Effect of a Thermal Treatment on the Activity of Carbon-Supported Pt, Pt+W and Pt+Mo Electrocatalysts for Methanol Oxidation Reactions

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Previous studies on carbon supported Pt, Pt+W and Pt+Mo indicated that Pt+Mo was the most active electrocatalyst at low potentials and that Pt+W has similar properties as pure Pt in methanol oxidation. Those samples were thermy treated at 900 °C in a hydrogen gas atmosphere for 6 hours to observe the effect on metal particle sizes and on their distribution on carbon support. It was found that thermally treated Pt+Mo/XC-72 remains the most active catalyst at all potentials compared to the other heated samples. The heat treatment caused the sintering of small particles leading to a decrease in activity of the catalysts except Pt+Mo/XC-72. The heat treated samples were characterised by voltammetry, X-ray diffraction, transmission electron microscopy and energy dispersive X-ray analysis techniques. The methanol oxidation reaction was followed by in-situ FTIR spectroscopy to identify products and adsorbed species on the surface of electrode.

1. Introduction

Power production using the combustion of fossil fuels is known to yield substantial amounts of sulfur dioxide (particularly if the fuel is coal), nitrogen oxides in addition to carbon dioxide. If the combustion is incomplete, it yields carbon monoxide, a variety of hydrocarbons and soot. Investigations have led to a better understanding of the environmental effects of combustion by-products especially in connection with, for example, acid rain and green house effect. However, in fuel cells most of these harmful by-products are not observed. For instance, the end products for direct methanol fuel cells, DMFC, are water and carbon dioxide as shown below:

$$\text{CH}_3\text{OH} + \frac{3}{2}\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$$

To date the most successful catalyst for the DMFC is based on the Pt-group metals, in particularly Pt itself. The high cost and the rapid poisoning of platinum metal has motivated researchers to find an alternative, more active and affordable catalyst. For this purpose, the basic idea is to modify Pt by the addition of a second metal to change its adsorption properties. Such a modification can be performed in different ways i.e.; the alloying of Pt with a second metal such as Ru, Sn \cite{1,2}; the modification of the Pt surface by foreign metal ad-atoms \cite{3} or the enhancement of effective surface area by dispersion of the precious metal into conducting materials such as carbon or a conducting polymer \cite{4,5}.

Previous studies showed that electro-deposition of Mo or W on Pt highly improves the methanol oxidation reaction kinetics in acidic solution \cite{6-8}. However, our studies on untreated carbon supported Pt, Pt+W and Pt+Mo showed only a small enhancement of the activity of Pt+Mo at low potentials while no effect was detected for W addition on the Pt/XC-72 \cite{9}. It is well known that metal particle size and distribution are very important parameters regarding the catalytic properties of catalysts. For this purpose, carbon supported Pt, Pt+W and Pt+Mo were treated under hydrogen gas at 900 °C for 6 hours. It was found that the size of the metallic particles is enlarged by thermal sintering which results in a reduction of the catalytic activity except Pt+Mo/C-72.

2. Experimental Section

2.1. Preparation and characterisation of thermally treated Pt/XC-72, Pt+Mo/XC-72 and Pt+W/XC-72

1.0 g of carbon powder XC-72 was suspended in 400 ml of water in an ultrasonic bath for 30 min and heated to...
80 °C. PtCl₄ (0.306 g) dissolved in ~150 ml of water was slowly added and the solution heated for 2.5 h. After addition of 9.5 ml concentrated HCHO, the heating process was continued for a further 2 h. The sample was collected by filtration, washed with 1.5 l of boiling water to remove any residual chloride ions and dried at 100 °C overnight. Finally, the catalyst was reduced for 6 h at 900 °C under hydrogen gas in order to obtain the heated carbon-supported platinum catalyst. The heated carbon-supported Pt+W and Pt+Mo catalysts were prepared in an identical manner using 0.195 g PtCl₄ and 0.116 g Na₂WO₄·2H₂O; and 0.195 g PtCl₄ and 0.163 g Na₂MoO₄·2H₂O, respectively.

2.2. Electrochemical measurements

Electrodes were prepared from 25 mg powder sample sonicated in 0.5 ml of Nafton® solution (5% from Aldrich), diluted in 2.5 ml of water. 0.15 ml of N,N-dimethyl formamide was added in order to obtain a smooth electrode surface, particularly for IR measurements. 20 µl of the resulting ink was dropped on a glassy carbon or gold disk electrode (0.7 cm diameter), then heated at 40 °C for 20 min and finally at 100 °C for 1 h to eliminate the solvents.

The electrocatalytic activity of Pt/C, W/C, Pt+W/C, Mo/C and Pt+Mo/C for the electrooxidation of methanol was measured at room temperature using a Venking PGSO-95 potentiostat / galvanostat in 0.15 M HClO₄ (Merck Suprapur grade) aqueous solution, containing 0.5 M CH₃OH (Merck pro analysis). The solution was previously deoxygenated with nitrogen gas of high purity (L’Air Liquid). The counter electrode was a glassy carbon sheet and a Pd/H₂ electrode was used as a reference electrode, but all the curves were given in the Reversible Hydrogen Electrode, RHE, scale.

2.3. Infrared measurements

A Bruker IFS 66v spectrometer with a HgCdTe detector (infrared associates) was used to record in situ infrared reflectance spectra with a resolution of 4 cm⁻¹. Two different techniques were used to obtain the spectra. The first one, Single Potential Alteration Infrared Spectroscopy, SPAIRS, consists of recording spectra during a voltamogram at a low sweep rate, typically 1 mV/s, calculated after the averaging of 128 interferograms. The spectrum at a given potential is calculated as \( \frac{R(E_2) - R(E_1)}{R(E_1)} \), where \( E_1 \) and \( E_2 \) were chosen in the potential region of interest.

2.4. X-ray powder diffraction measurements

X-ray powder diffraction experiments were performed on a Siemens D500 diffractometer at room temperature (Cu Kα radiation, 1.54056 Å). NaCl was employed as an internal standard.

3. Results and Discussion

The averaged crystallite particle sizes of all samples were determined by both X-ray diffraction and transmission electron microscopy, Table 1. The averaged particle size of the crystallite species can be found from powder diffraction data using the Scherrer formula. The basic parameters for this formula are the instrumental constant, the wavelength of the incident X-ray and its angle and the breadth of the diffraction peak at half height. Whilst such line broadening is useful in determining the average particle size in a system with a narrow particle size distribution, it is of limited value where a wide range of particle sizes and/or morphologies are present, and in general will overestimate the particle size. Electron microscopy enables the direct observation of individual crystallites and provide sufficient care is taken can give both the average particle size and the size distribution.

Reduction of the samples by hydrogen gas at 900 °C for 6 h causes a sintering of the small metal crystallites and in all cases the average particle size increases substantially, Table 1. From an examination of the three heated samples by electron microscopy it is also clear that a relatively wide range of particle sizes is present. A striking feature in the electron micrographs is the presence of a number of extremely large crystallites in the heat treated samples. These are more common and are presumably due to thermal sintering of the crystallites within the agglomerates. It might be expected that the increase in particle size would result in a lowering of the catalytic performance which is observed in all cases except in the Pt+Mo/C where the activity of the treated sample is 3.5 times larger than of the untreated one (see below). Electron micrographs of the treated Pt/XC-72 powder sample showed a number of extremely large particles, ~700 nm diameter. The majority of the particles are between ~3 - 7 nm, however, a significant number of larger particles of ~40 - 60 nm diameter were also evi-
Table 1. The average crystallite particle size in nm determined by (a) X-ray line broadening and (b) transmission electron microscopy.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(a)</th>
<th>(b) Transmission electron microscopy</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Very few</td>
<td>A few</td>
</tr>
<tr>
<td>Pt/XC-72 u*</td>
<td>5.9</td>
<td>~60 - 125</td>
</tr>
<tr>
<td>Pt/XC-72 h*</td>
<td>17.2</td>
<td>~700</td>
</tr>
<tr>
<td>Pt+Mo/XC-72 u*</td>
<td>4.7</td>
<td>~500</td>
</tr>
<tr>
<td>Pt+Mo/XC-72 h*</td>
<td>15.2</td>
<td>~700</td>
</tr>
<tr>
<td>Pt+W/XC-72 u*</td>
<td>7.5</td>
<td>~150 - 250</td>
</tr>
<tr>
<td>Pt+W/XC-72 h*</td>
<td>13.2</td>
<td>~400</td>
</tr>
</tbody>
</table>

u* = Unheated samples; h* = heated samples.

dent in Fig. 1. In addition to these, a small number of quite large particles, ~100 - 125 nm, were observed. Transmission electron micrographs of powder samples of Pt+W/XC-72 showed the particle distribution to be reasonably similar in Pt/XC-72, but in different size. In Pt+W/XC-72 the larger number of the crystallites were between ~0.4 - 5 nm diameter, and there was a substantial number of somewhat larger clusters such as ~10 - 50 nm in diameter. A trivial number of larger particles, ~100 - 200 nm, and a tiny amount of quite large particles, ~400 nm, were also detected. The particles observed in transmission electron microscopy studies of the Pt+Mo/XC-72 powder sample showed an analogous trend to that found in the other powder samples. In this material, most of the particles are between ~1.3 - 5 nm in diameter and there were also appreciable amounts of slightly larger particles, ~10 - 20 nm. As was found for the other samples, the electron micrograph of Pt+Mo/XC-72 showed the presence of a very small number of extremely large particles, up to ~700 nm in diameter, and small amounts of ~200 - 400 nm in diameter were also present. The X-ray powder diffraction patterns...
of the three treated samples are given in Fig. 2. They were all indicative of a pure platinum lattice. The X-ray diffraction pattern showed no evidence for the substitution of W or Mo into the Pt structure but rather distinct peaks due to Pt and MoO₃ were observed for Pt+Mo/XC-72. Although the crystallites have segregated into two phases, energy dispersive X-ray analyses, EDAX, indicated that platinum and molybdenum species were always associated with each other although not always in a constant ratio. For example, in Fig. 3, the sample is platinum rich (80%Pt+20%Mo) in region A, while it has a small platinum content (50%Pt+50%Mo) in region B; it was also possible to analyse individual large crystallites in region C, and the data indicate a large crystallite to be almost pure Pt. X-ray diffraction and EDAX analyses were used in an attempt to identify the tungsten species present in Pt+W/XC-72. The absence of tungsten and/or tungsten oxide peaks in the X-ray diffraction pattern could be due to the material having an amorphous structure and/or the small crystallite size in the sample. Further, if alloying of Pt+W occurred, a shift in the peak position should be observed in the X-ray diffraction pattern. However, the X-ray diffraction pattern of Pt+W/XC-72 showed only a typical Pt peak like the Pt/XC-72 sample. For the Pt+W/XC-72 catalyst EDAX measurements showed no evidence for the incorporation of the second metal into the Pt crystallites. Indeed in all analyses only Pt centres were observed. Increasing the spot size showed the presence of both platinum and tungsten, up to 15%, especially for the regions which do not contain large agglomerated particles.

In order to better characterise the effect of Mo or W on the Pt behaviour, cyclic voltamme-

![Image](https://example.com/image.png)

Fig. 3. Electron micrograph of a heat treated Pt+Mo/C sample; right: EDAX analysis results for metal particles in regions A, B, and C of this catalyst.
try studies in 0.1 M HClO₄ at room temperature were undertaken. The cyclic voltammogram of heat treated Pt/XC-72, Pt+W/XC-72 and Pt+Mo/XC-72 are shown in Fig. 4. The voltammograms of Pt/XC-72 and Pt+W/XC-72 are very similar in all regions except for the hydrogen adsorption region where it is more clear for Pt/XC-72. Pt+Mo/XC-72 has a quite different cyclic voltammogram from that of the other catalysts. New sharp and broad redox features are observed which can be ascribed to molybdenum oxide redox reactions. The sharp cathodic and anodic features disappeared after several scans. That might show the dissolution of related molybdenum species. Although, the scanning process did not affect the position of the broad redox features of molybdenum but a small change in intensities, it produced similar hydrogen adsorption desorption region for Pt+Mo/XC-72 as Pt/XC-72. Nakajima and coworkers have found that molybdenum exist in +3, +4 and +6 oxidation states in the region of 0.05 - 0.25 V, 0.25 - 0.5 V and > 0.65 V respectively [6]. The broad anodic and cathodic features between ~0.2 - 0.6 V showed presence of several oxidation state of Mo and/or different site of molybdenum oxides, however, using only voltammogram results is not possible to give definite values of them.

Addition of methanol to the electrolyte displayed a typical methanol oxidation reaction for all samples, however it was difficult to define the starting potential for the methanol oxidation reaction. For
that reason, stationary potentiostatic measurements have been performed by recording current during 15 min at a constant potential. Current is quite constant after 15 min for each potential plateau taken every 50 mV in 0.1 M HClO$_4$ + 0.5 M CH$_3$OH at room temperature, Fig. 5. As already mentioned above, heat treatment process decreases the activity of the catalysts at almost all potentials except for Pt+Mo/XC-72. One of the reason might be the increase in the size of the metal particles leading to a decrease of the real active surface area of the electrodes. However, comparing the three samples, it is apparent that the activity can not be explained only in terms of the particle size and distribution. The oxidation state of metals may also play an important role for the oxidation of methanol, however, X-ray photoelectron studies have not been carried out in this work. Nevertheless, if there is a large difference in particle size and/or distribution, the reduced active surface area plays a main role for the
Fig. 9. SNIFTIR spectra of heat treated Pt/C in 0.15 M HClO₄ + 0.5 M CH₃OH as a function of the potential modulation: 1) [0.05 V - 0.35 V]; 2) [0.15 V - 0.45 V]; 3) [0.25 V - 0.55 V]; 4) [0.35 V - 0.65 V]; 5) [0.45 V - 0.75 V]; 6) [0.55 V - 0.85 V]; 7) [0.65 V - 0.95 V].

Fig. 10 (top). SNIFTIR spectra of heat treated Pt+Mo/C in 0.15 M HClO₄ + 0.5 M CH₃OH as a function of the potential modulation: 1) [0.05 V - 0.35 V]; 2) [0.15 V - 0.45 V]; 3) [0.25 V - 0.55 V]; 4) [0.35 V - 0.65 V]; 5) [0.45 V - 0.75 V]; 6) [0.55 V - 0.85 V]; 7) [0.65 V - 0.95 V].

Fig. 11 (bottom). SNIFTIR spectra of heat treated Pt+W/C in 0.15 M HClO₄ + 0.5 M CH₃OH as a function of the potential modulation: 1) [0.05 V - 0.35 V]; 2) [0.15 V - 0.45 V]; 3) [0.25 V - 0.55 V]; 4) [0.35 V - 0.65 V]; 5) [0.45 V - 0.75 V]; 6) [0.55 V - 0.85 V]; 7) [0.65 V - 0.95 V].

final electrocatalytic activity. Methanol oxidation reaction starts at the lowest potentials for Pt+Mo/XC-72 in comparison to the other catalysts studied, Fig. 5, that is a very important parameter to
consider for the use of such catalysts for practical applications (fuel cells).

SPAIRS and SNIFTIRS measurements were performed in the range between 1000 and 3100 cm\(^{-1}\) as a function of the electrode potential. The SPAIRS results for Pt/XC-72, Pt+Mo/XC-72 and Pt+W/XC-72 are given in Figures 6 to 8, respectively and the corresponding SNIFTIRS spectra in Figures 9 to 11. It is known that SPAIRS measurement is sensitive for the reaction products which are close to the electrode surface while the SNIFTIRS measurement is more sensitive to the adsorbed intermediate species as well as to the reaction products. The SPAIRS measurements were recorded between 0.05 and 0.6 V vs. RHE, for each 50 mV. The results showed an absorption band at 2345 cm\(^{-1}\) at 450 mV for Pt/XC-72 and Pt+Mo/XC-72, at 500 mV for Pt+W/XC-72. That band is attributed to the anti-symmetric stretching mode of CO\(_2\) formed during methanol oxidation reaction for all samples. The intensity of the CO\(_2\) band is the highest for Pt+Mo/XC-72 and the smallest for Pt+W/XC-72, Fig. 12b. The broad peak at about 1630 - 1640 cm\(^{-1}\) in all spectra is due to interfacial water, \(\delta(\text{HOH})\), but the presence of quinone species at the carbon powder surface can not be excluded. The adsorbed CO, which is linearly bonded to the electrode surface, CO\(_l\), was observed during SNIFTIRS measurements at about 2040 cm\(^{-1}\) for all samples, Figs. 9 - 11. It has the smallest intensity for the Pt+Mo/XC-72 electrode, which suggests a weak poisoning phenomenon due to the presence of Mo, and a larger one for Pt+W/XC-72, Fig. 12a. Methanol oxidation reaction product CO\(_2\) was also observed during SNIFTIRS measurements at about 2350 cm\(^{-1}\) for all samples. The same trend in the intensity of CO\(_2\) was observed here as a SPAIRS results. For those two bands, CO and CO\(_2\), the intensities are in agreement with each other because the highest the poisoning on the surface of the electrode is, the smallest the product formation is, as illustrated for Pt+W/XC-72 in Fig. 12a, b. The CO\(_2\) band behaviour was reproducible and abnormal (in sign) for Pt+Mo/XC-72 as observed for heat untreated Pt+Mo/XC-72. That might be due to the macrostructure of the electrode. The broad band at about 1630-1640 cm\(^{-1}\) was also observed for all samples as for SPAIRS results.

**Conclusions**

It is well known that the increase in the particle size of the metals, decrease the activity of the catalyst due to a decrease of the active surface area of the catalyst. This was observed for Pt/C and Pt+W/C but not for Pt+Mo/C. The stationary electrochemical measurements showed that Pt+Mo/C has the highest activity at all potentials among the heat treated samples. This result is also supported by SNIFTIRS measurements which showed the smallest poisoning by CO\(_{ads}\) with Pt+Mo/C and SPAIRS measurements which indicated the highest production of CO\(_2\) (main reaction product). The unexpected increase in the activity of Pt+Mo/C is most probably due to the different oxidation states of Mo in the heat treated and untreated catalyst. At this stage, it is too early to give a final interpretation and further studies such as X-ray photoelectron spectroscopy measurements will be necessary.

A final remark should be done concerning the apparent discrepancy observed by the two techniques.
which were used during this work. While the activity decreases from Pt+Mo/XC-72 via Pt+W/XC-72 to Pt/XC-72 according to the electrochemical measurements, the order is inverted for Pt/XC-72 and Pt+W/XC-72 by keeping Pt+Mo/XC-72 as the most active one, from SPAIRS and SNIFTIRS experiments. This apparent difference in activity estimation from two very different methods is, however, to consider very carefully. For example, it is clear from the SNIFTIRS technique that the intensity of the CO band can be directly related to the coverage in CO species, the intensity of CO\(_2\) is much more difficult to be interpreted quantitatively. Moreover, from stationary measurements, all reaction products from methanol oxidation have to be considered such as CO\(_2\), but also intermediate products such as formic acid and formaldehyde.

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