca. 4:1), and corresponds to the 6MP nominal composition. This would appear to indicate that the 6MP ring system is stable during the impregnation process. The binding energy of nitrogen (ca. 399 eV) had not changed. As a result of adsorption, the exposed platinum surface ( $Pt4f_{(7/2, 5/2)}$  signals) decreased from  $\sim 55$  down to  $\sim 30$  at.% during the first 10 min of equilibration and remained at approximately the same magnitude in the course of impregnation.

### 3.8.3. XPS of platinum surface during formic acid oxidation

We observed that the sulfur signal, and corresponding calculated atom concentration, decreased in the spectra of samples after they were used to catalyze formic acid oxidation. These

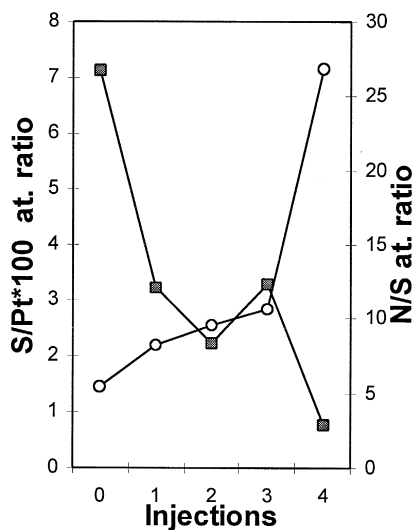


Fig. 10. The loss of protective layer from platinum surface is determined by the decrease in sulfur (■) concentration during formic acid oxidation. This process is accompanied by an increase in the nitrogen (○) concentration.

results indicate the loss of the protective layer from the catalyst surface during use. On the other hand, the nitrogen concentration was observed to increase (Fig. 10).

One explanation for these apparently disparate observations in the surface composition associated with catalyst usage is that the desorption of 6MP from the platinum surface is accompanied by the adsorption of the IDMPA molecules. Unfortunately, we were unable to distinguish nitrogen from IDMPA on Pt and 6MP on Pt by XPS. The N1s signals in spectra taken of the two pure materials, IDMPA and 6MP, are different. A binding energy of 401.5 eV was measured for IDMPA, whereas a broad signal that was curve resolved to yield two signals at 399.1 and at 400.6 eV for 6MP. A low concentration of phosphorus (with a binding energy of 133.7 eV) was observed for the sample of IDMPA adsorbed on a Pt black. This appears to be evidence for IDMPA adsorption. Nevertheless, despite the loss in 6MP, the reaction rate appeared to be maintained during the subsequent injections (Figs. 1 and 2). This can be explained by the results and conclusions

about significant protection offered by as low as 0.07 wt.% sulfur concentration and virtually no substantive difference between 0.17% and 0.3% (cf. Fig. 5). The original sulfur concentration on the sample used for the reaction studies was 0.17%. It is therefore unlikely that any difference in  $K$  would be observed for the sequence of reaction injections.

#### 4. Conclusions

- IDMPA suppresses the rate of formic acid oxidation on noble metal catalysts.

- Preadsorption of 6MP protects noble metals from complexation by aggressive chelating agents, thus increasing the reaction rate and retarding noble metal (Pd) leaching.

- We hypothesize that 6MP works through the formation of SAMs in which the thiol group binds to the noble metal. This can result in the formation of a network of oriented cyclic amines, which in acidic environments creates a charged barrier and sieve that can serve as a protective coating.

- The S/Pt ratio has a volcano-like relationship with activity. This suggests that the ratio between 6MP and noble metal is an important variable to achieve optimal catalytic activity.

- The reaction between 6MP and Pt is rapid. Nevertheless, a relatively long equilibration time is required to make the catalyst both active and robust. We propose that self-assembly is occurring within the adsorbed layer as a slow process

with the reaction between the noble metal and sulfur as only an initial step.

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