

Precious metal/hydrogen bronze anode catalysts for the oxidation of small organic molecules and impure hydrogen

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Abstract

The mechanism of 'hydrogen spill-over' on Pt/WO₃ electrode is reviewed and the application of this catalyst system for the anodic oxidation of small molecules and impure H₂ is discussed. The results obtained to date suggest that the catalyst operates as a bifunctional catalyst and its performance is significantly better than Pt–Ru or Pt–Sn anode catalysts.

Keywords: Small organic molecules; Hydrogen; Catalysts; Oxidation; Anodes

1. Introduction

There is a worldwide interest in the application of fuel cells for transportation applications. However, it is necessary to develop inexpensive and active anode catalysts capable of oxidising small organic molecules, such as methanol or impure hydrogen produced by reforming of methanol. This paper gives an account of the work done by Tseung and co-workers over the past thirty years on precious metal/alloy/hydrogen bronze anode catalysts and discusses the significance of the findings.

2. Some practical and theoretical considerations

In order to develop inexpensive anode catalysts for the above applications, it is necessary to find solutions to the following problems.

(i) Since hydrogen is difficult to carry (heavy hydrogen cylinders), the choice of a convenient fuel between hydrocarbons and reformed fuels (hydrogen containing up to 2% carbon monoxide). This restricts the choice of the electrolyte either to acid or polymer electrolyte membrane. This in turn means precious metals have to be used, since other metals are not resistant to acids or form non-active oxide films of their surfaces.

(ii) The oxidation of small organic molecules and impure hydrogen involves the formation of adsorbed carbon monoxide (CO_{ads}) on precious metal surfaces, and it is necessary to develop composite/alloy catalysts which can efficiently oxidise CO_{ads} at low overpotentials.

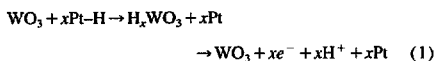
Traditionally, in order to increase their utilisation, precious metals are supported on high surface area, conducting carbon or graphite surfaces. These catalysts can either be prepared by freeze-drying [1] or by impregnation of precious metal salts, followed by chemical reduction with reducing agents. The crystallite size of the precious metals can be as small as 20 Å. To increase the activity of platinum anode catalysts for the oxidation of CO_{ads}, Pt–Ru [2] and Pt–Sn [3] bifunctional catalysts are used. Such catalysts rely on the fact that the CO_{ads} on the Pt sites reacts with surface hydroxyl species (OH_{ads}), at the adjacent RuO₂ or SnO₂ sites.

Though such measures have significantly improved the activity of the anode catalysts, there is still room for improvement. This paper gives a brief account on work on Pt/WO₃ and Pt–Ru/WO₃ which show great promise in improving the performance of anode catalysts for the oxidation of small organic molecules and impure hydrogen.

3. The hydrogen spill-over effect on Pt/WO₃

Since there is a limit to the size of platinum crystallites supported on high surface carbon, it is worth considering whether it is possible to use active catalyst supports which enable some of the catalytic steps for the oxidation of hydrogen to be spilled over to the active support, thus improving the overall efficiency of the hydrogen oxidation reaction. One interesting possibility is to use hydrogen tungsten bronzes as the active support. These compounds were first reported by Glemser and Naumann [4] and have the general formula, H_xWO₃ (0.3 < x < 0.5). They are acid resistant, metallic con-

ductors, and are blue in colour. Such compounds could function as intermediates in the anodic oxidation of hydrogen [5], providing an alternative path for the reaction:



However, these mere facts that such reactions do proceed does not prove conclusively that the 'hydrogen spill-over' mechanism is operating on Pt/WO₃ electrodes, since differences in platinum crystallite size, electrode structure and conductivity may contribute to a variation in performance. A more fool-proof method was therefore devised [6,7]. This involved the preparation of stock samples of platinum-supported WO₃ or TaC by freeze-drying (20 wt.% Pt). The stock samples were then admixed with various amounts of WO₃ or TaC and the hydrogen oxidation activity plotted as mA/mg Pt at a fixed overpotential. If the active support did not participate in the electrochemical oxidation of hydrogen, then the activity/mg Pt would be independent of the platinum loading of the electrode. This was indeed the case for the TaC-supported catalysts, but the results for the Pt/WO₃ was quite different. The lower the platinum loading, the higher the specific activity (mA/mg Pt), thus confirming that there is indeed a 'hydrogen spill-over' effect.

However, it should be noted that in order to optimise the Pt/WO₃ system, it is necessary to maximise the number of Pt/WO₃ interfaces. This is difficult using WO₃ powders prepared by the decomposition of tungstic salts, since WO₃ sinters at relatively low temperatures, resulting in relatively large particles (~0.1 μm).

4. Preparation of Pt/WO₃ by co-electrodeposition

One possible way of increasing the number of Pt/WO₃ interfaces is by co-electrodeposition. This is achieved by deposition of a homogeneous solution of dissolved tungsten and chloroplatinic acid on gold foils [8,9]. The dissolved tungsten solution was prepared by reacting tungsten powder with excess hydrogen peroxide. After all the tungsten was dissolved, the remaining hydrogen peroxide was decomposed by a platinumised platinum electrode. Direct transmission electron microscopy and X-ray powder diffraction examination showed that the platinum crystallites are in the order of ~40 Å whilst the WO₃ is amorphous. However, since it is not possible to produce Pt/WO₃ powders by co-electrodeposition, dissolved tungsten was admixed with chloroplatinic acid and high surface area carbon, freeze-dried and vacuum decomposed at 350 °C to form Pt/WO₃/C catalyst powders for the preparation of Teflon-bonded electrodes. Since the WO₃ is supported on high surface area carbon supports, the particle size is much smaller than that of WO₃ prepared by thermal decomposition of tungsten salts. Furthermore, the conductivity of the catalyst powder is significantly improved because of the addition of conducting carbon powder.

5. Oxidation of adsorbed carbon monoxide on Pt-Ru: and Pt-Ru/WO₃ co-deposited electrodes [10]

Cyclic voltammetric studies showed that the oxidation of carbon monoxide in 0.5M H₂SO₄, 25 °C, on Pt-Ru/WO₃ started at ~100 mV versus saturated hydrogen electrode (SHE) and the peak current density at 450 mV versus SHE was over 100 mA/cm², whereas a Pt-Ru electrode started to oxidise carbon monoxide at ~300 mV versus SHE and the peak oxidation current density was less than 30 mA/cm². This significant difference in performance may be related to the fact that RuO₂ will only be formed at higher anodic potentials whereas WO₃ is already present at 0 mV versus SHE. This ensures that there are OH_{ads} species on the surface of WO₃ even at low overpotentials and these react with CO_{ads} on adjacent platinum sites.

6. Anodic oxidation of methanol and formic acid on Pt/WO₃ and Pt-Ru/WO₃

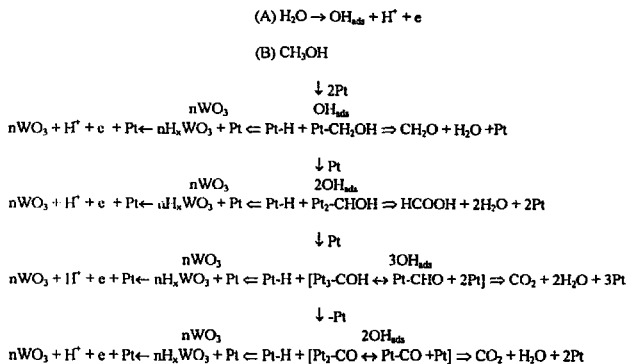
The oxidation of methanol and formic acid involves many steps, the first of which is a dehydrogenation reaction. It is expected that the performance of Pt/WO₃ and Pt-Ru/WO₃ should be significantly more active than platinum. This is indeed the case [8-12]. A 1 mg Pt/1 mg WO₃ co-deposited electrode on gold foil gave a steady performance at 100 mA/cm² at 200 mV versus saturated calomel electrode (SCE), 0.5 M H₂SO₄, 1 M CH₃OH at 60 °C. On the other hand, a platinumised gold electrode of similar platinum loading gave 10 mA/cm² at 450 mV versus SCE and became severely poisoned within 20 min. A schematic reaction scheme for the oxidation of methanol or Pt/WO₃ is shown in Fig. 1.

Since formic acid is one of the intermediates of the methanol oxidation in acid media, it is of interest to study the activity of Pt/WO₃ for the oxidation of formic acid. It may be possible to oxidise formic acid at room temperature. Pt/WO₃ can oxidise formic acid at room temperature at 50 mA/cm² at ~350 mV versus SHE for a test period of 180 h without change in performance, whereas a platinumised electrode was poisoned and only gave 43 mA/cm² at 480 mV versus SHE. The performance on the Pt-Ru/WO₃ electrode was even better, 100 mA/cm² at 300 mV versus SHE.

A schematic reaction scheme for the oxidation of formic acid is shown in Fig. 2.

7. Anodic oxidation of impure hydrogen [13]

Table 1 compares the performance of Pt/C, Pt-Ru/C, Pt/WO₃ and Pt-Ru/WO₃/C Teflon-bonded electrodes for the oxidation of impure hydrogen (containing 100 ppm of CO). All the electrodes decayed continuously with the exception of Pt-Ru/WO₃/C and it is expected that further optimisation will result in higher performance.

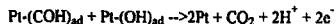
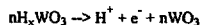
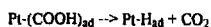
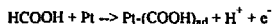


where $n = 1/x$.

Fig. 1. Reaction scheme for the oxidation of methanol on Pt/WO₃ electrode in acid solution.

Table 1
Anodic performance of Teflon-bonded Pt/C, Pt/WO₃/C, Pt-Ru/C and Pt-Ru/WO₃/C at 200 mV vs. SHE, 80 °C, 0.5 M H₂SO₄, no *iR* correction

Electrode (loading mg cm ⁻²)	Performance over test periods (mA cm ⁻²)	Comments
Pt/C; 1.7 Pt	30 at 18000 s	Continuous drop in performance
Pt/WO ₃ /C; 1.43 Pt	100 at 12000 s	Continuous drop in performance
Pt-Ru/C; 1.8 Pt-Ru	100 at 16000 s	Continuous drop in performance
Pt-Ru/WO ₃ /C; 1.8Pt-Ru	220 at 22000 s	No change in performance during test



where $n=1/x$

Fig. 2. Reaction scheme for the oxidation of formic acid on Pt/WO₃ electrode in acid solution.

8. Conclusions and further work

The above results suggest that the Pt/WO₃ and its analogues are a new class of anodic oxidation catalysts which warrant further fundamental studies and optimisation.

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