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Methanol electrooxidation on carbon-supported Pt–WO_{3-x} electrodes in sulphuric acid electrolyte

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Electrooxidation of methanol has been studied in sulphuric acid electrolyte at 60° C on carbon-supported Pt–WO_{3-x} electrodes employing varying amounts of WO_{3-x}. It is found that the electrodes containing (3 : 1) Pt–WO_{3-x} composite catalyst exhibit a higher catalytic activity towards methanol electrooxidation than platinized carbon electrodes without WO_{3-x}. In the light of the XPS and XRD data on the carbon-supported (3 : 1) Pt–WO_x sample, it is speculated that the WO_x is present in the form of an oxyhydroxide, which can promote surface oxy-species on platinum by proton transfer.

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1. Introduction

As the air quality in our cities continues to deteriorate owing to the emission of partially combusted hydrocarbons from internal combustion engines, attention has turned to electrochemical power as a possible source of pollution-free traction. In principle, electrically powered vehicles can either be battery or fuel-cell driven, the primary difference being the fact that batteries necessarily carry their own fuel at all times, and need recharging when that fuel is exhausted, whereas fuel cells require an external source of chemical fuel, which, in the liquid form, can be resupplied extremely quickly [1–5].

The primary advantages of fuel cells, aside from the possibility of rapid refuelling and low intrinsic pollution, are mechanical simplicity and modularity of construction, giving a robust and reliable product. The primary *disadvantage* is the necessity, in the more technologically developed fuel cells, for the use of hydrogen gas as the fuel. Unfortunately, hydrogen is difficult both to store and to transport; it can be absorbed within certain alloys, but this leads to a substantial weight penalty, or it can be transported as a liquid, though this has obvious safety hazards. A more satisfactory solution would be to use a liquid fuel that could be reformed to hydrogen, but this adds appreciably to the costs of the fuel cell, and the most satisfactory approach would be to electro-oxidize a liquid fuel directly at the anode. However, the only liquid fuel that has any substantial electroactivity for conversion to CO_2 and water is methanol, since this possesses no C–C bonds and has the further advantage of being cheap and plentiful, but even for this material, it has proved exceptionally difficult to find catalysts of the required activity [6–15].

The requirement for activity is dictated by a rational choice of figures of merit for any fuel cell to be used in traction, since power/weight and energy/weight ratios must be as high as possible. To ensure that the fuel cell is no larger and heavier than the internal combustion engine it seeks to replace, a power density value of at least $0.2\,W\,cm^{-2}$ must be sought, which, given the known performance of the air cathode, requires that the anode should sustain a current density of $>400\,mA\,cm^{-2}$ at less than 300 mV vs NHE. These figures have not yet been attained for electrodes described in the literature, and further effort to identify more active promoters is needed.

Recently, Shen and Tseung [16, 17] have reported that electrochemically codeposited Pt–WO_{3-x} electrodes on a gold substrate exhibit high catalytic activity toward methanol electrooxidation in sulphuric acid. In this communication, we report the fabrication of chemically codeposited, carbon-supported Pt–WO_{3-x}(Pt–WO_{3-x}/C) electrodes of a type that can be employed in practical fuel cells. Electrodes have been made with varying compositions of Pt and WO_{3-x}, and their behaviour toward electrooxidation of methanol in sulphuric acid explored.

2. Experimental details

2.1. *Preparation and characterization of catalysts*

The samples of Pt–WO_x/C catalyst with several

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Table 1. Electrode-kinetic parameters for methanol (1 M) oxidation in sulphuric acid electrolyte on Pt/C and Pt–WO_{3-x}/C electrodes

Electrode type	*Electrode-kinetic parameters*				*Ohmic drop*	
	Tafel data *Slope*/mV	$n\alpha$	*Graphical data* *Slope*/mV	$n\alpha$	*Experimental*/ $\Omega\,cm^2$	*Graphical*/ $\Omega\,cm^2$
Pt/C	102	0.65	47	0.60	0.45	0.55
(6 : 1) Pt–WO_{3-x}/C	117	0.56	46	0.61	0.50	0.62
(3 : 1) Pt–WO_{3-x}/C	88	0.76	36	0.61	0.42	0.48
(3 : 2) Pt–WO_{3-x}/C	135	0.49	59	0.78	0.70	0.85

Pt : WO_x ratios were prepared by liquid-phase reduction of homogeneous solution of chloroplatinic acid and ammonium metatungstate, $(NH_4)_6H_2W_{12}O_{40}$, precursor with sodium borohydride. Ketjenblack carbon (2.5 g) was suspended in 100 ml of water at 80° C. An aqueous solution (50 ml) containing 2.1 g chloroplatinic acid that contained 1 g of platinum and an appropriate amount of $(NH_4)_6H_2W_{12}O_{40}$ (see Table 1) was slowly added to the carbon suspension at 80° C, and allowed to impregnate for 1 h. The resulting slurry was heated with mechanical stirring at about 100° C until an ink-like paste was obtained. It was subsequently dried in an air oven at 110° C for 4 h. The dried mass was finely powdered, mixed with 100 ml of water at 80° C and reduced by dropwise addition of 0.2 M $NaBH_4$ (50 ml) at a pH value of about 1. The resulting slurry was maintained at 80° C for 24 h. It was subsequently filtered, washed copiously with hot distilled water and dried in an air oven at 110° C for 4 h. The spectral analysis of filtrates conducted on a U-3410 Hitachi spectrophotometer at various steps suggested that both platinum and metatungstate were not lost while washing the catalyst samples.

The X-ray diffraction (XRD) patterns of Pt/C and Pt–WO_x/C catalysts as prepared and after heat treating them in air were recorded at room temperature on a Stoe X-ray powder diffractometer using Cu K_α radiation source. The sizes of the platinum particles in various catalyst samples were obtained from X-ray diffraction peak broadening and application of the Debye–Scherrer equation both prior and subsequent to electrode polarization after washing the electrodes abundantly with hot distilled water.

X-ray photoelectron spectra (XPS) of (3 : 1) Pt–WO_x/C sample were recorded at 30° C on a VSW Scientific Instrument Spectrometer with Al K_α radiation. The vacuum in the analysis chamber of the instrument was better than 0.1 μPa. The spectrometer was calibrated by recording the Pt 4f spectrum on argon-etched, high-purity platinum foil. The Pt–WO_x/C sample was pressed against a stainless steel sample holder and dried at 100° C in a low-pressure (~ 10 Pa) oven for 1 h. Subsequently, the sample was introduced into the spectrometer through a separate differentially-pumped, fast-entry chamber and then into the desorption chamber kept under ultra high vacuum for desorption of any volatile species adsorbed on the carbon support before transferring it to the analyser chamber. The spectrum was background corrected by the Shirley method [18] followed by its deconvolution by Gaussian–Lorentz routines. The quantitative evaluation of each species was also carried out by dividing the integrated peak area by atomic sensitivity factors obtained from published ionization cross sections, the mean free-electron escape depth, and the transmission functions of spectrometer expressed as the relative intensity ratio to carbon [19, 20].

2.2. *Preparation and characterization of electrodes*

Dual-layer gas-diffusion electrodes were prepared for electrochemical oxidation of methanol in 2.5 M sulphuric acid. These comprised a Pt–WO_x/C catalyst deposited on a wet-proofed carbon paper acting as a diffusion layer for the removal of carbon dioxide produced during the electrooxidation of methanol. The electrodes were prepared by first mixing the catalyst with water at 60° C in an ultrasonic water bath accompanied with mechanical stirring for about 30 min. An appropriate amount of isopropyl alcohol was added and the resulting slurry was allowed to wet for 2 h. The flocculate was spread by doctor-blade technique over a Toray carbon paper (Toray TGP90) wet proofed with a solution of Dupont fluoroethylene propylene polymer (FEP 120) up to a loading of 5 mg cm^{-2}. The electrodes were pressed at 70° C under 15 kg cm^{-2} for 5 min, and then dried in an air oven at 100° C for 1 h followed by heating in the same oven at 360° C for 15 min. The Pt loading in the electrodes was maintained at 0.8 mg cm^{-2}.

The test electrode was mounted to a holder and assembled into a thermostated three-electrode cell with a platinum-flag counter electrode and a Hg/Hg_2SO_4, SO_4^{2-} reference electrode. The electrochemical cell was filled with 2.5 M H_2SO_4 electrolyte which was purged with nitrogen for about 1 h with constant mechanical stirring and temperature maintained at 60° C. Subsequently, methanol was added to give a 1 M MeOH concentration in the H_2SO_4 electrolyte. The galvanostatic polarization data for methanol electrooxidation on various catalytic electrodes were obtained and IR-corrected employing the current-interrupter method. The experiments were performed on several electrodes to ascertain the reproducibility of the data. The polarization data have been converted with respect to a normal hydrogen electrode (NHE) for convenience. The geometric area of the

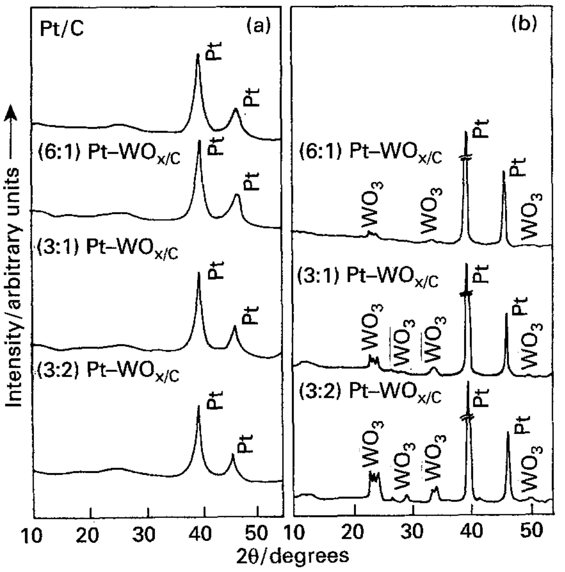


Fig. 1. XRD patterns of the various Pt–WO$_x$/C and Pt/C samples (a) as prepared, and (b) after heat treatment in air at 450° C for 30 min.

electrode (1.5 cm^2) was used to calculate the current densities.

3. Results and discussion

Figure 1(a) and (b) show the XRD patterns of various Pt–WO$_x$/C catalysts recorded before and after their heat treatment in air. Although it is hard to detect the presence of any WO$_{3-x}$ from the XRD patterns of the as prepared Pt–WO$_x$/C catalysts shown in Fig. 1(a), the XRD patterns obtained subsequent to their heat treatment in air at 450° C for 30 min clearly reflect the presence of a crystalline WO$_3$ phase as shown in Fig. 1(b). The sizes of the platinum particles in the as prepared (6 : 1) Pt–WO$_x$/C, (3 : 1) Pt–WO$_x$/C and (3 : 2) Pt–WO$_x$/C catalysts were found to be 6.0, 6.7, 8.0 and 7.4 nm, respectively. On subsequent heat treatment of these catalysts in air at 450° C for 30 min, the platinum particle size was found to have increased to approximately 18.0 nm. Interestingly, no crystalline WO$_x$ phase could be detected in the XRD patterns of any of the Pt–WO$_{3-x}$/C samples recorded at various stages of their heat treatment in air below 450° C suggesting that only amorphous or nanocrystalline WO$_x$ species were present on these electrodes following their heat treatment in air at 360° C as described in the electrode preparation protocol of Section 2.2. It is, however, noteworthy that software analysis of the XRD data on various Pt–WO$_x$/C catalysts showed the partial presence of a WO$_2$ phase in amounts that varied with the WO$_3$ content of the catalyst. The W 4*f* X-ray photoelectron spectrum of the (3 : 1) Pt–WO$_x$/C catalyst sample given in Fig. 2 suggests that the lower binding energy doublet with W 4$f_{7/2}$ at 34.7 eV agrees well with the published value of W(IV) oxide while the binding energy of W 4$f_{7/2}$ component of the higher binding energy doublet at 36.8 eV is close to the chemical shift reported for W(VI) oxide [21]; the relative concentrations of W(IV) and W(VI) oxides in the catalyst being 41% and 59%, respectively. Thus, the XPS and XRD data complement each other. The Pt 4*f* spectrum of the sample was much akin to the spectra of Pt/C samples reported elsewhere [22] and hence it is not included here. The lower binding-energy doublet with Pt 4$f_{7/2}$ at about 71 eV agrees well with the published value of 71.1 eV for Pt-metal [23]. By contrast, the binding energy of Pt 4$f_{7/2}$ component of the higher binding energy doublet at about 73 eV is close to the chemical shift reported for the oxidic platinum species [24–26]. The relative intensity of the oxidic platinum doublet is found to be much lower (12%) in relation to the Pt-metal (88%).

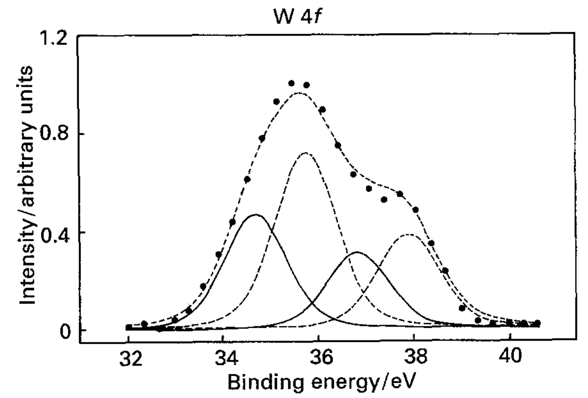


Fig. 2. W 4*f* X-ray photoelectron spectrum of (3 : 1) Pt–WO$_x$/C sample.

Figure 3 shows the galvanostatic current–potential data for oxidation of methanol on Pt/C and various Pt–WO$_{3-x}$/C electrodes together with their respective current–potential data obtained by least-squares regression to fit the measured data as described elsewhere [27]. The latter provides the evaluation of the limiting-current values averting the need to reach high current–potential region where the secondary reactions could vitiate the data. Interestingly, although the rest potential of the Pt/C electrode is closer to the reversible value of 0.043 V vs NHE for

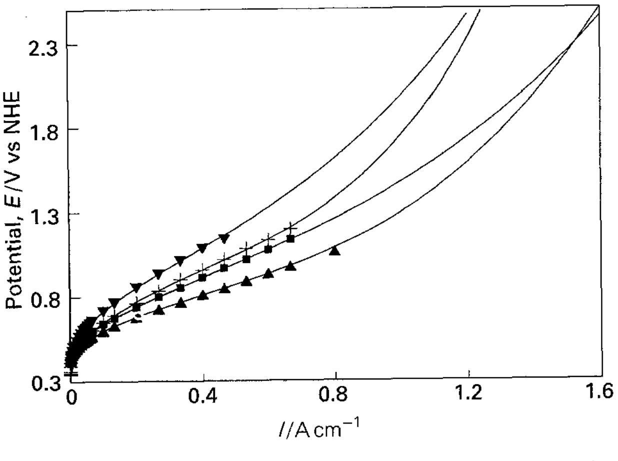


Fig. 3. Measured (symbols) and simulated (full lines) galvanostatic steady-state polarization current–potential data for methanol (1 M) oxidation on various Pt–WO$_{3-x}$/C and Pt/C electrodes in sulphuric acid electrolyte at 60° C. Pt–WO$_{3-x}$/C: (■) 6 : 1, (▲) 3 : 1 and (▼) 3 : 2. (+) : Pt/C.

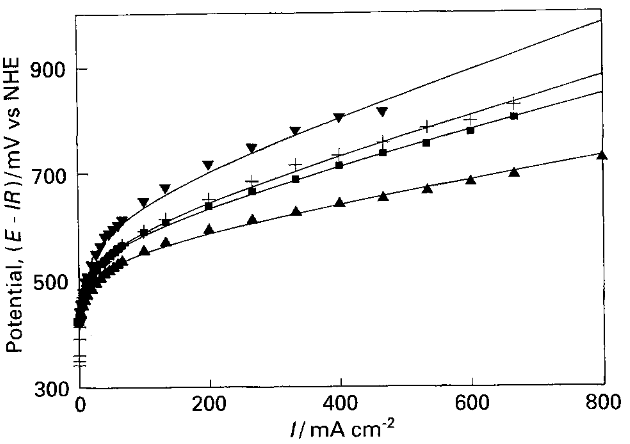


Fig. 4. The IR-compensated galvanostatic steady-state polarization data for methanol (1 M) oxidation on various Pt–WO$_{3-x}$/C and Pt/C in sulphuric acid electrolyte at 60° C. Pt–WO$_{3-x}$/C: (■) 6 : 1, (▲) 3 : 1 and (▼) 3 : 2. (+) : Pt/C.

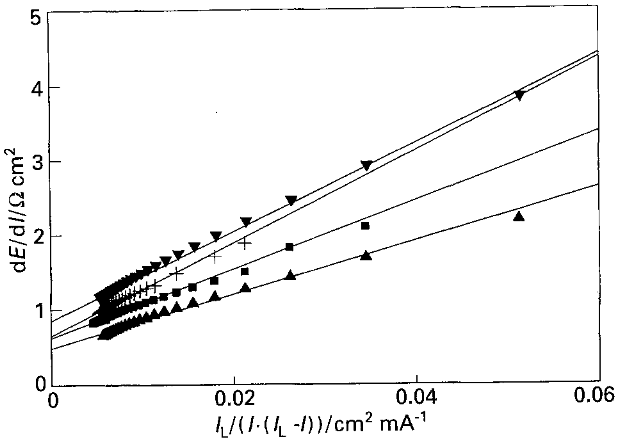


Fig. 6. The dE/dI against $I_l/(I(I_l - I))$ plots for methanol (1 M) oxidation on various Pt–WO$_{3-x}$/C and Pt/C electrodes in sulphuric acid electrolyte at 60° C. Pt–WO$_{3-x}$/C: (■) 6 : 1, (▼) 3 : 2 and (▲) 3 : 1. (+) : Pt/C.

the methanol electrooxidation reaction in sulphuric acid, compared to any of the Pt–WO$_{3-x}$/C electrodes, it exhibits higher polarization in comparison to both (3 : 1) and (6 : 1) Pt–WO$_{3-x}$/C electrodes at high load current densities. Among the various Pt–WO$_{3-x}$/C electrodes studied here, the (3 : 1) Pt–WO$_{3-x}$/C electrode exhibits the highest catalytic activity toward methanol electrooxidation. By contrast, the performance of the (3 : 2) Pt–WO$_{3-x}$/C electrode is poorer in relation to both (3 : 1) and (6 : 1) Pt–WO$_{3-x}$/C electrodes as well as Pt/C electrode. The (3 : 2) Pt–WO$_{3-x}$/C electrode also exhibits a high ohmic-drop (see Table 1). The IR-compensated polarization data for various Pt–WO$_{3-x}$/C and Pt/C electrodes are shown in Fig. 4. The data show a reduction of about 150 mV in the polarization value at 800 mA cm^{-2} load current for (3 : 1) Pt–WO$_{3-x}$/C electrode in relation to the Pt/C electrode.

The electrode kinetic-parameters for electrooxidation of methanol on various Pt–WO$_{3-x}$/C electrodes were derived from both the Tafel plots (Fig. 5) and the plots of dE/dI against $I_l/[I(I_l - I)]$ obtained analytically as shown in Fig. 6. In the former, experimentally measured current–potential data and uncompensated resistance value were employed in the calculations in conjunction with the anodic limiting-current values (I_l) obtained analytically by the least-squares fitting of the current–potential data. In the latter, least-squares regression generates a mathematical function simulating the electrochemical behaviour and its first and second derivatives were used to obtain the electrode kinetic-parameters and ohmic resistance values [27]. The electrode kinetic-parameters thus obtained for methanol oxidation on various Pt–WO$_{3-x}$/C electrodes are given in Table 1. A good agreement is seen between the kinetic data derived from the Tafel plots and the analytical method. According to these data, the lowest Tafel slope is observed for the (3 : 1) Pt–WO$_{3-x}$/C electrode that also exhibits the higher catalytic activity toward methanol electrooxidation in relation to both (3 : 2) and (6 : 1) Pt–WO$_{3-x}$/C as well as Pt/C electrodes. The higher Tafel slope obtained for the (3 : 2) Pt–WO$_{3-x}$/C electrode may indicate that the catalytic Pt-sites are particularly hindered by excess of WO$_{3-x}$.

Interpretation of the Tafel slopes for complex electrochemical reactions is fraught with difficulty, particularly for porous electrodes catalysing reactions which involve the participation of several surface-bound intermediates. The electrooxidation of methanol is now known to involve the initial formation of surface-bound CO at low potentials [4], formed by the chemisorption of CH$_3$OH, provided the concentration of methanol exceeds ~ 0.5 M [28], and we have argued elsewhere [28] that values near 90 mV per decade on bulk platinum can be associated with attack on CO at the edges of adsorbed islands, whereas higher values appear to be associated with CO migration to active sites as the rate limiting step, with attack on CO at these sites being very rapid. We have also argued that promotion of platinum by base metal oxides can be understood in terms of a proton-shift model, in which the base metal is bonded to the platinum surface through M–O–Pt bonds

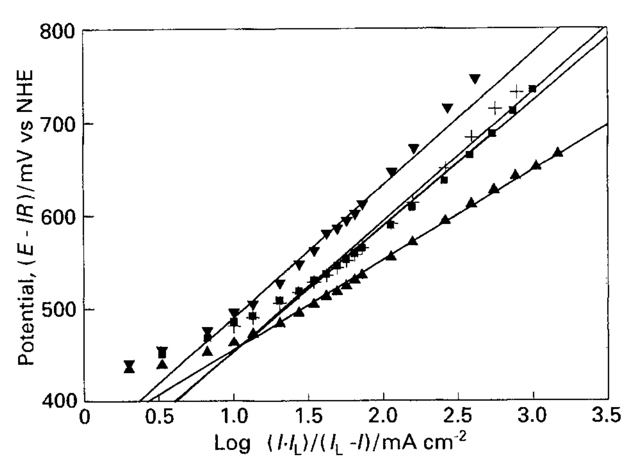
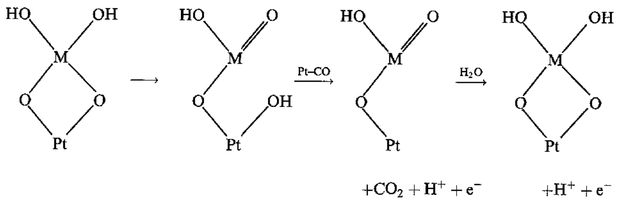


Fig. 5. Tafel plots for methanol (1 M) oxidation on various Pt–WO$_{3-x}$/C and Pt/C electrodes in sulphuric acid electrolyte at 60° C. Pt–WO$_{3-x}$/C: (■) 6 : 1, (▲) 3 : 1 and (▼) 3 : 2. (+) : Pt/C.

which can break as [29]:



Such a mechanism creates active sites at the Pt–MO_x interface, and if these are optimal in number, then the rate limiting step will be attack on CO rather than migration of CO. This accounts for the Tafel slopes observed above; for the (6 : 1) sample, the high Tafel slope suggests that migration may be playing a role, perhaps unsurprisingly given the low coverage of WO_x. At higher WO_x coverage, the Tafel slope decreases as expected, but it would appear that if the loading of WO_x becomes too large, adsorption sites for methanol become blocked and the coverage strongly decreases, leading to an increase in Tafel slope.

The intersection on the ordinate in Fig. 6 represents the value of uncompensated resistance for the respective electrode and the linear increase in dE/dI with the load current gives the associated contribution of charge-transfer resistance to the electrode polarization. The present data clearly suggest that a high uncompensated resistance plays an important rôle in the relatively poorer electrochemical performance of the (3 : 2) Pt–WO_{3-x}/C electrode.

It remains to consider the reason why the WO_{3-x} promoted electrodes from this study proved to be more active than those from a previous study [29]. There it was postulated that if the W were tetrahedrally coordinated, or equivalently if the WO_3 on the surface were cross linked so that there were no free W–OH bonds, then the mechanism shown above could not operate. XPS data reported in [29] showed no evidence for any W(IV), in contrast to data for the electrodes in this study. The facile conversion of W(VI) to W(IV) will require an open oxy-hydroxide structure with substantial numbers of free W–OH bonds, whereas it appears that our earlier studies were on WO_3 material with a less open structure. Reduction of this material would be through proton insertion to give a hydrogen bronze of mixed IV--VI valence rather than discrete IV and VI oxidation states. It is thus evident, as was implicit in our earlier paper [29], that the morphology of the base-metal oxide is quite crucial in determining its promoter activity for platinum.

It might be thought that the promotional activity of WO_x is related to the W(VI)/W(IV) redox couple acting as a surface mediator for the oxidation of surface methanolic residues. However, the E^0 value for the couple is -0.03 V vs NHE [30, 31], and it is evident from our data that promotion is taking place at far more positive potentials, where the concentration of W(IV) would be negligible and its thermodynamic effect extremely small.

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