Kinetics of Methanol Oxidation Over Platinum Wire Catalysts

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The oxidation of methanol at atmospheric pressure over platinum wire catalysts has been studied over a wide range of experimental conditions (T = 310-660 K, $P_{O_2}/P_{CH_3OH} = 2-100$). Two experimental techniques were used. In the conventional flow-reactor experiments kinetic parameters were obtained from measurement of gas-phase concentrations, while in the microcalorimeter experiments kinetic parameters were derived from the rates of heat generation at the catalyst surface.

At 373 K, for $P_{O_2}/P_{CH_3OH} = 25$, a point within the experimental range common to both techniques, the specific rates of oxidation determined by each method were 120 nmol s⁻¹ cm⁻² (conventional flow reactor) and 100 nmol s⁻¹ cm⁻² (microcalorimeter). The use of the microcalorimeter enabled kinetic measurements to be made over the full experimental range. It was found that the observed kinetics were dependent on both temperature and oxygen : methanol ratio. Thus in the general rate expression :

$$R = k P_{\rm CH_3OH}^m P_{\rm O_2}^n$$

the values of *m* and *n* were found to vary between 0 and $\frac{1}{2}(P_{O2}/P_{CH_3OH} \le 5, T \le 380 \text{ K})$, through 1 and $\frac{1}{2}(P_{O2}/P_{CH_3OH} = 8-15, T = 325-390 \text{ K})$, to 1 and 0 (*T* > 405 K, all ratios).

Non-steady-state kinetics were also observed for $P_{O_2}/P_{CH_3OH} = 5$ at temperatures between 380 and 405 K.

A mechanism, which is consistent with the observations, is proposed involving the interaction of gaseous methanol with adsorbed atomic oxygen to produce adsorbed methoxy species. These species react with further oxygen to produce formaldehyde or carbon dioxide.

There have been a number of reports on the gas-phase oxidation of methanol over metal oxide catalysts ¹⁻³ where interest centres on the production of partial oxidation products, particularly formaldehyde. The gas-phase oxidation of methanol over transition metals has received less attention although the oxidation over palladium has been studied ⁴ and recent work ⁵ enabled a detailed mechanism to be derived for the oxidation over copper (110). The adsorption over platinum ⁶ and the decomposition over nickel, copper and platinum ⁷⁻⁹ have also been investigated.

There have been two reports on the oxidation of methanol over platinum. The first ¹⁰ dealt with the oxidation of methanol-rich mixtures over platinum gauze in a flow reactor. Large yields of formaldehyde were observed but no kinetic data were derived. The second report ¹¹ described the oxidation of oxygen-rich mixtures over platinum supported on alumina in the form of a microcalorimeter. No partial oxidation products were detected and reaction orders in oxygen of 0 and $-\frac{1}{2}$ were reported.

In order to obtain a more comprehensive picture of the oxidation over platinum wire we have studied the kinetics of methanol oxidation over a wide range of experimental conditions. In addition, we have used two contrasting experimental techniques. The use of a conventional flow reactor enabled kinetic parameters to be derived from measurements of equilibrium gas-phase concentrations of reactants and

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products. Kinetic parameters were also obtained from measurements of the rates of production of heat at the catalyst surface using a microcalorimetric method.

EXPERIMENTAL

CONVENTIONAL FLOW REACTOR

The conventional atmospheric pressure flow system included a Pyrex glass reactor (length 240 mm, diameter 14 mm) with an axial thermocouple well. The reactor was held vertically in a high-thermal-capacity electrical furnace and the temperature monitored with a Chromel/Alumel thermocouple to an accuracy of ± 2 K.

Nitrogen, oxygen and air were supplied from high-pressure cylinders and mixed using calibrated Rotameters. The gases were passed through activated charcoal (12-22 mesh, activated at 473 K) and magnesium perchlorate. Methanol vapour was introduced to the feed by bubbling one of the gases through two thermostated Dreschels containing methanol (B.D.H. AnalaR). A total flow rate of 200 cm³ min⁻¹ was used. The gas flow was sampled before and after passage through the reactor.

A mass spectrometer (VG Micromass 6) was used to identify the reaction products. Methanol was analysed by a gas chromatograph (Pye Unicam 104) with a flame ionisation detector (f.i.d.). A Porapak T column at 423 K was used for analysing methanol in the presence of large concentrations of formaldehyde. The accuracy of the technique was estimated to be $\pm 2 \%$. Formaldehyde was analysed by gas chromatography and calibrated using a colorimetric technique.¹² For the colorimetric analysis the reaction products were collected in distilled water. The absorbance of the solution, after adding the appropriate reagents, was measured at 520 nm. The accuracy of both techniques was estimated to be $\pm 5 \%$. Methyl formate was analysed by gas chromatography to an accuracy of $\pm 20 \%$. Carbon dioxide was analysed by infrared absorption at 4255 nm using a Perkin–Elmer 157 G spectrophotometer with a gas cell having a path length of 100 mm. The accuracy of this technique varied from ± 1 to $\pm 7 \%$ over the partial pressure range 0.6-0.05 k Pa.

Methanol conversion levels were kept to below 25% when calculating reaction rates. The rate was calculated using the equation ¹³

$$\frac{m}{F} = \int_{0}^{x} \frac{1}{r(x)} dx \tag{1}$$

where m is the catalyst mass, F is the flow rate, x is the fractional conversion and r is the reaction rate. Under all the conditions used the rate was found to increase exponentially with temperature, thus the influence of diffusion effects on the observed kinetics was excluded.

The platinum catalyst used was in the form of high purity (99.99 %) wire gauze (Johnson Matthey). The mass was 0.569 g, the wire diameter 0.164 mm and the geometric surface area $1100 \text{ mm}^2 \text{ g}^{-1}$. Small pieces of the gauze were supported on a glass-wool plug surrounding the thermocouple well. The catalyst was washed in chromic acid and distilled water and pretreated in air at 773 K for 1 h.

MICROCALORIMETER

The microcalorimetric technique has been described in detail previously.¹⁴ The catalyst was positioned in the centre of a 14 mm diameter glass tube with the gas flow directed vertically upwards. The gas supplies and methods of mixing were the same as those used in the flow reactor.

Methanol was analysed by gas chromatography (f.i.d.) using Porapak P at 423 K to an accuracy of ± 1 %. Methanol conversions were found not to exceed 6 % over the experimental conditions used. The lower formaldehyde concentrations formed in the microcalorimeter were measured by passing the gas stream through a water trap and analysing the resulting solution colorimetrically using Schiff's test.¹⁵ The absorbance of the solution was measured at 570

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nm. The accuracy of the analysis was \pm 5 %. Carbon dioxide concentrations were measured to an accuracy of \pm 1 % using a Wösthoff CO/CO₂ meter. This method is based on the change in electrical conductivity of 0.002 mol dm⁻³ NaOH solution in the presence of carbon dioxide.

The catalyst, an 11-turn coil of 5×10^{-2} mm platinum wire (Johnson Matthey, purity 99.999 %) with a pitch of 12.5×10^{-2} mm, formed the calorimeter. The coil was washed in chromic acid and distilled water and pretreated in air at 773 K for 10 min. Treatment for a longer period (1 h) or at a higher temperature (1173 K) had no effect on the catalytic activity.

For this form of microcalorimeter the change in electrical power consumption at constant temperature produced by the reaction on the catalyst surface represents the methanol oxidation rate and is given by

$$\Delta P = \sum_{i} r_i \,\Delta H_i \tag{2}$$

where r_i is the rate of surface reaction leading to species *i* and ΔH_i is the corresponding heat of reaction generated at the catalyst surface. Heats of reaction are constant over the experimental temperature range ¹⁴ and can be equated to the standard heats of oxidation. The term ΔH_{CO_2} , corresponding to the complete oxidation of methanol to carbon dioxide, dominates the right-hand side of eqn (2) and therefore measurement of ΔP can be used to obtain kinetic data for that reaction. Thus the rate of methanol oxidation to carbon dioxide is given by

$$r_{\rm CO_2} = \frac{\Delta P}{\Delta H_{\rm CO_2}} = km f(P_{\rm O_2}) f(P_{\rm CH_3OH})$$
(3)

where k is the rate constant, m is the mass of catalyst and $f(P_{O_2})$ and $f(P_{CH_3OH})$ are functions of the oxygen and methanol pressures, respectively.

RESULTS

After pretreatment, surface analysis of both catalysts by Auger electron spectroscopy established that no metallic impurities were present.

CONVENTIONAL FLOW REACTOR

In the absence of catalyst no reaction was observed over the entire range of experimental conditions used. Under the experimental conditions used the oxidation of methanol produces mainly carbon dioxide, formaldehyde and water, with trace amounts of methyl formate. The selectivity to methyl formate, defined as the ratio of the rate of formation of product to the total rate of consumption of methanol, did not exceed 1.4 %.

The effect of temperature, between 315 and 377 K, on the concentrations of methanol, carbon dioxide and formaldehyde is shown in fig. 1. The selectivity to formaldehyde as a function of temperature is also shown. At 328 K approximately 25 % of the methanol consumed is partially oxidised to formaldehyde whilst at 377 K only 11 % is partially oxidised.

The effect of methanol and oxygen pressure on the rates of methanol consumption and formaldehyde formation are shown in fig. 2 and 3. The kinetic data obtained are shown in table 1. Also included for comparison are results obtained using the microcalorimetric method (see below) under similar reaction conditions.

MICROCALORIMETER

Over the experimental conditions used no activity was observed when the platinum coil was replaced by a similar coil coated in borosilicate glass.



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FIG. 1.—Conventional flow reactor results: effect of temperature on (a) the concentrations of methanol (×), formaldehyde × 10 (●) and carbon dioxide (▲) and (b) selectivity to formaldehyde (■). Initial methanol pressure 0.83 kPa, initial oxygen pressure 21.3 kPa, total flow rate 200 cm³ min⁻¹.



FIG. 2.—Conventional flow reactor results : effect of methanol pressure on methanol consumption rate at 336 K (\odot) and formaldehyde formation rate at 343 K (\bigcirc). Initial oxygen pressure 21.3 kPa, total flow rate 200 cm³ min⁻¹.



FIG. 3.—Conventional flow reactor results : effect of oxygen pressure on methanol consumption rate at 336 K (●) and formaldehyde formation rate at 343 K (○). Initial methanol pressure 0.83 kPa, total flow rate 200 cm³ min⁻¹.

TABLE 1.—CONVENTIONAL FLOW REACTOR	OR RESULTS : KINETIC DATA OBTAINED AT HIGH OXYGEN TO
METHANOL RATIOS.	TOTAL FLOW RATE 200 cm ³ min ^{-1}

	pressure dependence				temperature dependence		
rate in terms of	tempera- ture/K	methanol order $(P_{0_2} = 21.3 \text{ kPa})$	methanol concentration range/kPa	oxygen order $(P_{CH_3OH} = 0.83 \text{ kPa})$	oxygen concentration range/kPa	apparent activation energy/kJ mol ⁻¹ $(P_{CH,OH} = 0.83 \text{ kPa}, P_{O_2} = 21.3 \text{ kPa})$	temperature range/K
methanol consumption	336	1.0±0.1	0.42-1.23	0.4 ± 0.1	4.8-34.0	33±5	326-345
formaldehyde formation	343	0.9 ± 0.1	0.25-1.38	0.4 ± 0.1	4.1-30.0	31 ± 5	326-345
carbon dioxide formation						33 ± 10	326-345
methanol oxidation $(\Delta P,$ microcalori- metric method)	363	0.9±0.1	0.20-1.03	0.5 ± 0.1	2.0-12.0	34±4	325-390

Simultaneous, independent, product analysis established that, under the conditions used, formaldehyde and carbon dioxide were the only carbon containing reaction products. However, since the methanol conversion rate in the microcalorimeter experiments is an order of magnitude lower than the methanol conversion rate in the flow reactor experiments the expected concentrations of methyl formate are below the limit of detection. It thus follows from eqn (2) that

$$\Delta P = r_{\rm CO_2} \Delta H_{\rm CO_2} + r_{\rm CH_2O} \Delta H_{\rm CH_2O}$$
(4*a*)

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thus

$$10^{-6} \Delta P = 676 r_{\rm CO_2} + 157 r_{\rm CH_2O} \tag{4b}$$

where ΔP is expressed in mW and the heats of oxidation of methanol to carbon dioxide and methanol to formaldehyde are taken ¹⁶ to be 676 and 157 kJ mol⁻¹, respectively. The rates of formation of carbon dioxide and formaldehyde, r_{CO_2} and r_{CH_2O} , are expressed in mol s⁻¹.

Throughout the experiments the rates of formaldehyde formation were calculated from measurement of formaldehyde concentrations. This enabled the rates of formation of carbon dioxide to be calculated using eqn (4b). It was found throughout that ΔP could be equated to $r_{CO_2}\Delta H_{CO_2}$ without the introduction of significant errors.

The selectivity to formaldehyde, S, was obtained from the expression

$$S = r_{\rm CH_2O} / (r_{\rm CH_2O} + r_{\rm CO_2}).$$
(5)

The effects of temperature on ΔP and selectivity to formaldehyde for $P_{O_2}/P_{CH_3OH} = 25$ are shown in fig. 4. Below 420 K ΔP is strongly dependent on temperature: above 420 K the rate becomes increasingly less temperature dependent. Conversely, the selectivity to formaldehyde falls rapidly with increasing temperature but, like the rate, becomes less temperature dependent at temperatures >420 K.

Fig. 5 shows the effect of temperature on ΔP and the selectivity to formaldehyde for $P_{O_2}/P_{CH^3OH} = 5$. ΔP increases slowly from 320 to 385 K followed by a very rapid increase from 385 to 405 K. ΔP then increases approximately exponentially with temperature in the range 405-428 K, becoming less temperature dependent beyond 428 K.

When rate measurements were taken immediately after thermal equilibrium was established a hysterisis loop ABCD was obtained. When the rates were measured as a function of increasing temperature from 320 K, at 405 K a low value of ΔP at B was measured. Increasing the temperature beyond 405 K and then reducing to 405 K



FIG. 4.—Microcalorimeter results: effect of temperature on ΔP (\bullet) and selectivity to formaldehyde (×). Methanol pressure 0.83 kPa, oxygen pressure 21.3 kPa, total flow rate 400 cm³ min⁻¹.



FIG. 5.—Microcalorimeter results: effect of temperature on ΔP (\odot) and selectivity to formaldehyde (×). Methanol pressure 1.03 kPa, oxygen pressure 5.3 kPa, total flow rate 400 cm³ min⁻¹, steady-state conditions (———); non-steady-state conditions (———).

produced a high value, D. As can be seen from fig. 5, the converse behaviour was observed for the selectivity to formaldehyde.

Reaction orders with respect to methanol and oxygen pressure were measured at 363 and 405 K. Fig. 6 shows the effect of methanol pressure on ΔP at oxygen pressures of 21.3 and 5.3 kPa. Fig. 7 shows the effect of oxygen pressure on ΔP at methanol pressures of 0.42 and 1.03 kPa. Thus at 405 K the reaction is first order in methanol and zero order in oxygen for all ratios of oxygen to methanol studied. However, at 363 K the reaction orders are dependent on the oxygen: methanol ratio. For ratios from 2 to 5 the orders are 0 (methanol) and $\frac{1}{2}$ (oxygen). For ratios from 8 to 15 the orders are 1 (methanol) and $\frac{1}{2}$ (oxygen), while for ratios greater than 15 the orders are 1



FIG. 6.— Microcalorimeter results : effect of methanol pressure on ΔP at 363 and 405 K for oxygen pressures of 21.3 (—••—) and 5.3 kPa (—×—). Total flow rate 400 cm³ min⁻¹.

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FIG. 7.—Microcalorimeter results : effect of oxygen pressure on ΔP at 363 and 405 K for methanol pressures of 1.03 (—•) and 0.42 kPa (—×—). Total flow rate 400 cm³ min⁻¹.

(methanol) and 0 (oxygen). The orders obtained at 405 K for $P_{O_2}/P_{CH_3OH} = 5$ pertain to the higher value, D, in fig. 5. An apparent activation energy of 35 ± 5 kJ mol⁻¹ was determined between 343 and 390 K at a methanol pressure of 0.83 kPa and an oxygen pressure of 21.3 kPa.

Further experiments using the microcalorimeter were undertaken at temperatures of 568 and 953 K to compare the rates of methanol consumption determined calorimetrically [using eqn (3)] with the rates obtained by the simultaneous measurement of gas-phase concentrations. The reaction conditions used were $P_{\rm CH_3OH} = 0.83$ kPa and $P_{\rm O_2} = 21.3$ kPa at a total flow rate of 400 cm³ min⁻¹. The microcalorimetric rates (compared with the gas-phase concentration rates) for the two temperatures were 77 ± 1 (76 \pm 9) and 95 ± 1 (94 ± 3) nmol s⁻¹, respectively.

DISCUSSION

Experiments established that, in the absence of any catalyst, no gas-phase reactions took place. However, these experiments were not capable of detecting reaction products formed by the gas-phase reactions of species generated by the catalyst surface. Such processes have been postulated ¹⁷ and if they occur they can seriously interfere with measurements relating to surface reactions.

The microcalorimetric technique coupled with simultaneous analysis of reactants and/or products is capable of throwing some light on this problem. There is excellent agreement between the microcalorimetric oxidation rate (derived from ΔP) and the oxidation rate obtained simultaneously from the monitoring of methanol concentration in the gas stream. This agreement may indicate the absence of such interfering reactions since reactions in the gas-phase would not be expected to be totally recorded by the microcalorimeter. Furthermore, using eqn (1) and (3) it is possible to calculate the specific rates per unit geometric area at any temperature for each method. At 373 K, a temperature covered in both techniques, and using $P_{CH_3OH} = 0.83$ kPa and $P_{O_2} = 21.3$ kPa, the values are 120 nmol s⁻¹ cm⁻² (conventional flow reactor) and 100 nmol s⁻¹ cm⁻² (microcalorimeter). The remarkable agreement between these specific rates provides further evidence that only reactions on the catalyst surface significantly contribute to the reaction products and gives confidence that the kinetic measurements reported here are uninfluenced by experimental artefacts.

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The reaction orders and activation energies obtained by each technique, under similar conditions, are given in table 1. Over this experimental range the rate of methanol oxidation, R, derived from either technique, may be expressed as

$$R = k P_{\rm CH_3OH} P_{\rm O_2}^{\pm}.$$
 (6)

Defining the rate constant as $k = Ae^{-E/RT}$ yields E = 33 kJ mol⁻¹.

However, the results obtained using the microcalorimeter over a wider experimental range show that, at higher temperatures and at lower P_{O_2}/P_{CH_3OH} values, different rate expressions may apply.

At $P_{O_2}/P_{CH_3OH} = 25$ (fig. 4) rapid attainment of steady-state rate values were observed over the whole temperature range. Reaction orders were invariant, first order in methanol and zero order in oxygen.

At $P_{O_2}/P_{CH_3OH} = 8-15$ rapid attainment of steady-state rate values were again observed throughout. However, reaction orders varied with temperature. At 363 K the reaction rate was first order in methanol and $\frac{1}{2}$ order in oxygen, whereas above 405 K the rate was first order in methanol and zero order in oxygen.

At $P_{02}/P_{CH_3OH} \le 5$ (fig. 5) non-steady-state reaction rates were observed between 380 and 405 K. Within the temperature range both reaction rates and orders varied with time. Thus between A and B zero reaction orders were observed in both methanol and oxygen whereas for rates between A and D the reaction was first order in methanol and zero order in oxygen.

At temperatures above 430 K the rate of reaction becomes almost independent of temperature. At the same time the reaction orders in methanol and oxygen become 1 and 0, respectively. This is indicative of the reaction becoming controlled by the rate of diffusion of methanol to the catalyst surface. In order to estimate the diffusive flux we have assumed that the catalyst behaves as a perfect sink for methanol and can be represented as a sphere of diameter equal to the length of the coil. Diffusive flux may then be calculated using a model for diffusion to a hot sphere, which incorporates the temperature dependence of both the thermal conductivity and diffusion coefficients of the gas mixture.¹⁸ Such a calculation at 430 K and $P_{CH_3OH} = 1.0$ kPa predicts a maximum value for ΔP of 48 mW, in reasonable agreement with the experimental value of 55 mW. Thus at temperatures approaching 430 K the diffusive flux contribution to the rate expression cannot be ignored and deviation of surface kinetics towards diffusion kinetics is inevitable. This can be seen in the plots of oxygen dependence given in fig. 7.

It is therefore apparent that the rate expression [eqn (6)] applies only over the experimental range specified in table 1.

The formation of partial products, reported here, is in general agreement with earlier work on bulk platinum catalysts.¹⁰ However, methanol oxidation over a supported platinum (Pt/Al₂O₃) microcalorimeter ¹¹ was found to proceed almost exclusively to carbon dioxide and water. Furthermore, in the latter study it was found that, although the methanol dependence was first order, the dependence on oxygen was $-\frac{1}{2}$ rising to zero order with increasing oxygen pressure. It was postulated ¹¹ that oxygen competes with methanol for one type of site, important at lower oxygen pressures. At higher oxygen pressures a second, non-competitive, site dominates the observed reaction leading to zero-order kinetics. These results may be reconciled if we postulate that in the deposition of platinum on alumina some high energy sites with a strong affinity for oxygen are produced along with a majority of sites with similar character to those found in bulk platinum. In this case reaction at low temperatures and/or low oxygen pressures will be dominated by the high energy sites where oxygen strongly inhibits methanol adsorption leading to the observed negative dependence on

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oxygen. The excess of oxygen is also responsible for the low selectivity for partial products. At higher oxygen pressures this area is saturated with oxygen and reaction is dominated by sites similar to those found here on bulk platinum catalysts. The tendency towards zero-order kinetics with increasing pressure on both catalysts, without modification of the apparent activation energy, suggests that the surface becomes effectively saturated with oxygen without excluding the adsorption of methanol. This is supported by ultra-high-vacuum studies of oxygen adsorption on polycrystalline platinum ¹⁹ where the saturation coverages were found to be less than unity.

A mechanism for the oxidation of methanol over platinum can be postulated which is consistent with the experimental results. Thus:

$$O_2(g) + 2\Box \stackrel{K_1}{\underset{k_{-1}}{\leftarrow}} 2O(a) \tag{I}$$

$$CH_3OH(g) + O(a) + \Box \xrightarrow{k_2} CH_3O(a) + OH(a)$$
 (II)

$$CH_3O(a) + O(a) \xrightarrow{k_3} CH_2O(a) + OH(a)$$
 (III)

$$\operatorname{CH}_2\operatorname{O}(a) \xrightarrow{k_4} \operatorname{CH}_2\operatorname{O}(g) + \Box$$
 (IV)

$$CH_2O(a) + O(a) \ etc. \xrightarrow{k_5} CO_2(g) + H_2O(g) + \square$$
 (V)

$$20H(a) \xrightarrow{k_6} H_2O(g) + O(a) + \Box$$
 (VI)

where \Box denotes an adsorption site.

Dissociative adsorption of oxygen on platinum has been widely reported.^{19, 20} Step (II) has been postulated in the oxidation of methanol over palladium ⁴ and copper.⁵

It is proposed that step (III), the abstraction of hydrogen from adsorbed methoxy species to form adsorbed formaldehyde, is rate limiting. Some support for this comes from the work on the decomposition of methanol over platinum black,⁹ nickel ⁷ and copper ⁸ catalysts where the initial abstraction of the hydroxyl hydrogen is postulated as being rapid compared with the subsequent abstraction of methyl hydrogen to form formaldehyde.

If adsorbed atomic oxygen is in equilibrium with the gas phase $(k_1, k_{-1} \gg k_2 \text{ etc.})$, then

$$k_1 P_{O_2} \theta_{\Box}^2 = k_{-1} \theta_{O_2}^2. \tag{7}$$

The fractional coverage of $CH_2O_{(a)}$ is small if either the rate of desorption (IV) or the rate of reaction (V) is greater than the rate of formation (III). Then:

$$1 = \theta_{\rm CH_3O} + \theta_{\rm O} + \theta_{\Box} \tag{8}$$

therefore

$$k_1 P_{O_2} \theta_{\Box}^2 = k_{-1} (1 - \theta_{CH_3O} - \theta_{\Box})^2$$
(9)

therefore

$$\theta_{\Box} = \frac{k_{-1}^{\frac{1}{2}} \left(1 - \theta_{\mathrm{CH}_{3}\mathrm{O}}\right)}{(k_{1} P_{\mathrm{O}})^{\frac{1}{2}} + k_{-1}^{\frac{1}{2}}} \tag{10}$$

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$$=\frac{1-\theta_{\rm CH_{3}O}}{1+(bP_{O_2})^{\frac{1}{2}}}$$
(11)

and

$$\theta_{\rm O} = (1 - \theta_{\rm CH_3O}) \frac{(bP_{\rm O_2})^{\frac{1}{2}}}{1 + (bP_{\rm O_2})^{\frac{1}{2}}}$$
(12)

where

 $b = k_1/k_{-1}.$

The steady-state coverage of methoxy species is maintained by reactions (I) and (III) therefore

$$\frac{\mathrm{d}\theta_{\mathrm{CH}_{3}\mathrm{O}}}{\mathrm{d}t} = k_2 P_{\mathrm{CH}_{3}\mathrm{OH}} \theta_{\Box} \theta_{\mathrm{O}} - k_3 \theta_{\mathrm{CH}_{3}\mathrm{O}} \theta_{\mathrm{O}} = 0$$
(13)

and substituting eqn (11) into (13) gives

$$\theta_{\rm CH_{3}O} = \left[\frac{k_2 P_{\rm CH_{3}OH}}{1 + (bP_{O_2})^{\frac{1}{2}}}\right] \left[k_3 + \frac{k_2 P_{\rm CH_{3}OH}}{1 + (bP_{O_2})^{\frac{1}{2}}}\right]^{-1}.$$
 (14)

The rate of reaction (III) is given by

$$R_3 = k_3 \theta_{\rm CH_3O} \,\theta_{\rm O} \tag{15}$$

$$=\frac{k_{3}\theta_{\rm CH_{3}O}\left(1-\theta_{\rm CH_{3}O}\right)\left(bP_{O_{2}}\right)^{\frac{1}{2}}}{1+\left(bP_{O_{2}}\right)^{\frac{1}{2}}}$$
(16)

$$= \left\{ \frac{k_{3}(bP_{O_{2}})^{\frac{1}{2}}}{1 + (bP_{O_{2}})^{\frac{1}{2}}} \right\} \left\{ \frac{k_{2}P_{CH_{3}OH}}{k_{3}[1 + (bP_{O_{2}})^{\frac{1}{2}}] + k_{2}P_{CH_{3}OH}} \right\} \times \left\{ 1 - \frac{k_{2}P_{CH_{3}OH}}{k_{3}[1 + (bP_{O_{2}})^{\frac{1}{2}}] + k_{2}P_{CH_{3}OH}} \right\}.$$
(17)

If $(bP_{O_2})^{\frac{1}{2}} \ll 1$ and $k_2P_{CH_3OH} \ll k_3$, eqn (17) becomes

=

$$R_3 = k_2 P_{\rm CH_3OH} \, (bP_{\rm O_2})^{\frac{1}{2}}.$$
 (18)

If $k_2 P_{CH_3OH} \gg k_3$, then R_3 tends to zero.

Thus this mechanism predicts the observed kinetics for high oxygen to methanol pressure ratios. The rapid drop in methanol oxidation rate with temperature below 405 K for $P_{O_2}/P_{CH_3OH} = 5$ is predicted if we assume that the adsorption of methanol, step (II), is less activated than the subsequent oxidation, step (III), resulting in the methanol saturated surface under these conditions. Since the temperature dependence of the overall oxidation reaction is the temperature dependence of the rate constant for adsorption, the low activation energy observed is consistent with this assumption. Further evidence in support of the weakly activated adsorption of methanol comes from work on the decomposition of methanol over platinum black ⁹ and other transition metal catalysts ^{7, 8} where the rate of adsorption was found to be relatively insensitive to temperature when compared with the rate of hydrogen abstraction from the methoxy species.

The non-steady-state behaviour (fig. 5) indicates that the methanol covered surface is the less stable and that its transition to an oxygen covered surface is a slow process under these experimental conditions. This suggests that the processes which generate vacant sites for the adsorption of oxygen [steps (IV)-(VI)] are relatively inefficient.

The kinetics of methanol consumption and those of carbon dioxide formation were found to be identical, indicating the probability of a common rate limiting step, postulated to be step (II). Thus any mechanism for the successive oxidation of intermediates involving processes which are rapid by comparison with step (II) is consistent with our results. However, successive hydrogen abstraction from CH₃O(a) seems unlikely since the formation of CO(a) may be expected to inhibit the reaction;⁹ no inhibition occurred in the present work. Both surface formates and CHO species have been suggested as intermediates in the decomposition of formic acid and formaldehyde, respectively, on platinum group metals,^{21, 22} though there is evidence to suggest that a species H₂COO exists on copper (110)⁵ and silver (110).⁵ Secondaryion mass-spectrometry studies of the adsorption of methanol on rhodium ²³ indicate the presence of CH₃O, CH₂O, CHO and CO species. We therefore suggest that the most likely mechanism for CO₂ formation is oxygen insertion into the CHO species to form COOH which then decomposes to carbon dioxide.

The selectivity to formaldehyde as a function of increasing temperature at the high P_{O_2}/P_{CH_3OH} ratio (fig. 4) shows a smooth decrease from 50 to 15%. This indicates that the rate of oxidation of adsorbed formaldehyde (step V) is more temperature dependent than its rate of desorption (step IV). When $P_O/P_{CH_3OH} = 5$ the selectivity to formaldehyde increases rapidly whilst ΔP decreases rapidly as the temperature is reduced from 405 to 384 K. The rapid fall in the rate has been postulated as the result of an excess surface coverage of methanol. It follows that there would be insufficient oxygen for complete oxidation resulting in the observed rise in selectivity to formaldehyde.

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