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Effect of High Surface Coverage on the Rate of Methanol Oxidation at Platinum Electrode

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The rates of the methanol oxidation and the CO_{ad} formation at Pt electrodes in solutions of CH_3OH+ 0.5 mol dm^{-3} H_2SO_4 were investigated under the conditions minimizing the harmful effect of impurities. Under the particular conditions, the both rates decreased remarkably towards zero at a limiting coverage of about 0.8. Namely, the CO_{ad} hindered both the formation of the CO_{ad} itself and the oxidation of methanol *via* some unidentified intermediate other than CO_{ad}. This fact was explained by assuming an aggregate with two vacant sites indispensable for the CO_{ad} formation and the methanol oxidation to CO_2.

It is well known[1—4] that the stationary-state rates of the methanol oxidation on platinum electrodes in acid media increase and, in succession to a maximum, decrease with an increase in the methanol concentration, and that the decrease is remarkable at low potentials and high methanol concentrations. Similar maxima and the subsequent decreases of rate are also observed on each system of formaldehyde,[5] ethanol,[6] ethylene,[7,8] and so on. For the case of ethylene, Bockris *et al.*[8] gave an explanation on the basis of their hydroxyl-radical mechanism. Bagotzky *et al.*[1] however, observed variations in the rate of the methanol oxidation with potential differing from those predicted by the hydroxyl-radical mechanism. Biegler *et al.*[4] related the retardation of the methanol oxidation to the effect of high surface coverage with adsorbate formed from methanol, while Bagotzky *et al.*[1] showed that it also occurred even at low coverages. Breiter[9] proved that the presence of chloride ion, even in its very low concentrations, resulted in the inhibition of the methanol oxidation. Belanger[10] also reported similar effects of several anions such as nitrate as well as halogen ions.

In short, there were certain serious disagreements among groups of workers about the experimental data, particularly about the rates in the range of medium to limiting coverages. Thus it appeared of necessity to establish in the first place reliable data that were practically uninfluenced by impurities.

The data obtained with such a particular attention were different from those of the previous workers[1,4] in certain respects, *e.g.*, whether there were stationary-state rates in the methanol oxidation to CO_2. Above all, the rates of the formation of the adsorbate, CO_{ad}, and the overall oxidation of methanol decreased remarkably, in many cases towards zero, as soon as the coverage with CO_{ad} attained to a limiting value of 0.8, though the definition of the coverage here differed from that adopted by the previous investigators.[1,4] The phenomenon was explained by assuming that at the high coverage the CO_{ad} would damage the aggregates, each consisting of two vacant sites, indispensable for the formation of the CO_{ad} itself and for the oxidation of methanol *via* some unidentified intermediate other than CO_{ad}.

Experimental

The cells, electrodes, reagents, and the procedures were the same as those described in the previous paper.[11]

The coverages with adsorbate, θ_1 and θ_2, were expressed as

$$\theta_1 = (Q_H^0 - Q_H)/Q_H^0 \qquad (1)$$

$$\theta_2 = Q^{ox}/(Q^{ox})_{max} \qquad (2)$$

where Q_H^0 was the electric quantity required to cover fully the electrode surface with a monolayer of adsorbed hydrogen atoms in the absence of the carbon-containing adsorbate, Q_H was that in the presence. Q^{ox} was the quantity required to oxidize an amount of the adsorbate, and $(Q^{ox})_{max}$ was the maximum Q^{ox}. Q_H and Q_H^0 were determined by the conventional hydrogen-deposition method, in which the scan rates of potential were 20 and 100 V s^{-1} at the concentrations of methanol below and above 0.3 mol dm^{-3}, respectively. Q^{ox} and $(Q^{ox})_{max}$ were determined by the method described previously.[11]

In order to minimize the disturbing effect of adsorbed impurities on the rate of methanol oxidation, the temperature was lowered to 0 °C, and roughened electrodes were used. Under these conditions, the decrease of Q_H^0 due to the adsorption of impurities did not exceed 3% within the oxidation time of 400 s.

The potentials were referred to the reversible hydrogen electrode in 0.5 mol dm^{-3} H_2SO_4, and the current densities were expressed for the unit true surface area, which was determined by the hydrogen-deposition method.

Results and Discussion

As seen in Fig. 1, the rate of oxidation never became stationary within about 400 s at the methanol concentrations above about 0.1 mol dm^{-3}. Although longer times resulted eventually in stationary rates, then Q_H^0 decreased more than 3% and the disturbing effect of impurities became perceptible. Figure 2 shows the time dependence of the CO_{ad} coverage under the same conditions as in Fig. 1. The coverage reached an approximately constant value of 0.8 at

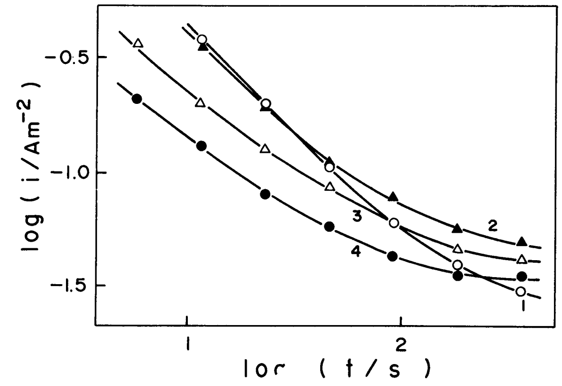

Fig. 1. Variation in oxidation rate with time ($CH_3OH + 0.5\,mol\,dm^{-3}$ H_2SO_4, 0.6 V, 0 °C). Methanol: (1) 3.0; (2) 1.0; (3) 0.1; (4) $0.03\,mol\,dm^{-3}$.

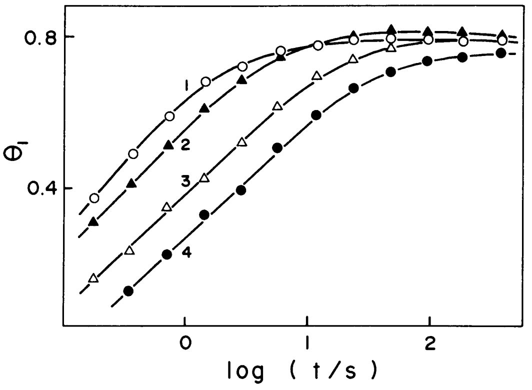

Fig. 2. Variation in surface coverage with time ($CH_3OH + 0.5\,mol\,dm^{-3}$ 0.6 V, 0 °C). Methanol: (1) 3.0; (2) 1.0; (3) 0.1; (4) $0.03\,mol\,dm^{-3}$.

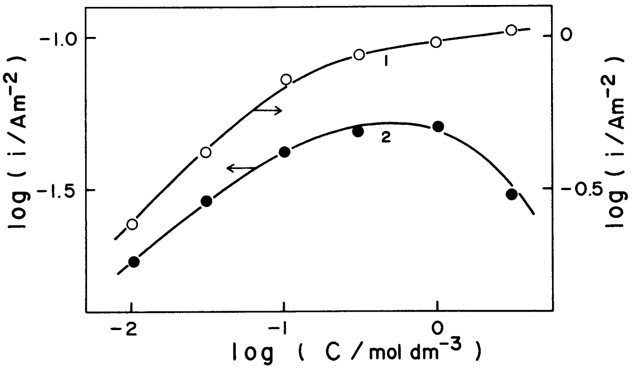

Fig. 3. Variation in oxidation rate at 360 s with methanol concentration ($CH_3OH + 0.5\,mol\,dm^{-3}$ H_2SO_4, 0 °C). Potential: (1) 0.75; (2) 0.60 V.

all the methanol concentrations of 0.03—3 $mol\,dm^{-3}$. Respective curves in Fig. 3 show the typical rate-variations with the methanol concentration. The current densities plotted were ones at a particular time of 360 s when the coverages had already become stationary. Retarding of the oxidation rate at higher concentrations is obvious, and it becomes remarkable at lower potentials. These trends are in consistent with the observations by Bagotzky,[1] Biegler[4] *et al.* Contrary to their observations, however, the rates were not always stationary.

It is known[1,4,12] that the decay of current observed in the initial stage of the methanol oxidation at constant potentials is associated with the formation and accumulation of adsorbates. In order to know the time dependence of the oxidation rate uninfluenced by such a nonstationary current, i_N, subtraction of i_N from the observed current is necessary; the remainder is denoted hereafter by i_R. The present authors[11] showed that the formation and oxidation of the adsorbate that is experimentally identifiable could be written as

$$CH_3OH_{sol} = CO_{ad} + 4H^+ + 4e \qquad (3)$$

$$CO_{ad} + H_2O = CO_2 + 2H^+ + 2e \qquad (4)$$

Because part of the adsorbates formed are simultaneously oxidized unless the potential is very low, i_N at every moment solely contributes to the increase in the CO_{ad} coverage, θ_2. Expressing the mole number of CO_{ad} at its saturated coverage by N_s, and the Faraday constant by F,

$$i_N = 4FN_s d\theta_2/dt \qquad (5)$$

according to Eq. 3. The i_N can also be expressed in terms of an electric quantity, Q_s^{ox} required to oxidize N_s moles of CO_{ad} to CO_2.

$$Q_s^{ox} d\theta_2/dt = 2FN_s d\theta_2/dt \qquad (6)$$

From Eqs. 5 and 6,

$$i_N = 2Q_s^{ox} d\theta_2/dt \qquad (7)$$

The time dependence of $i_R/(1-\theta_1)$ under the same conditions as those in Fig. 1 is shown in Fig. 4. Strictly speaking, no stationary rate was seen. In the course of the gradual fall of current, the coverages attained to a constant limiting value of about 0.8 at all the methanol concentrations when the potential was 0.6 V. The solid circle on each curve indicates the time at which the coverage attains to 0.75, and the time became shorter with an increase in the methanol concentration.

Relations between $i_R/(1-\theta_1)$ and θ_1 at various methanol concentrations and at a constant potential of 0.6 V are shown in Fig. 5. The fall of the rate became extremely remarkable with an increase of the coverage in its range of about 0.75 to 0.80. At the concentration of 0.03 $mol\,dm^{-3}$, the coverage could not reached 0.8, and no further fall of current could be measured. Because the rate of Reaction 3 is relatively small at low concentrations and exponentially decreases with an increase in θ_1, the coverage would be unable to come up to 0.8 within the limited measurement time. The electrode potential also exerted an effect upon the value

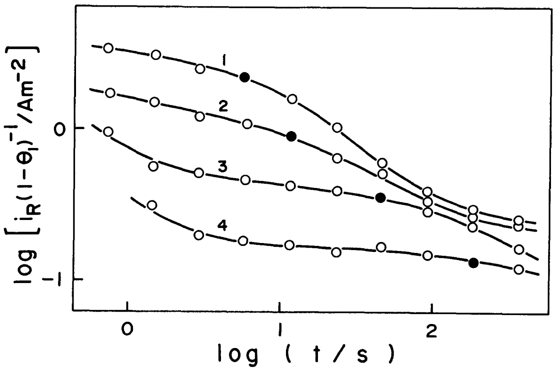

Fig. 4. Variation in oxidation rate with time ($CH_3OH+0.5\,mol\,dm^{-3}$ H_2SO_4, 0.6 V, 0 °C). Methanol: (1) 1.0; (2) 0.3; (3) 0.1; (4) 0.03 mol dm^{-3}. Solid circle indicates when coverage attains to *ca.* 0.75.

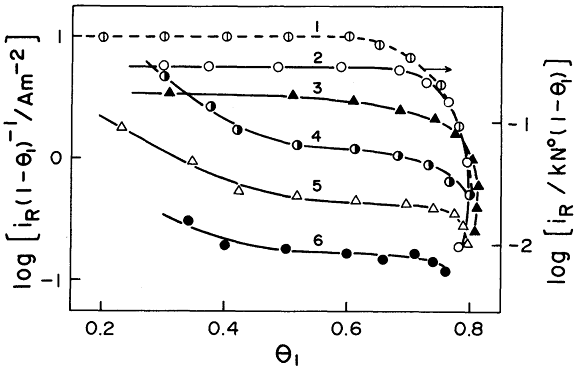

Fig. 5. Variation in oxidation rate with coverage ($CH_3OH+0.5\,mol\,dm^{-3}$ H_2SO_4, 0.6 V, 0 °C). Methanol: (2) 3.0; (3) 1.0; (4) 0.3; (5) 0.1; (6) 0.03 mol dm^{-3}; Curve 1: theoretical.

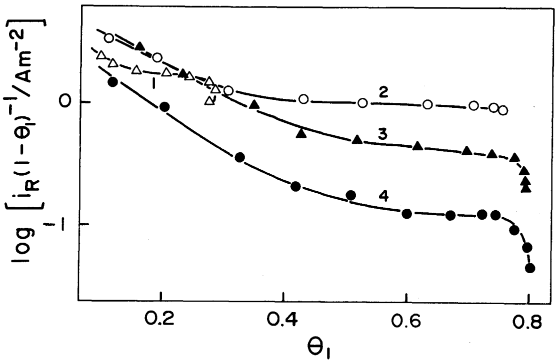

Fig. 6. Variation in oxidation rate with coverage ($0.1\,mol\,dm^{-3}$ $CH_3OH+0.5\,mol\,dm^{-3}$ H_2SO_4, 0 °C). Potential: (1) 0.75; (2) 0.65; (3) 0.60; (4) 0.55 V.

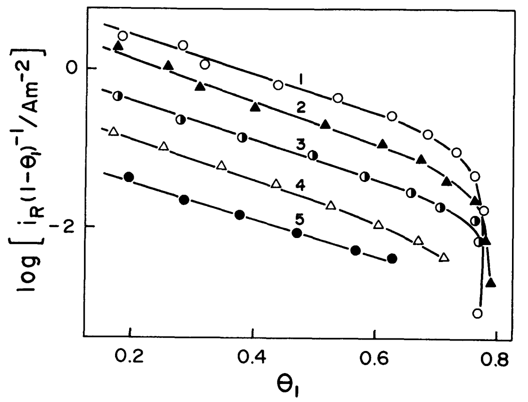

Fig. 7. Variation in CO_{ad} formation rate with coverage at 0.4 V ($CH_3OH+0.5\,mol\,dm^{-3}$ H_2SO_4, 0 °C). Methanol: (1) 3.0; (2) 1.0; (3) 0.3; (4) 0.1; (5) 0.03 mol dm^{-3}.

of limiting coverage and the subsequent rate fall as illustrated in Fig. 6. Limiting coverages were 0.75 at 0.65 V, 0.3 at 0.75 V, and intermediate values ranging from 0.75 to 0.3 at the potentials from 0.65 to 0.75 V. In every case of higher potentials above 0.65 V, the current hardly continued falling after the limiting coverage, though an indication of the fall was observed. A potential increase accelerates the oxidation of the CO_{ad} exponentially,[13] but doesn't the formation so much.[1,4] Therefore, the both rates would become balanced at a coverage lower than 0.8.

Similar remarkable falls of the rate of CO_{ad} formation took place whenever the coverage approached a limiting coverage of about 0.8 as shown in Fig. 7. The formation currents, i_F, were ones, except for Curve 2, corrected for the simultaneous oxidation of CO_{ad} by the method described in the preceding paper.[11] Coincidence in the value of the limiting coverages between the methanol oxidation and the CO_{ad} formation suggests that their causes would be similar.

Rate Fall before and after the Coverage of 0.8. As shown above, both the rates of the CO_{ad} formation and the overall methanol oxidation under the particular conditions markedly decrease, in some cases towards zero, immediately after the CO_{ad} coverage attains to a limit of about 0.8. A few explanations[1,4,7,8] have been given for the decrease in the oxidation rate at high coverages before the limits, but not an explanation for the unusual fall after the limiting coverage of 0.8. The definition of the coverage adopted here differs from those used by previous workers;[1,4] the value of 1 in their definition corresponds to about 0.8 in ours.

We have the data proving the oxidation rate of the CO_{ad} itself to be very small at its high coverages compared with the rate of the overall methanol oxidation to CO_2, the detail of which will be reported before long. Therefore, we are with Breiter *et al.*[12,14,15] about the opinion that different paths of CO_2 production exist in parallel. And we consider that at high coverages methanol is oxidized to CO_2 mostly without passing through the intermediate CO_{ad}.

Generally, such an adsorbate as is hard to react further can diminish the rate of an electrode reaction down to zero at a high coverage, if the adsorbate hinders sterically the approach of reactant species to the vacant sites adjacent to the preoccupied site, or if it prevents the availability of a site-aggregate that is indispensable for the electrode reaction to occur. The

CO_{ad} formed in the methanol oxidation is unlikely to exert the steric hindrance, because the coverage with the CO_{ad} formed from an aqueous solution of CO[16,17] is able to attain to 1. The aggregate-damaging effect is now under intensive investigation[18—20] in connection with the catalytic activity of an electrode modified with adatoms. This effect is operable provided the following conditions are satisfied.

(1) For the reaction under consideration to occur, an aggregate consisting of some of the vacant sites is necessary.

(2) The aggregate-damaging adsorbates are uniformly distributed on the surface.

(3) One molecule of the adsorbate occupies less sites than has one aggregate.

The CO_{ad} forming in the methanol oxidation can satisfy these requirements, the reasons are as follows.

(1) It would be reasonable to consider that the CO_{ad} formation takes place in a series of successive stages at which 4 hydrogen atoms of a methanol molecule are abstracted. Thus one or more sites are necessary in addition to the site(s) for the CO_{ad} eventually formed. Such site-aggregates would also be required for another path of the methanol oxidation to CO_2, though any stable intermediate is not yet experimentally identified.

(2) When the potential and the methanol concentration were below 0.5 V and 1 mol dm^{-3} respectively, no oxidation of methanol to CO_2 took place, and therefore the currents for the CO_{ad} formation, i_F, were directly measurable. The plots of log i_F $(1-\theta_1)^{-1}$ *vs* θ_1 were approximately linear within the limits of $0.1<\theta_1<0.75$ (Fig. 7), and expressed as

$$i_F = k(1-\theta_1)\exp(-3.84\,\theta_1) \qquad (8)$$

where k is a potential dependent constant. This experimental rate equation is substantially the same as the theoretical one[21] derived on the assumption that the heat of adsorption on a uniform surface increases linearly with an increase in the coverage. In other words, the CO_{ad} formation will occur in order of the increasing heat of adsorption, which will result in a uniform distribution of the CO_{ad}. At higher potentials above 0.5 V, an approximately uniform distribution would also be expected.

(3) Gilman *et al*[13,17] reported that the CO_{ad} formed from an aqueous solution of CO showed two states of binding with Pt surface atoms, *i.e.*, one-site (or linear) and two-site (or bridged) adsorptions. Since the value of $2\,(Q^{0}_{H}-Q_{H})/Q^{ox}$ represents the number of sites occupied by one CO_{ad}, the number can be determined from the slope of plots, Q^{ox}/Q^{0}_{H} *vs.* $(Q^{0}_{H}-Q_{H})/Q^{0}_{H}$, the latter equals to θ_1. Figure 8 shows the case in which the methanol concentration is 1 mol dm^{-3} and the potential 0.35—0.75 V. The number of sites, 1.89, indicates that most adsorbates at $\theta_1<$ about 0.6 are the bridged type, and the number 1.08 that the adsorbates at about $0.6<\theta_1<0.8$ are mainly linear type.

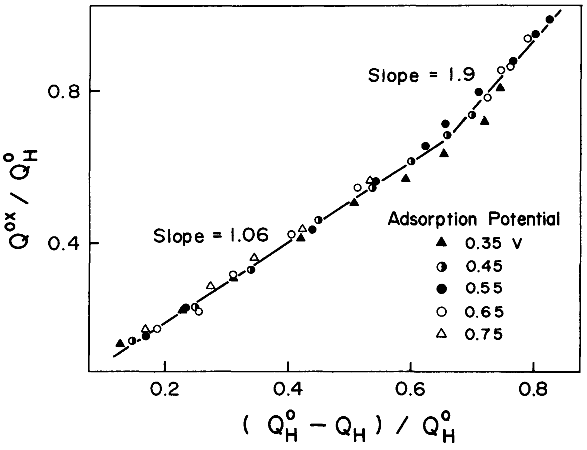

Fig. 8. Variation in Q^{ox} with coverage (1 mol dm^{-3} $CH_3OH+0.5$ mol dm^{-3} H_2SO_4, 0 °C).

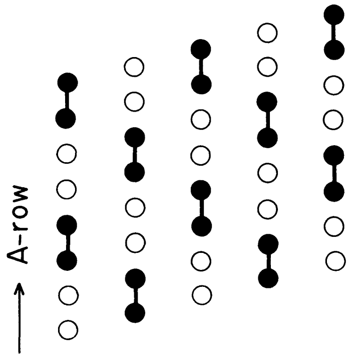

Fig. 9. Uniform distribution of bridged CO_{ad} at $\theta_1=0.5$ under minimum repulsion among CO_{ad} molecules.

To sum up, the CO_{ad} probably has such an aggregate-damaging effect as diminishes the rates of both the methanol oxidation to CO_2 and the further formation of CO_{ad} itself at its high coverage less than 1.

It is shown below first that the number of the aggregates, each consisting of 3 or more adjacent vacant sites, should be reduced to zero at $\theta_1=0.5$, if the bridged CO_{ad} species are distributed uniformly. And then that the linear adsorbates forming at $\theta_1>0.6$ should make all the aggregates consisting of two vacant sites each vanish at the coverage of 0.8.

The actual surface of the Pt electrodes used in the experiment was a mixture of crystal faces with the different indices and not a completely flat plane. However it can be represented by an orderly gathering of parallelograms as a simplest approximation, the apices representing the lattice sites (Fig. 9). In Fig. 9, rows of the nearest sites are called A-rows, and those of the next nearest ones B-rows.

A bridged CO_{ad} is considered[22] to be attached with its carbon atom to a pair of Pt sites. Since the atomic radius of Pt is larger than that of C, it must be energetically favorable for a bridged CO_{ad} to occupy those two sites which are nearest with each other. Thus

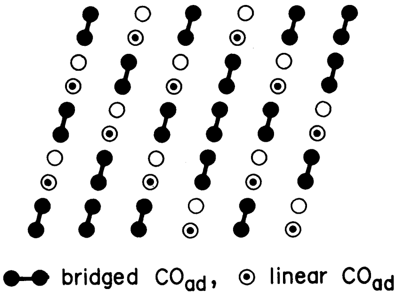

Fig. 10. An example of vacant-site distribution when coverage with bridged CO_{ad} (●–●) is 0.6 and that with linear CO_{ad} (⊙) 0.2.

the adsorbates will preferentially line up in the A-rows.

The negative value of the exponent, $-3.84\,\theta_1$, in Eq. 8, indicates that there are mutual repulsions between the CO-adsorbates, the adsorbed methanol molecules, or the both species, and that the repulsions make the adsorption energy of the CO_{ad} increasingly high with an increase in θ_1. In an A-row, the bridged CO_{ad} should align at intervals of some vacant sites in order to make the mutual repulsion small. If the maximum amount and the minimum repulsion of the adsorbates over the whole surface are required, every two pairs of sites situated directly abreast with a CO_{ad} should always be vacant as shown in Fig. 9. In this distribution of the adsorbates, the number of the aggregates with 3 or more adjacent vacant sites each is zero at $\theta_1=0.5$. However the experiment shows that the rate of the methanol oxidation does not fall to zero at the coverage of 0.4 to 0.75. It can thus be concluded that the number of sites in the aggregate indispensable to the oxidation of methanol to CO_{ad} or CO_2 is probably 2.

By assuming that the respective adsorbates at $\theta_1\leq0.6$ and >0.6 are exclusively bridged and linear types, the number of the remaining aggregates with two vacant sites each, A_2, can be deduced in the following way. Although the uniform distribution of the bridged adsorbates is probable at $\theta_1=0.5$ as shown in Fig. 9, a local irregularity cannot be avoidable at $\theta_1=0.6$. The distribution of the solid circles in Fig. 10 gives an example. At this coverage, A_2 is equal to a half of the remaining vacant sites, *i.e.*, $(1-0.6)\,S_t/2$; S_t is the total number of sites on the electrode surface. When $\theta>0.6$ and the linear adsorbates are distributed as uniformly as possible (Fig. 10), one linear adsorbate damages one aggregate. Consequently, A_2 is expressed as

$$A_2 = (1-0.6)S_t/2 - M_1 \tag{9}$$

where M_1 is the number of the linear adsorbates, and equal to $(\theta_1-0.6)\,S_t$. Then the expression 9 becomes

$$A_2 = S_t(0.8-\theta_1) \tag{10}$$

If i_R, the current for the oxidation of methanol to CO_2, is proportional to A_2, then

$$\log i_R(1-\theta_1)^{-1} = \log(kS_t) + \log(0.8-\theta_1)(1-\theta_1)^{-1} \tag{11}$$

This theoretical equation shows that the rate of the oxidation decreases towards zero as θ_1 approaches 0.8, as indicated by Curve 1 of Fig. 5. This is in substantial agreement with the experimental fact. The rate decreases in the CO_{ad} formation at 0.8 can also be explained in the same way.

To sum up, the aggregate consisting of two vacant sites is indispensable for the formation of CO_{ad} and the overall oxidation of methanol. The CO_{ad} exerts the aggregate-damaging effect at the coverages of about 0.8, leading to the decrease of the both rates towards zero.

Additional Remarks about the Coverages by Different Definitions. As described above, the maximum coverage with the CO_{ad} varies according to whether the starting species, from which the CO_{ad} is formed, is methanol or carbon monoxide in a solution. Generally speaking, the maximum coverage with a particular adsorbate does not always take an invariable value even if the adsorbates are identical, which are eventually formed from different starting species *via* different paths. It is therefore not appropriate to use the following coverages, θ_2 and θ_3, for the purpose of comparison of the coverage values, unless the starting and the adsorbate species are respectively the same. In such cases, the coverage defined by Eq. 1 should be used.

$$\theta_3 = (Q_H^0-Q_H)/[Q_H^0-(Q_H)_{min}] \tag{12}$$

where Q_H and Q_H^0 are previously stated when θ_1 is defined, and $(Q_H)_{min}$ are for the maximum amount of adsorbate, and $[Q_H^0-(Q_H)_{min}]$ corresponds to the maximum number of available hydrog hydrogen sites.

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