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Non-uniform surface kinetics with two types of sites: the case of ethanol oxidation on molybdenum oxide

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Temkin's theory of rates of catalytic reactions on non-uniform surfaces is extended to the MoO_3-catalyzed oxidation of ethanol to acetaldehyde. Two types of sites are assumed to be present, an oxygen atom site that can be modeled with uniform properties and a metal atom site characterized by non-uniform properties both for ethanol chemisorption to an ethoxide intermediate and the conversion of this intermediate to acetaldehyde. The rate-limiting step is the cleavage of a C–H bond in the absorbed ethoxide intermediate. Non-uniform surface kinetics leads to a kinetic rate expression of the form $v = kP_{C_2H_5OH}^{1-m}P_{O_2}^{(1-m)/4}P_{H_2O}^{-(1-m)/2}$. Such a rate expression, with $m = 0.14$, is shown to provide a good fit to kinetic data for the selective oxidation of ethanol on a silica supported molybdenum oxide catalyst.

Keywords: non-uniform surface; kinetics; ethanol; oxidation; molybdenum oxide

1. Introduction

The selective oxidation of ethanol to acetaldehyde

$$C_2H_5OH + \tfrac{1}{2}O_2 \rightleftharpoons CH_3CHO + H_2O$$

is catalyzed by several metal oxides. Molybdenum oxide and metal molybdates are exceptionally good catalysts for this and other catalyzed oxidations of alcohols [1–6]. The oxidation of alcohols catalyzed by metal oxides is generally assumed to involve two types of sites, metal atom sites and oxygen atom sites, each of which serves a specific function. The two types of sites are in close proximity and the ratio of their surface concentrations is fixed by the structure of the metal oxide surface.

The Temkin theory of rates of catalytic reactions on surfaces with non-uniform distributions of sites was introduced in 1957 and first applied to the kinetics of ammonia synthesis over iron [7–9]. Non-uniform surface kinetics has been applied since to several other reactions on metal surfaces in which only one type of site was involved, including ammonia decomposition on tungsten [10] and molybdenum [11] and ethylene hydrogenation on supported palladium–gold clusters [12]. Golodets [13] has discussed its application to oxidation reactions involving the reaction of gas phase or weakly adsorbed hydrocarbons with non-uniformly chemisorbed oxygen.

The underlying premise of non-uniform surface kinetics is that different sites on catalyst surfaces exhibit different heats of adsorption for reactants. This in turn leads to surface coverages that are described by Freundlich or Frumkin–Temkin isotherms rather than Langmuir isotherms. Subsequent catalytic steps also occur at different rates on different sites depending on the strengths of the bonds for the initially adsorbed species, yielding a Brønsted-type relationship between equilibrium constants and rate constants for elementary steps involving non-uniformly bound species. Non-uniform surface kinetics leads to power law rate expressions that are conveniently applied to many reactions that are not well described by Langmuir–Hinshelwood rate expressions derived from uniform surface kinetics. Boudart [14] and Boudart and Djéga-Mariadassou [15] have discussed the basis for non-uniform surface kinetics.

The Temkin formalism is based on a two-step catalytic sequence:

$$M_1 + A_1 \rightleftharpoons B_1 + M_2$$

$$M_2 + A_2 \rightleftharpoons B_2 + M_1$$

where A_1 and A_2 are reactants, B_1 and B_2 are products, and M_1 and M_2 are active centers in the sense of Taylor [16]. An implicit assumption in Temkin's derivation is that M_1 and M_2 represent the unoccupied and occupied states of the same site. A modification of the above sequence, with the first step equilibrated and the second

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step irreversible, has been used previously to explain the kinetics of ethanol oxidation to acetaldehyde [1]

$$M_1 + A_1 \rightleftharpoons B_1 + M_2$$

$$M_2 \rightarrow B_2 + M_1$$

where the symbol $\rightleftharpoons$ represents an equilibrated step and the symbol $\rightarrow$ represents a rate-determining step.

In this work we address the case where there are two types of sites, one of which is a Temkin (non-uniform) site and the other a Langmuir (uniform) site. Using the molybdenum oxide-catalyzed oxidation of ethanol as an example, we consider two types of sites on the same catalyst surface, metal atom sites which act as Temkin sites and oxygen atom sites which act as Langmuir sites.

2. Experimental

Kinetic measurements were carried out on 9% MoO_3/SiO_2. Details of the catalyst preparation [17] and reactivity [1] have been reported earlier. To summarize, 1 g of powder was pretreated in a mixture of O_2 (8 kPa), H_2O (4 kPa) and He (89 kPa) for 1 h at 623 K. The kinetic measurements were then taken at 523 K and atmospheric pressure using feed streams containing C_2H_5OH, O_2 and H_2O in helium at a total flow rate of 160 sccm (110 μmol s^{-1}). During these measurements, the partial pressure of one of the components was varied while the remainder were held constant. The range of partial pressures studied was 2–38 kPa for oxygen, 1–45 kPa for ethanol, and 1–65 kPa for water. In order to simplify the kinetic analysis, experiments were carried out under differential reaction conditions. Partial pressures of the products were measured by gas chromatography.

Turnover rates were calculated from the kinetic measurements using oxygen titration to determine the density of sites on the molybdenum oxide surface [17]. Briefly, oxygen uptakes were measured by a pulse method on samples pre-reduced in hydrogen at temperatures (600–640 K) below those at which bulk reduction occurred. The method was independently calibrated by laser Raman spectroscopy at low loadings and by X-ray diffraction line broadening at high loadings.

3. Results

Turnover rates for the oxidation of ethanol to the three main products (acetaldehyde, diethyl ether and ethylene) at 523 K are plotted as a function of oxygen, water vapor, and ethanol partial pressures in fig. 1. The selectivity to acetaldehyde was about 80%. The main secondary product was diethyl ether, with a selectivity of about 15%. Ethylene was produced with a selectivity of about 5%, while acetic acid and ethyl acetate were produced with selectivities less than 2%.

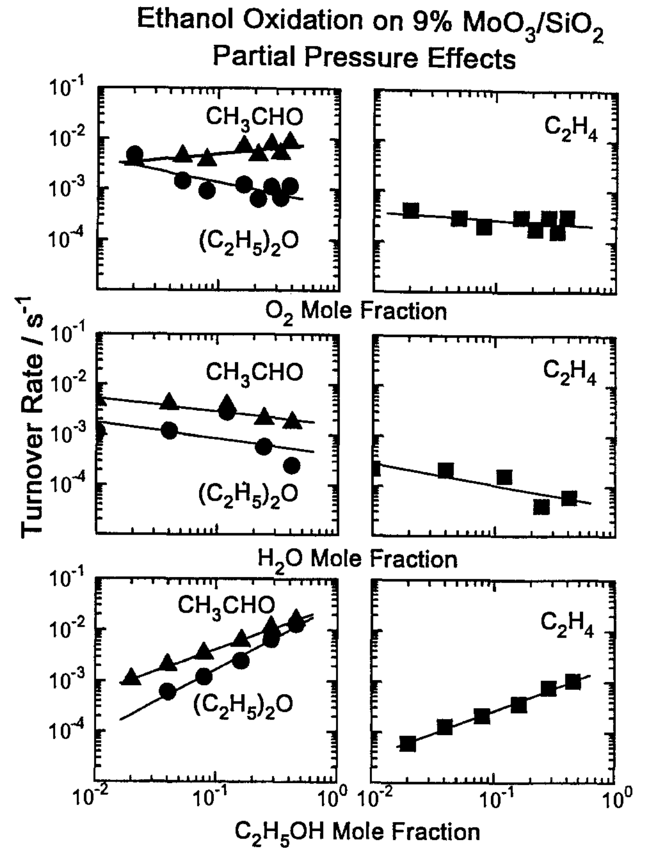

Fig. 1. Turnover rate for ethanol oxidation at 523 K and 1 atm total pressure: (a) dependence on O_2 mole fraction in the feed stream ($P_{H_2O} = 4.0$ kPa, $P_{C_2H_5OH} = 8.0$ kPa, balance helium), (b) dependence on H_2O mole fraction in the feed stream ($P_{C_2H_5OH} = 8.0$ kPa, $P_{O_2} = 8.0$ kPa, balance helium), (c) dependence on C_2H_5OH mole fraction ($P_{O_2} = 8.0$ kPa, $P_{H_2O} = 4.0$ kPa, balance helium).

Analysis of the reaction products as a function of oxygen, water vapor, and methanol partial pressures yielded the following expressions for the turnover rates v_i to acetaldehyde, ethylene, and diethyl ether:

$$v_{CH_3CHO} = k_\alpha P_{C_2H_5OH}^{0.86} P_{H_2O}^{-0.26} P_{O_2}^{0.24} ,$$

$$v_{C_2H_4} = k_\beta P_{C_2H_5OH}^{0.91} P_{H_2O}^{-0.43} P_{O_2}^{-0.15} ,$$

$$v_{(C_2H_5)_2O} = k_\gamma P_{C_2H_5OH}^{1.40} P_{H_2O}^{-0.31} P_{O_2}^{-0.37} .$$

The errors in the exponents are approximately ±0.05 for C_2H_5OH, ±0.10 for H_2O, and ±0.10 for O_2. Turnover rates to diethyl ether showed the strongest dependence on ethanol partial pressure. Turnover rates to all three products decreased with increasing water vapor partial pressure.

4. Discussion

4.1. Proposed reaction mechanism

The fundamental assumption in the present analysis is that the metal atom sites and the oxygen atom sites can be treated independently. The oxygen atom sites are assumed to be uniform, and species adsorbed on these sites can be handled in the normal manner for Langmuir adsorption. Ethanol adsorption takes place on metal atom sites, leading to the formation of an ethoxide intermediate. Reactivity measurements coupled with in situ laser Raman spectroscopy determination of the concentration of chemisorbed ethoxy intermediates indicates that this step is non-uniform and suggests the applicability of non-uniform surface kinetics in describing chemical processes on the metal atom sites [18].

We consider the following sequence of elementary steps for the oxidation of ethanol to acetaldehyde:

$$C_2H_5OH + M^* + O^* \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} M^*{-}OCH_2CH_3 + O^*{-}H \qquad (1)$$

$$M^*{-}OCH_2CH_3 \xrightarrow{k_2} CH_3CHO + M^*{-}H \qquad (2)$$

$$M^*{-}H + O^* \xrightarrow{k_3} M^* + O^*{-}H \qquad (3)$$

$$2O^*{-}H \overset{K_4}{\rightleftharpoons} H_2O + O^* + \square \qquad (4)$$

$$2\square + O_2 \overset{K_5}{\rightleftharpoons} 2O^* \qquad (5)$$

where M^* is an empty metal atom site, O^* is an empty oxygen atom site, and $\square$ represents a vacancy on an oxygen atom site. The first two steps occur on the non-uniform metal atom sites and will be treated in the manner of Temkin. The first step is in accord with previous work on ethanol adsorption on molybdenum oxide [1,3,17,19]. The second step is based on recent theoretical work indicating that hydride elimination reactions involve the metal atom site rather than a nearby oxygen atom site [20,21]. The third step represents the transfer of a hydrogen atom from a metal atom site to an oxygen atom site. It is assumed to be fast and therefore kinetically insignificant. (From the standpoint of the mathematical derivation below, the second and third step could be combined into one step, leading to hydride elimination by reaction with a nearby oxygen atom site, as assumed in many previous studies on alcohol oxidation [3,4,22,23].) The final two steps take place on the oxygen atom sites and account for desorption of water and reoxidation of the surface. They are assumed to be equilibrated.

4.2. Derivation of the rate equation

A non-uniform surface may be considered to be formed from a number of domains or ensembles with different heats of adsorption for adsorption complexes [14]. In the above mechanism, these complexes are the ethoxide groups on the M^* sites. We consider (j) such ensembles. Within each ensemble the site balance can be written as

$$(M^*)_j + (M^*{-}OCH_2CH_3)_j = (M)_j\,, \qquad (6)$$

where the subscript (j) refers to the sites in ensemble (j).

Equilibration of step (1) yields:

$$(M^*{-}OCH_2CH_3)_j = (M^*)_j \frac{k_1 P_{C_2H_5OH}(O^*)}{k_{-1}(O^*{-}H)}\,. \qquad (7)$$

Combining eqs. (6) and (7) yields the concentration of adsorbed ethoxy in ensemble (j),

$$(M^*{-}OCH_2CH_3)_j = (M)_j \frac{k_1 P_{C_2H_5OH}(O^*)}{k_1 P_{C_2H_5OH}(O^*) + k_{-1}(O^*{-}H)}\,, \qquad (8)$$

which can alternately be stated in terms of the fractional occupancy of metal atom sites in ensemble (j) by ethoxy intermediates $\theta \equiv (M^*{-}OCH_2CH_3)_j/(M)_j$,

$$\theta = \frac{k_1 P_{C_2H_5OH}(O^*)}{k_1 P_{C_2H_5OH}(O^*) + k_{-1}(O^*{-}H)}\,. \qquad (9)$$

The turnover rate v_j in ensemble (j) can then be expressed as

$$v_j = k_2\theta = \frac{k_2 k_1 P_{C_2H_5OH}(O^*)}{k_1 P_{C_2H_5OH}(O^*) + k_{-1}(O^*{-}H)}\,. \qquad (10)$$

Following Boudart and Djéga-Mariadassou [14], the rate constants in each ensemble are related to the surface coverage θ by

$$k_1 = k_1^0 \exp[-\alpha f\theta]\,, \qquad (11)$$

$$k_{-1} = k_{-1}^0 \exp[(1-\alpha) f\theta]\,, \qquad (12)$$

$$k_2 = k_2^0 \exp[(1-\alpha) f\theta]\,, \qquad (13)$$

where k_1^0, k_{-1}^0 and k_2^0 are rate constants in the limit of zero coverage, α is the Brønsted transfer coefficient, which relates the forward and reverse kinetic rate constants of an elementary step to its equilibrium constant $k_i \propto K_i^\alpha$, and f is the difference in the affinity of step (1) between zero coverage and full coverage. Assuming a continuous site distribution, the average turnover rate v, which is the property measured in kinetic experiments, can be obtained by integrating the rates on each ensemble over the entire surface,

$$v = \frac{1}{(M)} \int v_j \, d(M)_j\,. \qquad (14)$$

Details of the integration procedure follow those discussed by Boudart and Djéga-Mariadassou [14]. A continous site distribution is assumed with the following form:

$$d(M)_j = a \exp(-\gamma A^0/RT)\, d(A^0/RT)\,, \qquad (15)$$

where a is a constant, γ is a constant that characterizes the site distribution ($\gamma = 0$ corresponds to a Frumkin–Temkin isotherm and $\gamma \neq 0$ corresponds to a Freundlich isotherm), and $d(M)_j$ is the concentration of sites in ensemble (j) with an affinity for adsorption of ethanol between A^0 and $A^0 + \mathrm{d}A^0$. The integrated solution is

$$v = \frac{\pi}{\sin(\pi m)} \frac{\gamma}{\exp(\gamma f) - 1} k_2 \left(K_1 P_{C_2H_5OH} \frac{(O^*)}{(O^*\!-\!H)} \right)^{1-m} , \tag{16}$$

where $m = \alpha - \gamma$.

The oxygen sites are treated with uniform surface kinetics. The site balance on the oxygen sites reflects contributions from oxygen terminated sites, oxygen vacancies on these sites, and oxygen sites with adsorbed hydrogen atoms (hydroxyl groups),

$$(O) = (\square) + (O^*) + (O^*\!-\!H) , \tag{17}$$

where (O) is the total number of oxygen atom sites. We will assume that under reaction conditions the oxygen atom sites are nearly fully covered with adsorbed oxygen ($(\square), (O^*\!-\!H) << (O^*)$). Then from steps (3) and (4) the concentrations of oxygen vacancies and adsorbed hydroxyl groups on the oxygen atom sites are

$$(O^*) \cong (O) , \tag{18}$$

$$(\square) = (O) \frac{1}{K_5^{1/2} P_{O_2}^{1/2}} , \tag{19}$$

$$(O^*\!-\!H) = (O) \frac{P_{H_2O}^{1/2}}{K_4^{1/2} K_5^{1/4} P_{O_2}^{1/4}} . \tag{20}$$

Substituting eqs. (18) and (20) into eq. (16) yields

$$v = k \frac{P_{C_2H_5OH}^{1-m} P_{O_2}^{(1-m)/4}}{P_{H_2O}^{(1-m)/2}} , \tag{21}$$

where

$$k = \frac{\pi}{\sin(\pi m)} \frac{\gamma}{\exp(\gamma f) - 1} k_2^0 K_1^{1-m} K_4^{(1-m)/2} K_5^{(1-m)/4} . \tag{22}$$

4.3. Comparison with experimental results

The kinetic results for the formation of the primary product, acetaldehyde, are well described by the kinetic rate expression derived for a non-uniform surface (eq. (22)) with $m = 0.14$,

$$v = k P_{C_2H_5OH}^{0.86} P_{H_2O}^{-0.43} P_{O_2}^{0.21} .$$

In the case of uniform surface kinetics, the proposed mechanism leads to a kinetic rate expression of the form

$$v = k_2 \theta = k_2 \frac{K_1 K_4^{1/2} K_5^{1/4} P_{C_2H_5OH} P_{O_2}^{1/4} P_{H_2O}^{-1/2}}{1 + K_1 K_4^{1/2} K_5^{1/4} P_{C_2H_5OH} P_{O_2}^{1/4} P_{H_2O}^{-1/2}} , \tag{23}$$

which in the limit of low coverage of ethoxide becomes

$$v = k_2 K_1 K_4^{1/2} K_5^{1/4} P_{C_2H_5OH} P_{O_2}^{1/4} P_{H_2O}^{-1/2} . \tag{24}$$

This is similar in form to eq. (20) for a non-uniform surface. The use of non-uniform surface kinetics over uniform surface kinetics is suggested by the better fit to the data as well as by analysis of reaction isotherms and coverages during reaction conditions, which show that the isosteric activation energy decreases with increasing coverage of ethoxide [18].

The secondary product ethylene is formed through β-hydrogen abstraction from the ethoxide intermediate. Selectivity to ethylene was about constant for the range of conditions studied. The formation of the secondary product diethyl ether occurs through reaction of two adsorbed ethoxide groups, while formation of both acetaldehyde and ethylene involve only one adsorbed ethoxide group. High partial pressures of ethanol increase the concentration of adsorbed ethoxide groups, resulting in an increase in the selectivity to diethyl ether (fig. 1).

The oxidation of ethanol to acetaldehyde is inhibited by water vapor, one of its reaction products. Chung et al. [24] studied the adsorption of water vapor by molybdenum oxide. They found that few surface hydroxyl groups are present on the surface above 458 K in the presence of 0.63 kPa water vapor partial pressure in helium, indicating that product inhibition for ethanol oxidation at 523 K does not occur due to competitive site blockage by adsorbed hydroxyl groups on the M* sites. Their work also indicated that oxygen has a blocking effect on the adsorption of water.

In our proposed mechanism, the rate of ethanol oxidation to acetaldehyde is dependent on the concentration of the adsorbed ethoxide intermediate. Inhibition due to water vapor arises from its effect on the concentration of the adsorbed ethoxide species rather than through competitive adsorption on the M* site. Inhibition in this matter has been termed "kinetic coupling" by Boudart [25]. This explanation for inhibition by water vapor is consistent with the low surface concentration of hydroxyl groups under reaction conditions [24]. Due to the need for oxygen vacancies to allow for water adsorption (step (4)), the mechanism is also consistent with the increase in water adsorption on partially reduced MoO_3 surfaces [24].

The mechanism of ethanol oxidation appears to be quite similar to that for methanol oxidation. Both reactions take place on MoO_3 surfaces other than (010) due to the need for vacant metal atom coordination sites for adsorption of alcohol [26,27]. Adsorption of ethanol and methanol leads to ethoxide [1,19] and methoxide [4,26,28] intermediates respectively. The rate limiting step for both reactions is cleavage of a C–H bond [18,22], and both reactions are inhibited by water vapor [4,6].

The kinetic derivations presented here for ethanol oxidation are specific to the particular sequence of steps considered, but the method is general and should be applicable to other kinetic sequences. An example of a related situation is the hydroisomerization of pentane by bifunctional Pt/Al_2O_3 catalysts, where acid sites on the Al_2O_3 can be treated as Temkin sites and active sites on the Pt can be treated as Langmuir sites. Non-uniform surface kinetics have been suggested for analyzing the kinetics of that reaction [15].

5. Conclusions

The kinetics of ethanol oxidation to acetaldehyde catalyzed by MoO_3 are described by a power law rate expression of the form $v = kP^{0.86}_{C_2H_5OH}P^{-0.26}_{H_2O}P^{0.24}_{O_2}$. Ethanol chemisorbs non-uniformly on metal atom sites to form ethoxide intermediates, and the rate-limiting step is the breakage of a C–H bond in the ethoxide intermediate. Application of non-uniform surface kinetics based on Temkin metal atom sites and Langmuir oxygen atom sites leads to a power law kinetic rate expression of the form $v = kP^{1-m}_{C_2H_5OH}P^{(1-m)/4}_{O_2}P^{-(1-m)/2}_{H_2O}$. This expression with $m = 0.14$ agrees well with the experimentally measured kinetic rate expression. Non-uniform surface kinetics has usually been applied to much simpler kinetic sequences occurring on one type of site. With some restrictions, it can also be applied to more complex kinetic sequences involving more than one type of active site, such as selective catalytic oxidation reactions on metal oxides surfaces.

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