

# Inhibition of Methanol Oxidation by Water Vapor—Effect on Measured Kinetics and Relevance to the Mechanism

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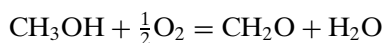
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The kinetics of methanol oxidation to formaldehyde was studied over an iron molybdenum oxide catalyst in a continuous flow reactor with external recycling at temperatures of 200–300°C. The kinetics of the reaction were well described by a power law rate expression of the form  $r = k P_{\text{CH}_3\text{OH}}^x P_{\text{O}_2}^y P_{\text{H}_2\text{O}}^z$ , where  $x = 0.94 \pm 0.06$ ,  $y = 0.10 \pm 0.05$ , and  $z = -0.45 \pm 0.07$ . The measured activation energy was  $98 \pm 6$  kJ/mol. When product inhibition by water vapor is not taken into account in such a power law kinetic rate expression, the apparent reaction orders in methanol and oxygen,  $x'$  and  $y'$ , and the activation energy  $E'$  are all lower than their true values:  $x' = (1-\delta)x$ ,  $y' = (1-\delta)y$ , and  $E' = (1-\delta)E$ , where  $\delta = -z/(1-z)$ . Methanol chemisorbs dissociatively to form methoxy and hydroxyl groups, and the rate-determining step is the decomposition of the methoxy intermediate. Product inhibition occurs through kinetic coupling, whereby water vapor chemisorbs dissociatively to form hydroxyl groups, which serve to reduce the steady state concentration of methoxy groups on the catalyst surface by reacting with them to reform methanol. © 1996 Academic Press, Inc.

## INTRODUCTION

The oxidation of methanol to formaldehyde



is carried out industrially over a catalyst consisting of a mixture of ferric molybdate,  $\text{Fe}_2(\text{MoO}_4)_3$ , and molybdenum trioxide,  $\text{MoO}_3$ . The process is carried out in excess air at temperatures around 350°C in multitubular fixed bed reactors. Conversion of methanol is nearly complete and the selectivity to formaldehyde is about 94% (1, 2).

The kinetics of methanol oxidation over iron molybdenum oxide catalysts has been the focus of several previous studies (3–12). Additional studies, most using model  $\text{MoO}_3$  catalysts, have addressed the reaction mechanism (13–24). Many other metal molybdates also catalyze the reaction (25–31), and the active sites are widely believed to be associated with surface Mo atoms for all of these catalysts. Methanol adsorption at these sites results in surface

methoxy groups,  $-\text{OCH}_3$ , as first proposed by Pernicone *et al.* (23) and confirmed by Groff (13). The rate-determining step involves the breakage of a C–H bond, as indicated by a strong kinetic isotope effect for  $\text{CD}_3\text{OD}$  relative to  $\text{CH}_3\text{OH}$ , but only a weak kinetic isotope effect for  $\text{CH}_3\text{OD}$  relative to  $\text{CH}_3\text{OH}$  (32, 33). Water is not strongly adsorbed (34, 35) and hydroxyl groups readily desorb as water (13). In spite of this, as first noted by Pernicone *et al.* (36), the rate is inhibited by water vapor even at low water vapor partial pressures. This product inhibition has been confirmed since then in several studies (3, 23, 27, 28).

The primary side product of the reaction is carbon monoxide at commercial conditions (1, 2, 27). Other side products are methyl formate [ $\text{HCOOCH}_3$ ], dimethoxymethane [ $(\text{CH}_3\text{O})_2\text{CH}_2$ ], and dimethyl ether [ $(\text{CH}_3)_2\text{O}$ ], but these are formed in appreciable quantities only at low temperatures (25, 27, 37). Selectivities to dimethoxymethane and dimethyl ether decrease with increasing methanol conversion and are lower when water is added to the feed stream. The same products and reaction rates are obtained in pulse experiments in the presence and absence of gas phase oxygen (23), indicating that lattice oxygen can participate in the reaction. However, the selectivity to formaldehyde decreases as the catalyst surface is reduced (16, 24).

## EXPERIMENTAL

Measurements of the rate of methanol oxidation to formaldehyde were obtained with an iron molybdate catalyst with a molar ratio of  $\text{MoO}_3$  and  $\text{Fe}_2(\text{MoO}_4)_3$  phases of 1.7 and a BET surface area of 5.9  $\text{m}^2/\text{g}$ . Experiments were performed in a continuous flow reactor with external recycling and on-line gas chromatographic analysis of both the reactants and the products, as described previously (27). Feed flow rates were in the range 30–400 sccm and the recycle flow rate was 3000 sccm, yielding recycle ratios of 7.5–100. Thus the reactor was well mixed and differential conversions per pass were obtained. Tests and calculations indicated an absence of heat and mass transfer effects. The experiments were done under widely varying conditions of feed-gas composition, temperature, and catalyst weight. A

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total of 72 runs was obtained with the following range of conditions: reactor temperature 200–300°C, catalyst weight 1.0–6.0 g, and partial pressures in the reactor of 0.07–42 kPa for methanol, 0.4–119 kPa for oxygen, 0.6–33 kPa for water, and 0.1–11 kPa for formaldehyde. Total pressure was 122 kPa with nitrogen being used as the inert gas. In most experiments, water was fed to the reactor in addition to the methanol, oxygen, and nitrogen.

## RESULTS

The conversion of methanol varied from 0.2 to 95%. Formaldehyde was always the predominant product with maximum selectivities (defined as moles of products per mole of methanol reacted) of 0.06 for carbon monoxide, 0.01 for carbon dioxide, 0.04 for dimethyl ether, and 0.05 for methyl formate. The rate of reaction to formaldehyde was well described by a power law kinetic rate expression of the form  $r = k P_{\text{CH}_3\text{OH}}^x P_{\text{O}_2}^y P_{\text{H}_2\text{O}}^z$ , where  $x = 0.94 \pm 0.06$ ,  $y = 0.10 \pm 0.05$ , and  $z = -0.45 \pm 0.07$ . The rate was independent of formaldehyde partial pressure. The measured activation energy was  $98 \pm 6$  kJ/mol. At 250°C, with a methanol partial pressure of 10 kPa, a water vapor partial pressure of 10 kPa, and an oxygen partial pressure of 20 kPa, the rate of reaction was  $3.8 \times 10^{-7}$  mole/m<sup>2</sup>/s. Assuming a site density for methanol adsorption of  $1.6 \times 10^{18}$  m<sup>2</sup>, as measured for Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> (14), this corresponds to a turnover rate of 0.14 s.

## DISCUSSION

### *Effect of Product Inhibition on the Determination of Kinetic Parameters*

At first it would appear that the use of a differential reactor with external recycle would always yield the correct kinetic results: reaction orders, activation energy, and kinetic isotope effect. However, as shown below, this is not true for a reaction inhibited by a product when that product has not been included in the rate expression. We use the methanol oxidation reaction as an example, but the method is general and applies equally to other reactions described by power law kinetic rate expressions with product inhibition.

In the discussion below, we use the term “true” to refer to the kinetic parameters calculated for the case where the inhibition component, in this case water, has been included in the rate expression, and the term “apparent” to refer to kinetic parameters calculated for the case where this term has been omitted from the rate expression.

For the methanol oxidation reaction, the true rate expression is of the form

$$r = k P_{\text{CH}_3\text{OH}}^x P_{\text{O}_2}^y P_{\text{H}_2\text{O}}^z, \quad [1]$$

where  $r$  [mol/m<sup>2</sup>/s] is the rate per unit surface area,  $P_i$  [kPa]

is the partial pressure of ( $i$ ),  $k$  [mol/kPa <sup>$x+y+z$</sup> /m<sup>2</sup>/s] is the true rate constant, and  $x$ ,  $y$ , and  $z$  are the true reaction orders in CH<sub>3</sub>OH, O<sub>2</sub>, and H<sub>2</sub>O, respectively. When inhibition by water vapor is not considered, the apparent rate expression is of the form

$$r = k' P_{\text{CH}_3\text{OH}}^{x'} P_{\text{O}_2}^{y'}, \quad [2]$$

where  $k'$  [mol/kPa <sup>$x'+y'$</sup> /m<sup>2</sup>/s] is the apparent rate constant, and  $x'$  and  $y'$  are the apparent reaction orders in CH<sub>3</sub>OH and O<sub>2</sub>, respectively.

Experimentally, in the absence of side reactions, the rate can be determined by measuring the mole fraction of formaldehyde  $x_{\text{CH}_2\text{O}}$  or water  $x_{\text{H}_2\text{O}}$  in the product stream:

$$r = F x_{\text{CH}_2\text{O}}/A = F x_{\text{H}_2\text{O}}/A, \quad [3]$$

where  $F$  [mol/s] is the molar flow rate into or out of the recirculation loop and  $A$  [m<sup>2</sup>] is the total surface area of the catalyst charge, which is related to the specific surface area  $a$  [m<sup>2</sup>/g] and the catalyst charge  $W$  [g] by  $A = aW$ .

Equation [3] can also be expressed as

$$r = F P_{\text{H}_2\text{O}}/AP, \quad [4]$$

where  $P$  [kPa] is the total pressure. Equating Eqs. [1] and [4] yields the partial pressure of water vapor in the recirculating reactor loop when there is no water in the feed stream

$$P_{\text{H}_2\text{O}} = (k P_{\text{CH}_3\text{OH}}^x P_{\text{O}_2}^y AP/F)^{1/(1-z)}. \quad [5]$$

Substituting Eq. [5] into Eq. [1] yields the apparent rate expression in terms of the methanol and oxygen partial pressures within the reactor

$$r = k^{1-\delta} P_{\text{CH}_3\text{OH}}^{x(1-\delta)} P_{\text{O}_2}^{y(1-\delta)} (F/AP)^\delta, \quad [6]$$

where  $\delta = -z/(1-z)$ .

Comparing Eqs. [2] and [6] yields the relationship between the true and apparent kinetic values when water inhibition has been ignored:

$$x' = x(1-\delta), \quad [7]$$

$$y' = y(1-\delta), \quad [8]$$

$$k' = k^{1-\delta} (F/AP)^\delta. \quad [9]$$

From Eq. [9], the true activation energy  $E$  and the apparent activation energy  $E'$  are related by

$$E' = (1-\delta)E, \quad [10]$$

while the true and apparent kinetic isotope effects, defined as the relative rate constants for deuterated species compared to their protonated counterparts, are related by

$$(k_D/k_H)' = (k_D/k_H)^{1-\delta}. \quad [11]$$

If in fact there is no water inhibition (that is,  $z = 0$ ), the apparent values equal the true ones.

When the rate is described by a power law kinetic rate expression with product inhibition, the result of neglecting that product inhibition in fitting kinetic parameters is that the experimentally determined apparent reaction orders in the reactant gases and activation energies are all smaller than the true values, while apparent kinetic isotope effects are less pronounced. The above discussion of the effect of product inhibition on measured kinetic parameters for power law kinetic rate expressions is general and can be applied to other reactions. The analysis has focused on a differential reactor with external recycling and a small gas feed and withdrawal. Similar effects occur in integral single-pass flow-through reactors (38).

The assumption that product inhibition is negligible in a kinetic study can be readily tested by adding an amount of product greater than that produced by the reaction to the feed stream and comparing the rate to that measured in the absence of product addition. The rates will be identical when product inhibition does not occur. Often, product addition to the feed stream is experimentally inconvenient or results in analytical complications in rate determination. This is necessarily the case when there is only one product produced in the reaction, such as in the formation of ammonia from nitrogen and hydrogen. Equation [9] provides a second method to check for the presence of product inhibition. When product inhibition is present ( $\delta > 0$ ), the measured rate increases with flow rate into the loop  $F$  when all other factors are held constant. When there is no product inhibition ( $\delta = 0$ ), and in the absence of external mass transfer limitations, the measured rate is independent of the flow rate  $F$ .

#### Application to Kinetic Studies

In the present study, a power law rate expression was found to fit the kinetic data well, and the following kinetic parameters were obtained:  $x = 0.94$ ,  $y = 0.10$ ,  $z = -0.45$ , and  $E = 98$  kJ/mol. In the absence of a water addition to the feed stream and without including the water vapor inhibition term in the rate equation, the following apparent kinetic parameters are predicted from Eqs. [7], [8], and [10]:  $x' = 0.65$ ,  $y' = 0.07$ , and  $E' = 68$  kJ/mol.

In a previous study of methanol oxidation in a flow-through reactor with external recycling (27), reaction orders for methanol and oxygen and activation energies were calculated for several iron molybdate catalysts without consideration of the inhibition by water vapor and without water vapor in the feed stream, yielding  $x' = 0.39$ – $0.61$ ,  $y' = 0.03$ – $0.14$ , and  $E' = 69$ – $79$  kJ/mol. The above analysis indicates that these kinetic parameters are apparent kinetic parameters rather than true ones. The analysis also suggests that kinetic parameters calculated in previous studies (5–8, 37) without incorporation of water vapor in the

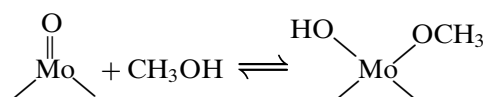
rate equation and without adding water vapor to the feed stream are also not true kinetic values. The activation energies for iron–molybdenum oxide catalysts ranged from 54–79 kJ/mol in those studies, values which are all less than the true activation energy of  $98 \pm 6$  kJ/mol measured here. This is in accord with the expectations from Eq. [10] for an apparent activation energy.

The kinetic isotope effect for methanol oxidation has been measured using methanol/oxygen feed streams and without consideration of inhibition by water vapor (32). At 260°C, kinetic isotope effects over a commercial iron molybdate catalyst were reported as follows:  $k'_{\text{CH}_3\text{OD}}/k'_{\text{CH}_3\text{OH}} = 0.94$  and  $k'_{\text{CD}_3\text{OD}}/k'_{\text{CH}_3\text{OH}} = 0.37$ . Since there was no consideration of the effect of inhibition by water vapor in these studies, these results represent apparent rather than true values. Equation [11] allows us to estimate the expected true value of the kinetic isotope effect when the reaction is carried out under controlled conditions of  $\text{CD}_3\text{OD}$ ,  $\text{D}_2\text{O}$ , and  $\text{O}_2$  relative to  $\text{CH}_3\text{OH}$ ,  $\text{H}_2\text{O}$ , and  $\text{O}_2$ , and for  $z = -0.45$ ,  $k_{\text{CD}_3\text{OD}}/k_{\text{CH}_3\text{OH}} = 0.24$ . Calculating the true kinetic isotope effect  $k_{\text{CH}_3\text{OD}}/k_{\text{CH}_3\text{OH}}$  is more difficult, since oxidation of  $\text{CH}_3\text{OD}$  leads to a mixture of  $\text{H}_2\text{O}$ ,  $\text{HDO}$ , and  $\text{D}_2\text{O}$  with  $\text{H/D} = 1.0$ . Indeed, we might expect slightly different rates for  $\text{CH}_3\text{OD}/\text{H}_2\text{O}/\text{O}_2$  and  $\text{CH}_3\text{OD}/\text{D}_2\text{O}/\text{O}_2$  feed streams. In any case, we expect  $k'_{\text{CH}_3\text{OD}}/k'_{\text{CH}_3\text{OH}}$  to fall between the measured value of 0.94 and the calculated value from Eq. [11] of 0.91. Both of these values differ only slightly from unity, supporting the original conclusion that breakage of an O–H bond is not the rate-determining step.

#### Reaction Mechanism

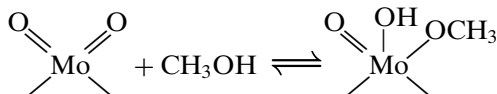
The mechanism of methanol oxidation is widely believed to occur through the dissociative reactive adsorption of methanol with a surface oxygen atom to form methoxy and hydroxyl groups, followed by the reaction of the methoxy intermediate with a second surface oxygen atom to form formaldehyde and a second hydroxyl. Reaction of the two hydroxyl groups leads to the formation of water. Dissociative adsorption of dioxygen completes the redox cycle. This reaction mechanism is in general agreement with the mechanism of partial oxidation of hydrocarbons catalyzed by metal oxides first proposed by Mars and van Krevelen (39).

A variety of specific steps has been proposed regarding the details of the bonding of methanol and hydroxyl groups on the surface. Pernicone *et al.* (23) propose that the adsorption step occurs at a single oxo site:

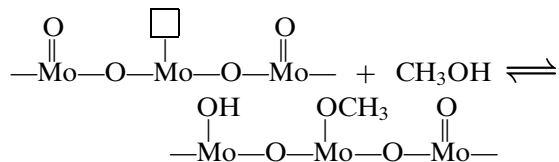


*Ab initio* quantum chemical calculations by Allison and Goddard (40, 41) indicate that adsorption onto single oxo sites is energetically unfavored, and that the adsorption

occurs on dioxo sites:

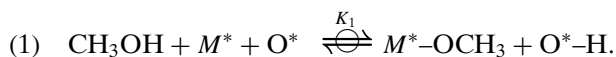


The authors propose that the (010) surface of  $\text{MoO}_3$  is comprised of such dioxo sites, and they suggest that this is the active surface for methanol oxidation. However, Ohuchi *et al.* (42) have carried out methanol adsorption experiments on  $\text{MoO}_3$  single crystals and shown that  $\text{CH}_3\text{OH}$  does not adsorb on the (010) surface. Chowdhry *et al.* (14) propose that the reaction occurs at coordinately unsaturated metal atom sites, which do not form on (010) surface but do form on (100) and (001) surfaces.  $\text{MoO}_3$  is a layered material, and the bulk structure and six-fold coordination of molybdenum are maintained at the (010) surface, while the layer edge surfaces expose molybdenum sites with lower coordination even though molybdenum remains in the +6 oxidation state (19). If the reaction takes place at coordinately unsaturated sites, the step can be written schematically as (27, 28)

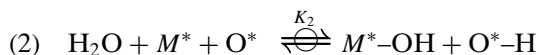


The alternating dioxo sites and surface oxygen vacancies in such a representation are consistent with cleavage of bulk  $\text{MoO}_3$  to form (100) and (001) surfaces. However, such surfaces may be energetically unfavored and undergo significant surface reconstruction. In this event, the details of the bonding of adsorbed species would vary accordingly. In the above representation, all of the Mo sites may be fully oxidized to  $\text{Mo}^{+6}$  under reaction conditions, or alternately, in the case of a partially reduced surface the reaction may occur on  $\text{Mo}^{+5}$  sites, as suggested by Niwa *et al.* (43).

Irrespective of the specific identity of the adsorption site, the methanol adsorption process involves two entities, a metal atom site to which the methoxy group is bound and an oxygen atom site to which the hydrogen atom is bound as a hydroxyl group. The equilibrated methanol adsorption step can be represented as



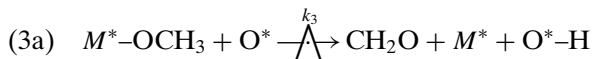
Water adsorption is expected to proceed in a manner similar to methanol adsorption:



The rate-determining step in the oxidation of methanol to formaldehyde is the conversion of the methoxy intermediate to formaldehyde through abstraction of a hydrogen atom (14, 15). *Ab initio* quantum chemical calculations by

Allison and Goddard (40, 41) suggest that the hydrogen atom is abstracted by a neighboring oxo site, and most other proposed mechanisms assume similar processes involving nearby oxygen atoms (4, 15, 18, 37, 43). Studies on supported  $\text{MoO}_3$  catalysts indicate the need for more than one site for the reaction to proceed (44, 45). *Ab initio* quantum mechanical calculations by Weber (46) indicate that hydride abstraction is catalyzed by the metal atom site itself. Once abstracted, the hydrogen atom quickly reacts with a nearby oxygen atom to form a hydroxyl group.

In proceeding, we will assume that the concentrations of adsorbed methoxy and hydroxyl species are small and the surface is rapidly reoxidized. Then the concentrations of empty metal atom sites ( $M^*$ ) and oxygen atom sites ( $O^*$ ) are independent of process conditions. The hydrogen atom abstraction step is rate-determining and irreversible, and it can be represented as



or



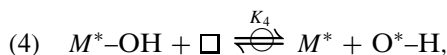
In either case, the turnover rate per metal atom site  $v$  can be expressed as

$$v = k_3 \theta_{\text{OCH}_3}, \quad [12]$$

and it is first order in the fractional surface coverage of metal atom sites with adsorbed methoxy  $\theta_{\text{OCH}_3}$ .

In order to complete the derivation of the rate equation, we must derive an expression for  $\theta_{\text{OCH}_3}$  in terms of the partial pressures of the reactants. Before proceeding, the question arises as to whether  $M^*-\text{OH}$  and  $O^*-\text{H}$  represent the same entity. In the case of bonding at an oxo or dioxo site, the bonding of the two hydroxyl groups would appear to be equivalent, while for bonding at a coordinately unsaturated site they might not be. We will proceed below along two lines, first considering the case where the metal atom and oxygen atom sites are distinct entities, and second the case where the oxygen and metal atom sites are equivalent in the sense that upon adsorption of water, adsorbed  $M^*-\text{OH}$  and  $O^*-\text{H}$  represent the same entity. For both cases, we will analyze the case where the surface coverages by adsorbed species are small.

If the sites are not equivalent, we expect an equilibrated reaction of the form



where  $\square$  represents an oxygen vacancy at an oxygen atom site. A similar reaction will relate the coverages of both types of sites with methoxy groups. We will use  $\theta_i$  and  $\phi_i$  to represent the fractional surface coverages of (*i*) on the metal and oxygen atom sites, respectively. Thus the fractional surface coverage of hydroxyl groups on the metal

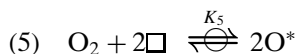
atom sites is represented by  $\theta_{\text{OH}}$ , while that on the oxygen atom sites is represented by  $\phi_{\text{H}}$ . The surface coverages of hydroxyl groups on the oxygen and metal atom sites are related through the equilibrium relationship

$$\phi_{\text{H}} = K_4 \theta_{\text{OH}} \phi_{\text{V}}, \quad [13]$$

where  $\phi_{\text{V}}$  represents an oxygen vacancy at an oxygen atom site. From Step (2), the concentrations of surface hydroxyl groups on the metal atom and oxygen atom sites are related to the water vapor partial pressure by

$$\phi_{\text{H}} \theta_{\text{OH}} = K_2 P_{\text{H}_2\text{O}}. \quad [14]$$

The surface is reoxidized through the reaction



and the fraction of oxygen atom sites which are vacant is related to the oxygen partial pressure by

$$\phi_{\text{V}} = \frac{1}{K_5^{1/2} P_{\text{O}_2}^{1/2}}. \quad [15]$$

Combining Eqs. [13]–[15] yields

$$\phi_{\text{H}} = \frac{(K_2 K_4)^{1/2} P_{\text{H}_2\text{O}}^{1/2}}{K_5^{1/4} P_{\text{O}_2}^{1/4}}, \quad [16]$$

$$\theta_{\text{OH}} = (K_2/K_4)^{1/2} K_5^{1/4} P_{\text{H}_2\text{O}}^{1/2} P_{\text{O}_2}^{1/4}. \quad [17]$$

From Step (1), the surface coverage of methoxy groups on the metal atom sites  $\theta_{\text{OCH}_3}$  is related to the methanol partial pressure and the surface concentration of hydroxyl groups on the oxygen atom sites  $\phi_{\text{H}}$  by

$$\theta_{\text{OCH}_3} = K_1 P_{\text{CH}_3\text{OH}}/\phi_{\text{H}}. \quad [18]$$

Substituting Eq. [16] for  $\phi_{\text{H}}$  yields

$$\theta_{\text{OCH}_3} = \frac{K_1 K_5^{1/4} P_{\text{CH}_3\text{OH}} P_{\text{O}_2}^{1/4}}{(K_2 K_4)^{1/2} P_{\text{H}_2\text{O}}^{1/2}}. \quad [19]$$

From Eq. [12], the turnover rate in terms of the partial pressures of methanol, oxygen, and water vapor is

$$v = k_3 \frac{K_1 K_5^{1/4} P_{\text{CH}_3\text{OH}} P_{\text{O}_2}^{1/4}}{(K_2 K_4)^{1/2} P_{\text{H}_2\text{O}}^{1/2}}. \quad [20]$$

The reaction is inhibited by water vapor and the ratio of the reaction orders in methanol and water vapor is  $-2$ .

Next we consider the case where, upon adsorption,  $\text{O}^*-\text{H}$  and  $\text{O}^*-\text{CH}_3$  represent the same entities as  $M^*-\text{OH}$  and  $M^*-\text{OCH}_3$ . We assume that low coverage of adsorbed hydroxyl and methoxy species translates to a surface in which the ratio of  $\text{O}^*$  and  $M^*$  is fixed. This corresponds, for example, to the case of a fully oxidized surface in which all

of the Mo atoms have been oxidized to  $\text{Mo}^{+6}$  and in which partially coordinated sites are still present. We use the representation  $\theta_i$  to describe the fractional surface coverage of (*i*), and  $\theta_{\text{OH}}$  represents all hydroxyl groups. Taking into account the equivalency of  $M^*-\text{OH}$  and  $\text{O}^*-\text{H}$ , equilibration of Step (2) yields

$$\theta_{\text{OH}} = K_2^{1/2} P_{\text{H}_2\text{O}}^{1/2}, \quad [21]$$

while equilibration of Step (1) combined with Eq. [21] yields

$$\theta_{\text{OCH}_3} = \frac{K_1 P_{\text{CH}_3\text{OH}}}{K_2^{1/2} P_{\text{H}_2\text{O}}^{1/2}}. \quad [22]$$

Substituting Eq. [22] into Eq. [12] yields the turnover rate

$$v = k_3 \frac{K_1 P_{\text{CH}_3\text{OH}}}{K_2^{1/2} P_{\text{H}_2\text{O}}^{1/2}}. \quad [23]$$

As can be seen from Eqs. [20] and [23], the ratio of the reaction orders in methanol and water vapor is  $-2$  irrespective of our assumptions concerning whether  $M^*$  and  $\text{O}^*$  remain distinguishable types of sites upon adsorption of methanol or water vapor. This value results from the assumption of equilibrated adsorption of methanol and water vapor, combined with the fact that adsorption of water vapor yields two hydroxyl groups while adsorption of methanol results in only one. The reaction order in oxygen differs slightly for the two models.

In deriving the above rate expressions, it has been implicitly assumed that reoxidation of the surface is rapid and that the steps leading to desorption of adsorbed water are identical to those leading to desorption as water of the two hydroxyl groups left behind on the surface following the conversion of methanol to formaldehyde. The equivalency of these two processes is not certain, since water adsorption/desorption does not reduce the surface, whereas methanol oxidation to formaldehyde with evolution of water does. Thus, the overall reaction may be more complex than the steps leading to Eqs. [20] and [23] would suggest. The rate equations have also been derived with the assumption that the surface coverages of adsorbed hydroxyl and methoxy species are low. This assumption appears to be valid above  $200^\circ\text{C}$ . Below  $200^\circ\text{C}$ , additional effects from competitive adsorption may influence the kinetics, further complicating the rate expression. Finally, the derivations of Eqs. [20] and [23] are based on uniform surface kinetics. The adsorption of methanol on  $\text{MoO}_3$  is well described by the Elovich equation (14), indicating that the heat of adsorption decreases about linearly with surface coverage. Consideration of surface nonuniformity leads to power law rate expressions with fractional reaction orders in methanol and water vapor of magnitude less than 1 and  $1/2$ , yet with their ratio remaining  $-2$  (47).

### Kinetic Coupling

The main point resulting from the derivation of Eqs. [20] and [23] is that inhibition of the methanol oxidation reaction by water vapor is a natural outcome of previously proposed reaction mechanisms. This inhibition occurs from the effect of water vapor on the steady state concentration of adsorbed methoxy groups. Product inhibition in this manner has been termed “kinetic coupling” by Boudart (48). Direct dehydrogenation of methanol to formaldehyde and dihydrogen is limited by thermodynamics at low temperatures. Oxygen acts to scavenge hydrogen atoms adsorbed as hydroxyl groups, forming water. Removal of the hydroxyl groups from the surface allows for further adsorption of methanol and for the overall reaction to proceed. Gas phase oxygen plays no direct role in the rate-determining step. Adsorbed or lattice oxygen can contribute equally to the removal of hydroxyl groups, and the reaction proceeds temporarily in the absence of dioxygen, resulting in partial reduction of the catalyst (16).

In many reactions, product inhibition occurs through site blockage resulting from competitive adsorption, and this has previously been assumed to be the mechanism through which water inhibits the rate for methanol oxidation (3, 12, 23, 27, 32). While methanol and water vapor adsorb in similar manners on similar sites, as discussed above, the bonding of methanol is much stronger. The lack of significant adsorption of water under reaction conditions was first noted by Farne and Pernicone (34). More recent results by Chung *et al.* (35) confirm that site occupancy by water vapor on MoO<sub>3</sub> is low above 200°C. Thus site blockage by adsorbed water does not appear to be significant under commercial operating conditions (300–350°C). However, at temperatures below 200°C site blockage by water adsorption may be an additional contributing factor to product inhibition.

### Consistency with Other Experimental Results

Selectivities to dimethyl ether and dimethoxymethane from methanol/oxygen feed streams without water are highest at low methanol conversions and low temperatures (4, 27), and they decrease strongly when water vapor is added to the feed stream. Chung *et al.* (49) and Machiels *et al.* (28) have described plausible reaction sequences leading to these side products. These sequences involve reactions between adsorbed methoxy groups, and their rates are at least second order in  $\theta_{\text{OCH}_3}$ . Since formaldehyde formation is first order in  $\theta_{\text{OCH}_3}$ , selectivities to these side products increase with increasing concentration of adsorbed methoxy. High water vapor partial pressure, present at high methanol conversions or when water is added to the feed stream, decreases  $\theta_{\text{OCH}_3}$  (Eqs. [19] and [22]) and, correspondingly, the selectivities to these two side products.

As the kinetic rate expression is written in Eq. [23] for the case of equivalent hydroxyl groups on metal atom

and oxygen atom sites, the small kinetic isotope effect  $k_{\text{CH}_3\text{OD}}/k_{\text{CH}_3\text{OH}} \cong 0.91\text{--}0.94$  results from the small changes in  $K_1$  and  $K_2$  for protonated and deuterated species. The much larger kinetic isotope effect  $k_{\text{CD}_3\text{OD}}/k_{\text{CH}_3\text{OH}} \cong 0.24$  can be attributed primarily to the difference in the rate constant  $k_3$  for breakage of a C–H bond compared to a C–D bond, although it too contains smaller contributions from  $K_1$  and  $K_2$ . The activation energy is

$$E = E_3 + \Delta H_1 - \frac{1}{2}\Delta H_2, \quad [24]$$

where  $E_3$  is the activation energy for conversion of the methoxy intermediate to formaldehyde,  $-\Delta H_1$  is the heat of adsorption of methanol, and  $-\Delta H_2$  is the heat of adsorption of water. The experimentally measured rate expression differs slightly from Eq. [23]. In particular, the reaction order in oxygen, while small, is nonzero. Thus, there are also additional small contributions to the activation energy beyond those considered in Eq. [24].

The oxidation of other alcohols by molybdenum oxide-based catalysts proceeds along similar lines as methanol oxidation. Farneth *et al.* (18) have studied the oxidation of methanol, ethanol, 2-propanol, and tertiary butyl alcohol on MoO<sub>3</sub> by temperature programmed reaction of the adsorbed alcohols. Due to steric hindrance, the surface density of the bulkier alcohols is slightly lower than for methanol. The higher order alcohols are also somewhat more reactive, which was attributed to the more facile removal of the  $\alpha$ -H in the rate-determining step. However, other aspects of the reaction are the same. Infrared spectroscopy indicates that ethanol is adsorbed as ethoxy on MoO<sub>3</sub> (50), and kinetic measurements of ethanol oxidation over supported MoO<sub>3</sub> catalysts yield a kinetic rate expression  $r = P_{\text{C}_2\text{H}_5\text{OH}}^{0.86} P_{\text{O}_2}^{0.24} P_{\text{H}_2\text{O}}^{-0.26}$  (47), which is similar in form to that observed for methanol oxidation. The formation of the secondary product diethyl ether during ethanol oxidation proceeds through steps analogous to the formation of dimethyl ether during methanol oxidation. There is one difference between methanol oxidation and the oxidation of higher alcohols—abstraction of  $\beta$ -H can lead to the production of olefins as secondary products for many higher alcohols, as evidenced by the formation of a small amount of ethylene during ethanol oxidation (47).

### CONCLUSIONS

When reaction rates are well described by power law kinetic rate expressions, neglect of product inhibition can confound the measurement of other kinetic properties. Under such circumstances, calculated reaction orders, activation energies, and kinetic isotope effects all differ from their true values.

Product inhibition can occur through kinetic coupling as well as through site blockage. The former case may occur when a reaction product participates in a reversible

step that occurs in the reaction sequence prior to the rate-determining step, and it often leads to product inhibition even in the presence of very low partial pressures of the inhibitor. The latter case occurs only when a reaction product is strongly adsorbed.

Methanol oxidation is inhibited by water vapor over iron molybdenum oxide catalysts, as well as over other molybdenum-oxide-containing catalysts. Power law kinetic rate parameters measured without consideration of product inhibition are therefore not the true values. The true activation energy ( $98 \pm 6$  kJ/mol) and reaction orders in methanol ( $0.94 \pm 0.06$ ) and oxygen ( $0.10 \pm 0.05$ ) are all higher than previously reported values, while the reaction order in water vapor is  $-0.45 \pm 0.07$ . The kinetic isotope effect at  $260^\circ\text{C}$ ,  $k_{\text{CH}_3\text{OH}}/k_{\text{CD}_3\text{OD}}$ , previously reported to be 0.37, is now estimated to be about 0.24. Wide ranging results are consistent with the source of product inhibition being kinetic coupling, including the lack of significant water adsorption at high temperatures, the  $-2$  ratio of reaction orders in methanol and water vapor, and the effect of water vapor on the selectivities of secondary products.

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