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Identification of the Adsorbate Formed on a Platinum Electrode from Methanol

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The kind of carbon-containing adsorbate formed on a platinum electrode from methanol in an acid medium was identified by an electrochemical method. Certain improvements were made in view of the harmful effects of the following factors on the Q^F value, the quantity of electricity required to form adsorbate. The factors: a) The amounts of dissolved oxygen in both solution and electrode itself; b) the concurrent oxidation of the adsorbate in the adsorption process; and c) the presence of by-products of the methanol oxidation, formaldehyde and formic acid. By appropriate procedures, these effects could be minimized or corrected. The ratio Q^F/Q^{ox}, where Q^{ox} was an electric quantity required to oxidize completely that amount of adsorbate corresponding to the Q^F, was found to be 1.8—2.0 when the potential was 0.30—0.54 V, and the methanol concentration 0.005—1 mol dm^{-3}. It was thus concluded that the adsorbate was almost exclusively CO_{ad}.

Different conclusions have been reported about the kind of carbon-containing adsorbate (M_{ad}) formed on a Pt electrode from methanol in acid media. The adsorbates proposed are COH_{ad},[1–7] CO_{ad},[8] a mixture of COH_{ad} and $COOH_{ad}$,[9] *etc.*,[10,11] but most investigators[12] seem to support the conclusion that COH_{ad} is, at least, the dominant species. Most of these conclusions were drawn from electrochemical data, such as the quantities of electricity participating in the formation (Q^F) and subsequent oxidation (Q^{ox}) of the adsorbate. More recently, B. Beden *et al.*[13,14] have identified CO_{ad} as the adsorbate by means of their newly developed technique[14,15] capable of observing *in situ* the vibrational IR spectra of an adsorbate on a Pt electrode. They claimed that there was no spectroscopic evidence for COH_{ad} under their experimental conditions.

Although such spectra would directly indicate the molecular structure of an adsorbate, the traditional electrochemical procedures seem to have an advantage of permitting wider experimental conditions.

The disagreement among investigators about the kind of adsorbate could have resulted from some small but decisive differences in their experimental electrochemical methods. D. Pletcher *et al.*,[16] for example, emphasized recently that the pretreatment of a Pt electrode surface crucially determined the experimental data about the methanol oxidation.

The present paper describes the disturbing effects of the following factors on the value of Q^F. a) Dissolved oxygen present in solution and inside the Pt electrode itself. b) Oxidation of the adsorbate accompanying the adsorption. c) Formaldehyde or formic acid, a possible by-product in the methanol oxidation. By using appropriate procedures in which these disturbing effects on Q^F were minimized or corrected, an electrochemical identification of the adsorbate in question was carried out. It was concluded that the adsorbate was almost exclusively CO_{ad} when the electrode potential was 0.30—0.54 V, the methanol concentration 0.005—1 mol dm^{-3}, and the temperature 0 °C.

Experimental

Test Electrodes. Q^F values were determined by the graphical integration of current-time curves for the M_{ad} formation process, and Q^{ox} values by the anodic pulse method of Breiter *et al.*[17,18] immediately after the adsorption process.

Generally, a large surface area is suitable for measuring small current densities in M_{ad} formation, but a very large pulse current is required to oxidize the M_{ad}. In order to facilitate the measurements of Q^F and Q^{ox} at a single electrode, one of the three test electrodes with roughness factors of about 1, 6, and 44 was used depending on the methanol concentration ranges of 2—1, 0.5—0.3, and below 0.2 mol dm^{-3}, respectively.

To prepare these roughened electrodes, platinum wires of 99.99% purity and 3×10^{-5} m^2 geometrical surface area each were platinized, then heat-treated at 300 or 500 °C in a hydrogen stream. The heat-treatment was necessary in order a) to remove oxygen in the metal itself; b) to prevent the coated Pt black from falling off; and c) to smooth the sharp regions of the Pt-black so that the distribution of currents might not become too uneven.

Electrolysis Cell. The cell consisted of three compartments. The first had a test electrode, around which a spiral platinum wire was concentrically placed as a counter electrode. This pair of electrodes was used to measure Q^{ox} by the pulse method. In the second compartment connected to the first by a narrow glass tube, another counter electrode was placed to keep the test electrode at a desired potential in co-operation with a potentiostat. The narrow tube served to suppress the migration of products formed at the counter electrode toward the test electrode. A palladium–hydrogen reference electrode[19] was in the third compartment connected to the first by way of a Teflon stopcock, which was closed during the deoxygenation of the solution in the other compartments under reduced pressure.

All the potentials described here were referred to a reversible hydrogen electrode in the same solutions.

Potential-pulse Sequence. A potential sequence used for the measurement of Q^F and Q^{ox} is shown in Fig. 1, differing mainly in the pretreatment of the electrode from those used by Bagotzky[3,20] and Biegler.[8,11]

Effects of dissolved oxygen were serious as shown in Fig. 2, where the electrode had a roughness factor of about 44. In the normal experiments, the solutions were deoxygenated under reduced pressure for 1 min and subsequently by nitrogen-gas bubbling for 30 min through fritted-glass disks (Step A in Fig. 1). Most of the dissolved oxygen remaining in the vicinity of the test electrode was removed during Step B, in which the potential was kept at 0.06 V for 5 min. By this procedure the current for oxygen reduction in the base solution, 0.5 mol dm^{-3} sulfuric acid, was confirmed to have diminished to about 10^{-4} A m^{-2} with a roughened electrode. For a smooth electrode, the effect of oxygen was difficult to minimize to this extent as is indicated in Curve 4 of Fig. 2. Consequently, the electrode was used only when the observed current for M_{ad} formation was larger than the residual reduction current of the dissolved oxygen remaining. In other words, it was used only when the methanol concentration was higher than 1 mol dm^{-3}. The test electrode underwent final cleaning-up at Step C and D. At 1.35 V, platinum oxides were formed, and most of the M_{ad} were removed by oxidation; at 0.06 V the platinum oxides were reduced without evolution of free hydrogen. The double rectangular pulses in Step C served to remove M_{ad} completely and to prevent the formation of a deep layer of surface oxides. A small amount of by-products, which might be formed at 1.35 V and at high concentrations of methanol, were allowed to diffuse away during Step D (0.06 V), the duration of which was 5 or 15 s. The longer duration was favorable for the complete disappearance of a non-steady current produced in the transit from C into D Steps. The shorter one, however, was superior at methanol concentrations above 0.3 mol dm^{-3}, because the amount of M_{ad} formed even at this low potential became perceptible at longer times. To diminish such concomitant events, all the measurements were made at a low temperature of 0 °C.

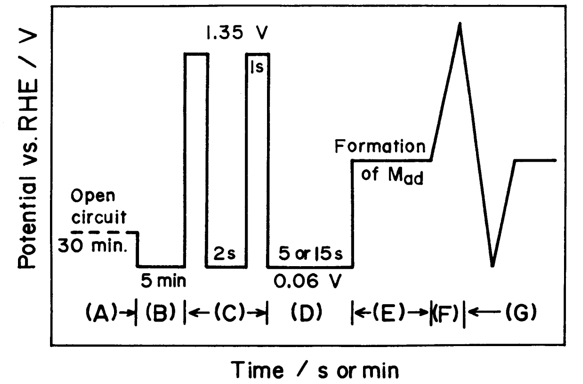

Fig. 1. Potential sequence for measurements of Q^F and Q^{ox}, A) Deoxygenation under reduced pressure and sudsequent N_2 bubbling, B) Reduction of remaining oxygen, C) Cleaning of electrode surface, D) Reduction of surface oxides and removal of oxidation products, E) M_{ad} formation and Q^F measurement, F) Q^{ox} measurement, G) for next run.

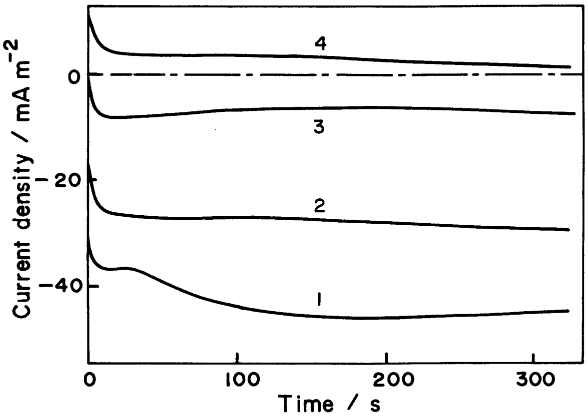

Fig. 2. Current decay on roughened electrode at 0.30 V in 0.03 mol dm^{-3} CH_3OH+0.5 mol dm^{-3} H_2SO_4 solution containing dissolved oxygen, Solution was saturated with air, oxygen was removed by degassing under reduced pressure and subsequent N_2 bubbling for: 1) 0; 2) 5; 3) 7; 4) 30 min.

The potential sequence was generated by means of a LB-75 M Wenking potentiostat and a handmade pulse generator. In the measurement of Q^F, the currents at Step E were stored in a HR-1200 transient converter (Kawasaki Electronics), which had a decimal 12-bit resolution, and recorded on a WX-4401 XY recorder (Watanabe Instruments Corp.,).

All the current densities described are for a unit true area of electrode surface, determined by the conventional hydrogen deposition method. In the measurement of Q^{ox} (Step F), the scan rates were 263, 99.4, and 27.6 V/s in the methanol concentration ranges of 2—1, 0.5—0.3, and below 0.2 mol dm^{-3}, respectively. Under these conditions, the observed currents were almost exclusively due to the oxidation of M_{ad}.

Results and Discussion

As most investigators[1-5,8,11] approve, the formation of an experimentally perceptible adsorbate from methanol in acid solution and the oxidation of the adsorbate may well be written as

$$M_{ad} \text{ formation: } CH_3OH = M_{ad} + n_1H^+ + n_1e \quad (1)$$

$$M_{ad} \text{ oxidation: } M_{ad} + H_2O = CO_2 + n_2H^+ + n_2e \quad (2)$$

M_{ad} denotes a carbon-containing adsorbate, n_1 and n_2 are the number of participating electrons. It should be noted that the equations do not necessarily represent the only path for methanol oxidation. According to the Eqns., $n_1+n_2=6$. If M_{ad} is, *e.g.*, CO_{ad} or COH_{ad}, n_2 should be 2 or 3, respectively. The ratio $n_1/n_2=Q^F/Q^{ox}$, where Q^F is a quantity of electricity required to form an amount of M_{ad}, and Q^{ox} is that required to oxidize this amount of M_{ad} to carbon dioxide.

Determination of Q^F *by Experimental* i-t *and* Q^{ox}-t *Relationships.* It is no doubt a prerequisite for obtaining a correct value of Q^F by integration of an experimental *i-t* relationship in the adsorption process that the *i* is solely due to the adsorption. As the criterion, previous investigators[3,8,11] employed either of the following theoretical *i-t* relationships:

$$i = k_1/t \quad (3)$$

$$1/i = 1/i_0 + k_2 t \qquad (4)$$

where k_1 and k_2 are constants. Equation 3 was derived by Bagotzky *et al*,[3,8,11] by using the next relation.

$$\theta_M = a + b \ln t \qquad (5)$$

where a and b are constants, and θ_M is a surface coverage with M_{ad}. They assumed that θ_M was in direct proportion to the number of M_{ad} species. The assumption, however, is not always correct, because every M_{ad} might not always occupy the same number of sites on the electrode surface; the details of which will be reported later. Thus, we prefer to use Q^{ox} instead of θ_M,

$$Q^{ox} = a' + b' \log t \qquad (6)$$

where a' and b' are constants. When the values of Q^{ox}/Q_H^o are within the range about 0.1 to 0.9, Eq. 6 is valid as shown in Fig. 3. Instead of Q^{ox}, Q^{ox}/Q_H^o is used for convenience of comparison with other data, Q_H^o being a quantity of electricity required fully to cover the surface with a monolayer of adsorbed hydrogen atoms. According to Eq. 6 or 5, Q^{ox} approaches minus infinity as t approaches zero, while it is required for the derivation of Eq. 4 that Q^{ox} approaches zero. It thus appears that Eq. 3 is preferable to Eq. 4.

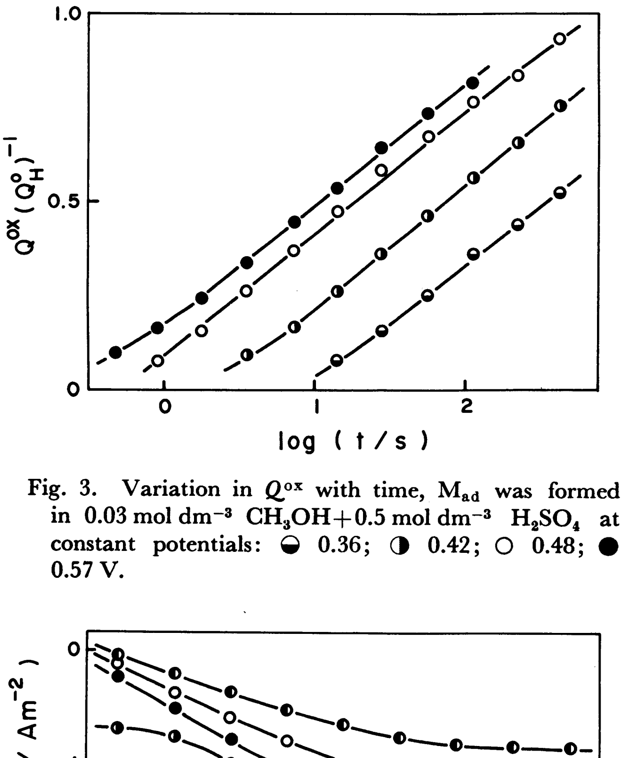

Fig. 3. Variation in Q^{ox} with time, M_{ad} was formed in 0.03 mol dm^{-3} CH_3OH+0.5 mol dm^{-3} H_2SO_4 at constant potentials: ⊖ 0.36; ◑ 0.42; ○ 0.48; ● 0.57 V.

Figure 4 shows typical *i-t* relations observed for the adsorption process under the same conditions as in Fig. 3. A linear part with a slope of −0.99 is seen in any curve obtained at a potential within the limits of 0.30—0.48 V, *e.g.*, the latter parts of curves 4 and 5, indicating the validity of Eq. 3. On the other hand, the former parts of the curves at low potentials show considerable deviations from that linear relation, and the lower the potential, the larger becomes the deviation. Although it might be ascribed to a change in the kinetics of adsorbate formation, the nature of the currents remains unknown. However the contributions of the currents to the value of Q^{ox} were so small that treating them as genuine adsorption currents brought no serious errors in obtaining the Q^F—Q^{ox} relationship (Fig. 6).

At potentials above 0.48 V, appreciable and stationary currents were observed even after 30 min from the start of adsorption. If adsorption on a electrode surface is completed, the adsorption current should fall to zero. Consequently, these stationary currents might be considered to be due to both the stationary oxidation of the adsorbate and, in some cases, the formation of by-products. Thus, the net adsorption currents at every moment were estimated by subtracting the stationary current still flowing at 30 min after the start of adsorption from the observed current.

Effects of Formaldehyde and Formic Acid on Q^F *and* Q^{ox}. Breiter *et al.*[21,22,23] reported that appreciable amounts of formaldehyde and formic acid were formed during the oxidation of methanol in acid so-

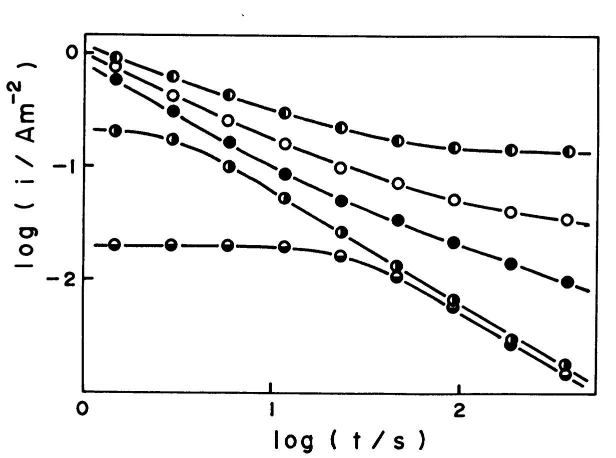

Fig. 4. Variation in current density at constant potential with time, 0.03 mol dm^{-3} CH_3OH+0.5 mol dm^{-3} H_2SO_4, Potential: 1) 0.65; 2) 0.60; 3) 0.55; 4) 0.45; 5) 0.35 V.

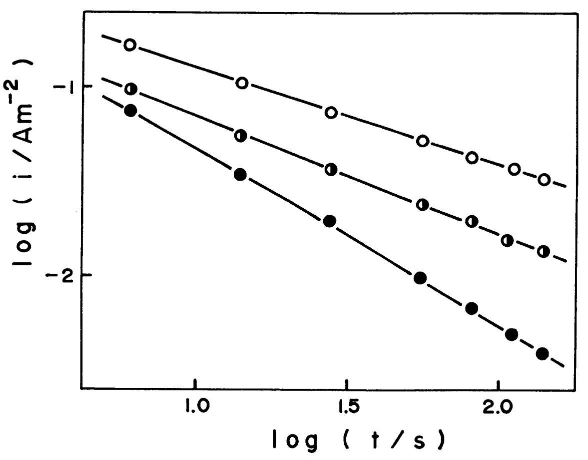

Fig. 5. Variation in M_{ad} formation current with concentration of formaldehyde in 0.03 mol dm^{-3} CH_3OH+0.5 mol dm^{-3} H_2SO_4+HCHO, Concn. of HCHO: ● 0; ◑ 0.01; ○ 0.03 mol dm^{-3}.

lution in which the concentration of methanol was relatively high. The effects of these substances on the *i*-*t* curves for M_{ad} formation process were significant even in their very low concentrations. Figure 5 shows how the presence of formaldehyde increases both the currents and the slopes of the log *i*—log *t* curves. The resulting Q^F were obviously larger than those in the absence of the aldehyde. Its presence, on the other hand, had only a small effect on the values of Q^{ox}, thus resulting in an increase in the Q^F/Q^{ox} values. The effects of formic acid were similar to those of formaldehyde. These contaminants originally present in methanol reagent can readily be removed. However there is no way of removing the substances that are unavoidably formed during the pretreatment for cleaning the electrode surface by potential pulses. Consequently, it seems best to design a pulse sequence which produces only as small amounts of these substances as possible. Such is the case with the sequence described in the experimental section. In addition, it was confirmed that[23] regardless of the potential the formation of these by-products only became perceptible, when the methanol concentration was above about 1 mol dm^{-3}. Their formation at a constant potential should be accompanied by a stationary current. Therefore, the background-current correction to obtain the net adsorption current would also eliminate that stationary current so long as the amount of by -products are not too large.

Q^F-Q^{ox} *Relationship.* Figure 6 shows the typical Q^F-Q^{ox} relations for the adsorption process under the same conditions as those in Figs. 3 and 4. There is a straight line relationship with a slope, Q^F/Q^{ox}, close to 2. In spite of the background-current corrections, upward deviations from linearity took place when the potential was above 0.48 V, while at the same time the Q^{ox} value was large. The cause of such deviation remains unknown. Figure 7 shows the variation in the slope of the linear part with potential. Within the potential range of 0.30—0.54 V, the slope varied only slightly, the average being 1.84. Biegler *et al.*[11] had reported that the slope depended on the potential. The virtual invariance of the slope value can be largely attributed to the current correction, which Biegler *et al.* did not made. The effects of methanol concentration on the slope value are illustrated in Fig. 8. In this instance the potential was 0.42 V, at which no background current was observed. The slope varied only slightly over a wide range of methanol concentration, 0.005—1 mol dm^{-3} the average being 1.89. Higher potentials resulted in slightly larger slopes. Lower potentials also led to slightly smaller values, and moreover narrowed the methanol-concentration range in which the slope remained practically constant.

As described above, the slope is almost constant over the considerably wide ranges of M_{ad}-formation time, potential, and methanol concentration. This fact indicates that only one kind of M_{ad} species is formed. As the M_{ad}, CH_3O_{ad}, CH_2O_{ad}, COH_{ad}, CO_{ad}, or $COOH_{ad}$ is to be expected from Eqs. 1 and 2, if the slope is 1/5, 1/2, 1, 2, and 5, respectively. Because the slope is close to 2, it is concluded that the adsorbate should almost exclusively be CO_{ad}, at least, under those conditions which have hitherto been specified. A slight deviation of the

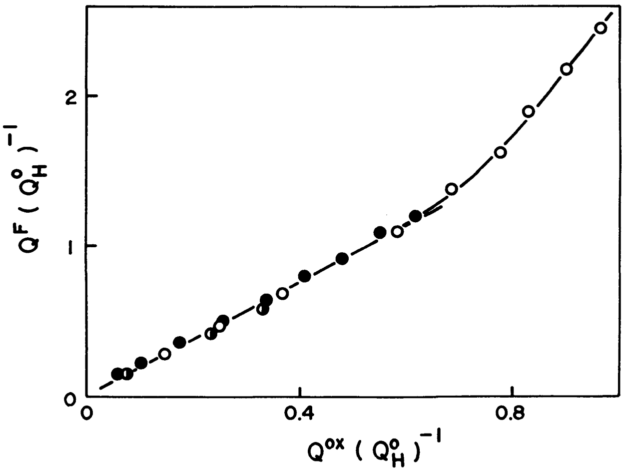

Fig. 6. Variation in Q^F with Q^{ox} in 0.03 mol dm^{-3} CH_3OH+0.5 mol dm^{-3} H_2SO_4, Constantials: ◑ 0.33; ● 0.42; ○ 0.51 V.

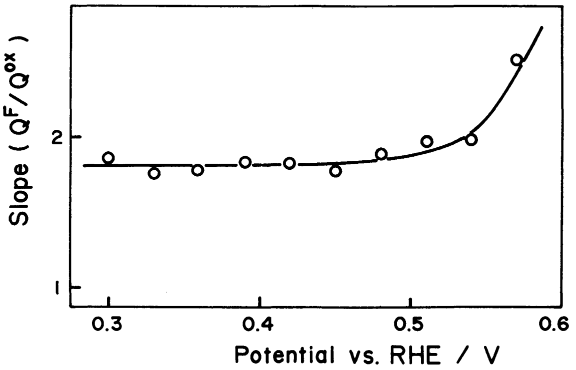

Fig. 7. Variation in slope (Q^F/Q^{ox}) with potential in 0.03 mol dm^{-3} CH_3OH+0.5 mol dm^{-3} H_2SO_4.

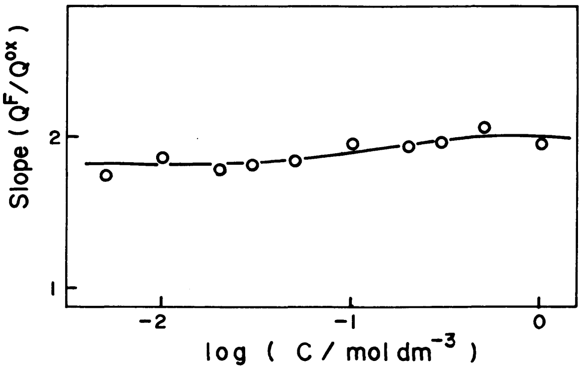

Fig. 8. Variation in slope (Q^F/Q^{ox}) with methanol concentration at 0.42 V in CH_3OH+0.5 mol dm^{-3} H_2SO_4.

slope value from 2 might have been caused by the coexistence of some other adsorbate such as COH_{ad}.

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