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Hydrogen spill-over effect on Pt/WO_3 anode catalysts

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Abstract

The experimental evidence and mechanism of 'hydrogen spill-over' on Pt/WO_3 is reviewed and the application of this catalyst system for the evolution of hydrogen, anodic oxidation, hydrogenation and the anodic oxidation of small molecules and impure H_2 is discussed. It is suggested that further work on preparation techniques to ensure the maximisation of Pt/WO_3 interfaces and other analogous systems should lead to even higher catalyst activity and applications. © 1997 Elsevier Science B.V.

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1. Introduction

Pt is universally acknowledged as the most active catalyst for catalytic reactions involving hydrogen. However, since Pt is expensive, there is a need to disperse them on high surface area supports, such as carbon and inert high surface area oxide powders. This paper reviews the work done by Tseung and his colleagues over the last 30 years on the use of WO_3 as an active support, whereby the hydrogen oxidation reaction can be spilled over to the WO_3 support, thus significantly enhancing the activity of the catalyst system. The use of Pt/WO_3 as an active bifunctional anode catalyst for the oxidation of methanol, formic acid, alcohol, glucose and CO is presented.

2. The hydrogen spill-over effect on Pt/WO_3

Since there is a limit to the size of platinum crystallites supported on high surface supports, it is worth considering whether it is possible to use active catalysts supports which enable some of the catalytic steps for the oxidation of H_2 to be spilled over to the support, thus improving the overall efficiency of the hydrogen oxidation reaction. One interesting possibility is to use the hydrogen tungsten bronzes as an active support. These compounds were first reported by Glemser and Naumann [1] and have the general formula H_xWO_3 ($0.3<x<0.5$). They are acid resistant, metallic conductors and blue in colour. Such compounds could function as intermediates in the anodic oxidation of hydrogen, providing an alternative path for the reaction: $WO_3+x\text{Pt–H}\rightarrow H_xWO_3+\text{Pt}\rightarrow WO_3+xe^-+xH$ [2–5]. However, these results alone could not prove conclusively that the 'hydrogen spill-over' mechanism is operating on Pt/WO_3 electrodes, since differences in Pt crystallite size, electrode structure and conductivity may contribute to the variation in performance. A more fool-proof method was therefore devised [3,4]. This involved the preparation of stock samples of Pt supported WO_3 or TaC by freeze drying (20 wt% Pt). The stock samples were then admixed

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with various amounts of WO_3 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 H_2, then the activity/mg Pt would be independent of Pt loading of the electrode. This was indeed the case for the TaC supported catalysts, but the results for the Pt/WO_3 was quite different, the lower the Pt 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 to optimise the Pt/WO_3 system, it is necessary to maximise the number of Pt/WO_3 interfaces. This is difficult using WO_3 powders prepared by the decomposition of tungstic salts, since WO_3 sinters at relatively low temperatures, resulting in relatively large particles (approx. 0.1 μm). Nevertheless, Pt/WO_3 electrodes have shown very much higher performance for the anodic oxidation of hydrogen than Pt supported on other inert catalyst supports [2,6]. Moreover, the hydrogen spill-over effect has also been shown to be operative in hydrogenation reaction [7] and hydrogen evolution reactions [8].

3. Alternative preparation techniques for Pt/WO_3 – coelectrodeposition of Pt–WO_3 films

As stated earlier, there is a need to optimise the number of Pt/WO_3 interfaces to achieve the highest activity. The main problem is the relatively low surface area of WO_3 powders produced by the decomposition of tungstic salts (approx. 3–5 M^2/g). Recently, we have found that by dissolving W powder with H_2O_2 in a solution containing alcohol and decomposing the excess H_2O_2 with platinised Pt gauze, it is possible to plate thin films of Pt/WO_3 [9]. Transmission electron microscopic and X-ray powder diffraction studies indicated that the Pt crystallites (approx. 40 Å) were uniformly dispersed on amorphous WO_3, thereby ensuring far greater number of Pt/WO_3 interfaces for a given weight of Pt/WO_3. The dissolved tungsten exists as $[(O_2)_2(O)WOW(O)(O_2)_2]^{2-}$ [10] ions in solution and these are electrodeposited as amorphous WO_3. Thin film electrodes however are only suitable for use in dissolved fuel fuel cells, since only gas diffusion Teflon bonded electrodes can function effectively for the oxidation of gaseous fuels, such as H_2.

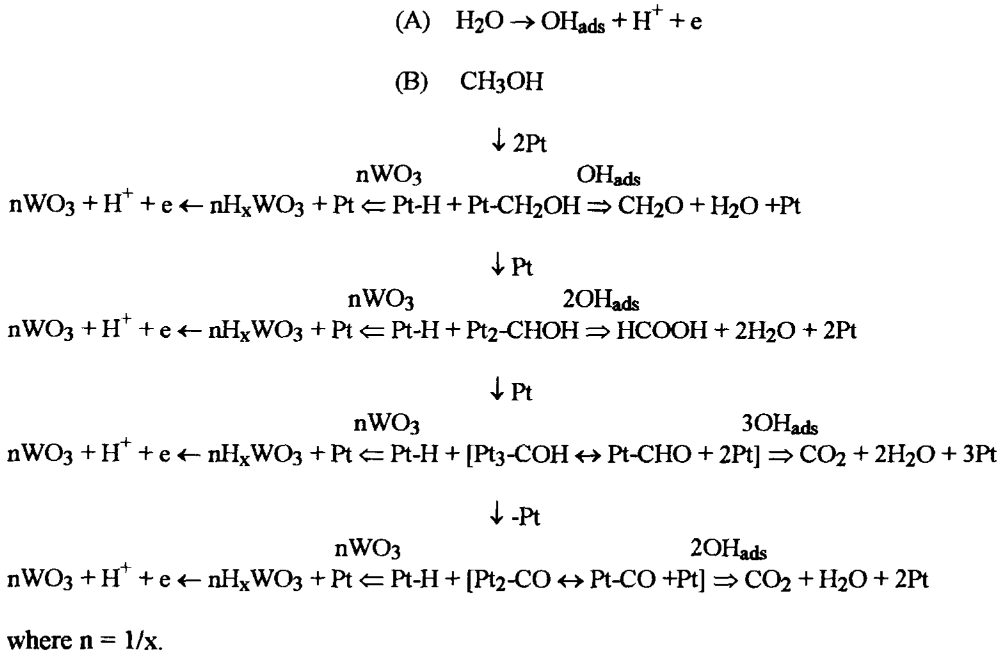
4. Applications of thin film electrodes for the anodic oxidation of dissolved fuel fuel cells

The oxidation of dissolved fuel, such as methanol, formic acid, ethyl alcohol produced CO_{ads} intermediates on precious metal surfaces, it is necessary to develop composite/alloy catalysts which can efficiently oxidise CO_{ads} at low overpotentials.

Traditionally, in order to increase the utilisation of precious metals, precious metals are supported on high surface area, conducting carbon or graphite surfaces. These catalysts can either be prepared by freeze-drying [11] 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 Pt anode catalysts for the oxidation of CO_{ads}, Pt–Ru [12] and Pt–Sn [13] bifunctional catalysts are used. Such catalysts rely on the fact that the CO_{ads} on the Pt sites reacts with OH_{ads} at the adjacent RuO_2 or SnO_2 sites.

Though such measures have significantly improved the activity of the anode catalysts, there are still room for improvements. Pt/WO_3 and Pt–Ru/WO_3 thin film electrodes should have significant advantages over conventional anode catalysts because the first stage of reaction involves dehydrogenation reaction where the hydrogen spill-over effect on the Pt surface is operative. Furthermore, since the conducting hydrogen tungsten bronze (H_xWO_3) is formed at 0 V vs. NHE, it can adsorb OH_{ads}, thereby facilitating the oxidation of CO_{ads} and other reaction intermediates at the Pt/WO_3 interface. On the other hand, SnO_2 is almost an insulator and RuO_2 does not form until the anodic potential is raised to about 300 mV vs. NHE.

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/WO_3 and Pt–Ru/WO_3 should be significantly more active. This is indeed the case [14–17]. A 1 mg Pt/1 mg WO_3 codeposited electrode on gold foil gave a steady performance at 100 mA/cm^2 at 200 mV vs. SCE, 0.5 M H_2SO_4, 1 M CH_3OH at 60°C. On the other hand a platinised gold electrode of similar Pt loading gave 10 mA/cm^2 at 450 mV vs. SCE and became severely poisoned within 20 mins. A schematic reaction scheme for the oxidation of methanol on Pt/WO_3 is shown in Fig. 1.



(A) $H_2O \rightarrow OH_{ads} + H^+ + e$

(B) CH_3OH

$\downarrow 2Pt$

$nWO_3 + H^+ + e \leftarrow nH_xWO_3 + Pt \xLeftarrow{nWO_3} Pt\text{-}H + Pt\text{-}CH_2OH \xRightarrow{OH_{ads}} CH_2O + H_2O + Pt$

$\downarrow Pt$

$nWO_3 + H^+ + e \leftarrow nH_xWO_3 + Pt \xLeftarrow{nWO_3} Pt\text{-}H + Pt_2\text{-}CHOH \xRightarrow{2OH_{ads}} HCOOH + 2H_2O + 2Pt$

$\downarrow Pt$

$nWO_3 + H^+ + e \leftarrow nH_xWO_3 + Pt \xLeftarrow{nWO_3} Pt\text{-}H + [Pt_3\text{-}COH \leftrightarrow Pt\text{-}CHO + 2Pt] \xRightarrow{3OH_{ads}} CO_2 + 2H_2O + 3Pt$

$\downarrow -Pt$

$nWO_3 + H^+ + e \leftarrow nH_xWO_3 + Pt \xLeftarrow{nWO_3} Pt\text{-}H + [Pt_2\text{-}CO \leftrightarrow Pt\text{-}CO + Pt] \xRightarrow{2OH_{ads}} CO_2 + H_2O + 2Pt$

where $n = 1/x$.

Fig. 1. Reaction scheme for the oxidation of methanol on Pt/WO_3 electrode in acid solution.

Since formic acid is one of intermediates of methanol oxidation in acid media, it is of interest to study the activity of Pt/WO_3 for the oxidation of formic acid, since it may be possible to oxidise formic acid at room temperature. Pt/WO_3 can oxidise formic acid at room temperature at 50 mA/cm^2 at ~350 mV vs. SHE for a test period of 180 h without change in performance, whereas a platinised electrode was poisoned and only gave 43 mA/cm^2 at 480 mV vs. SHE. The performance on Pt–Ru/WO_3 electrode was even better, 100 mA/cm^2 at 300 mV vs. SHE.

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

$HCOOH + Pt \dashrightarrow Pt\text{-}(COOH)_{ad} + H^+ + e^-$

$Pt\text{-}(COOH)_{ad} \dashrightarrow Pt\text{-}H_{ad} + CO_2$

$Pt\text{-}(COOH)_{ad} + HCOOH \dashrightarrow Pt\text{-}(COH)_{ad} + CO_2 + H_2O$

$Pt\text{-}H_{ad} + nWO_3 \dashrightarrow Pt + nH_xWO_3 + e^-$

$nH_xWO_3 \dashrightarrow H^+ + e^- + nWO_3$

$Pt\text{-}(COH)_{ad} + Pt\text{-}(OH)_{ad} \dashrightarrow 2Pt + CO_2 + 2H^+ + 2e^-$

where $n=1/x$

Fig. 2. Reaction scheme for the oxidation of formic acid on Pt/WO_3 electrode in acid solution.

Table 1
Anodic performance of Teflon bonded Pt/C, Pt/WO_3/C, Pt–Ru/C and Pt–Ru/WO_3/C at 200 mV vs. SHE, 80°C, 0.5 mol dm^{-3} H_2SO_4, no *iR* correction

Electrode (loading mg cm^{-2})	Performance over test periods (mA cm^{-2})	Comments
Pt/C; 1.7 Pt	30 at 18 000 s	Continuous drop in performance
Pt/WO_3/C; 1.43 Pt	100 at 12 000 s	Continuous drop in performance
Pt–Ru/C; 1.8 Pt–Ru	100 at 16 000 s	Continuous drop in performance
Pt–Ru/WO_3/C; 1.8 Pt–Ru	220 at 22 000 s	No change in performance during test

5. Oxidation of CO_{ads} on Pt–Ru and Pt–Ru/WO_3 codeposited electrodes [14]

Cyclic voltammetric studies showed that the oxidation of CO in 0.5 M H_2SO_4, 25°C, on Pt–Ru/WO_3 started at approx. 100 mV vs. SHE and the peak current at 450 mV vs. SHE was over 100 mA/cm^2, whereas a Pt–Ru electrode started to oxidise CO at approx. 300 mV vs. SHE and the peak oxidation was less than 30 mA/cm^2. The significant difference in performance may be related to the fact that RuO_2 will only be formed at higher anodic potentials whereas WO_3 is already present at 0 mV vs. SHE. This ensures that there are OH_{ads} species on the surface of WO_3 even at low overpotentials to react with CO_{ads} on adjacent Pt sites.

6. Anodic oxidation of impure H_2 [18]

Teflon bonded Pt/WO_3 and Pt–Ru/WO_3 gas diffusion electrodes were prepared from freeze-dried catalysts, using dissolved tungsten and precious metal salts as the precursor material.

Table 1 compares the performance of Pt/C, Pt–Ru/C, Pt/WO_3 and Pt–Ru/WO_3/C Teflon bonded electrodes for the oxidation of impure H_2 (containing 100 ppm of CO). All the electrodes decayed continuously with the exception of Pt–Ru/WO_3/C and it is expected that further optimisation will result in higher performance.

7. Stability of Pt/WO_3 electrodes [19]

In practice, any new electrocatalysts should be capable of delivering constant performance for thousand of hours. Recent work has shown that WO_3 is slightly soluble in 0.5 M H_2SO_4 at 60°C for 50 h. However, by coating the electrodes with a thin layer of Nafion dispersion, WO_3 is prevented from dissolving and the performance of the electrode is not affected.

8. Other analogous systems [20]

MoO_3, V_2O_5 and Nb_2O_5 all form hydrogen bronzes and is worth studying further.

9. Conclusions and further work

The above results suggest that the Pt/WO_3 and its analogues are a new class of anodic oxidation catalysts which warrant further fundamental studies and optimisation.

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