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Testing the Assumption of Surface Homogeneity in Modeling Catalytic Reactions

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Two techniques are described, which can be used to test the validity of the assumption of a uniform surface when modeling the kinetics of gas–solid catalytic oxidation reactions. These are applied to data previously obtained for the oxidation of toluene and *o*-xylene over a vanadium oxide catalyst. On the basis of these data, the introduction of terms accounting for nonuniformity of the catalyst surface is not warranted and the assumption of a homogeneous catalyst surface is shown to be adequate.

NOMENCLATURE

A_a	Arrhenius frequency factor for oxygen adsorption
A_{ij}	Arrhenius frequency factor for reaction step rate constant k_{ij}
C_i	Concentration of compound *i*
C_o	Concentration of oxygen
E_a	Activation energy for oxygen adsorption
E_{ij}	Activation energy for reaction step rate constant k_{ij}
k_a	Rate constant for oxygen adsorption, liter/(g · catalyst) (s)
k_{ij}	Rate constant for the reaction of compound *i* to compound *j*
m	Number of reaction steps in the network
n_{ij}	Moles of oxygen required per mole of compound *i* for the reaction of compound *i* to compound *j*
R	Universal gas constant
$S(E_a)$	Relative density of catalyst surface sites corresponding to activation energy E_a
T	Absolute temperature
ΣnkC	$\sum_i \sum_j n_{ij} k_{ij} C_i$
α_1,α_2	Site energy distribution parameters in the Freundlich isotherm
θ	Fraction of the surface covered

INTRODUCTION

Kinetic models for gas–solid catalytic oxidation reactions are usually developed assuming either equilibrium between adsorption and desorption (e.g., Langmuir–Hinshelwood or Rideal) or a steady state between adsorption and chemical reaction (e.g., steady state adsorption model). In either case it is common to assume that the energies of adsorption and desorption are independent of the extent of surface coverage. This is acknowledged to be a doubtful assumption at best.

There are two approaches to testing the validity of this assumption:

(i) Study the adsorption-desorption process in the absence of chemical reaction; and

(ii) evaluate surface homogeneity parameters at the same time as reaction parameters.

The first approach has been used by Stanislaus *et al.* (*1*). They studied a vanadium oxide catalyst for which the steady state adsorption model had been used to

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describe oxidation rate data and concluded that "the kinetics of oxygen chemisorption on a complex vanadium oxide catalyst must be described by more than one mechanism and perhaps as many as three." However, there are two main areas of concern in using their results. One lies in transferring the results obtained in the absence of chemical reaction to the situation in which both adsorption and reaction are occurring. The other lies in assessing the weight to be assigned to one of their three data sets which appears to be radically different from the others.

The purpose of this paper is to describe the second approach to testing the assumption of surface homogeneity and to illustrate its application to oxidation rate data gathered over a vanadium catalyst and represented by the steady state adsorption model (SSAM).

It should be noted that catalytic surfaces are not homogeneous. The question facing the kineticist is whether the inclusion of surface heterogeneity in the kinetic model is warranted, or whether the simpler assumption of homogeneity is adequate and indeed is all that can be justified. Therefore it is not homogeneity which is being tested, rather it is the assumption of homogeneity.

THEORY

The general form of the SSAM was presented by Boag *et al.* (*2*) as follows:

$$r_i = \left(\sum_j k_{ij}C_i - \sum_h k_{hi}C_h\right)\theta \qquad (1)$$

where r_i is the rate of disappearance of compound i and θ is the fraction of the surface covered by adsorbed oxygen, expressed as

$$\theta = k_aC_o/(k_aC_o + \Sigma nkC) \qquad (2)$$

The summation over j in Eq. (1) is over all network steps consuming compound i, and the summation over h is over all steps producing compound i.

$$\Sigma nkC = \sum_i \sum_j n_{ij}k_{ij}C_i$$

where i and j represent reactants in all reaction steps for $j > i$.

We now focus attention on the rate constant for the adsorption of oxygen, k_a. If k_a is written in the usual Arrhenius form

$$k_a = A_a \exp(-E_a/RT)$$

then

$$\theta = 1/[1 + \Sigma nkC/A_a \exp(-E_a/RT)\, C_o]. \qquad (3)$$

Assume that the energy of activation for the adsorption of oxygen is constant over a small region of the surface, p. The coverage within that region may be written as

$$\theta(E_{ap}) = 1/[1 + \Sigma nkC/A_a \exp(-E_{ap}/RT)\, C_o]. \qquad (4)$$

This assumes that A_a is independent of surface coverage. As the number of such regions increases and the size of each region decreases, the overall coverage tends to

$$\theta = \int S(E_a)\theta(E_a)dE_a \qquad (5)$$

where $S(E_a)$ is the relative density of sites having activation energy E_a, and the integration is over all possible values of E_a.

If the energy of activation is independent of the extent of surface coverage then $S(E_a)$ is a delta function at a particular value of E_a and Eq. (5) reduces to Eq. (3). This is the most common assumption in modeling gas–solid catalytic reactions.

The simplest assumption which can be made to extend the model to include heterogeneous surfaces is to assume that the energy of activation of adsorption increases linearly with θ, from $E_{a,\min}$ to $E_{a,\max}$. In other words the fraction of surface associated with E_a is uniformly distributed between $E_{a,\min}$ and $E_{a,\max}$. This is analogous to the Temkin adsorption isotherm. Using this assumption,

$$S(E_a) = 1/(E_{a,\max} - E_{a,\min}) \quad \text{for } E_{a,\min} < E_a < E_{a,\max}. \qquad (6)$$

Substituting Eq. (6) into Eq. (5) and integrating,

$$\theta = \frac{\ln[(\Sigma nkC + k_{a,\min} C_o)/(\Sigma nkC + k_{a,\max} C_o)]}{\ln[k_{a,\min}/k_{a,\max}]} \quad (7)$$

where $k_{a,\min} = A_a \exp(-E_{a,\min}/RT)$ and $k_{a,\max} = A_a \exp(-E_{a,\max}/RT)$.

Equation (7) can be used with Eq. (1) to give the rate of disappearance of any reactant. If there are m reaction steps in the proposed network then the model will contain $m + 2$ parameters to be estimated: $k_{a,\min}$, $k_{a,\max}$, and m reaction step rate constants k_{ij}. If the data are gathered at more than one temperature and if all reaction step rate constants k_{ij} are also written in Arrhenius form then the model will contain $2m + 3$ parameters: A_a, $E_{a,\min}$, $E_{a,\max}$, m frequency factors A_{ij} and m activation energies E_{ij}.

The second approach to testing the validity of the assumption that the surface is homogeneous can be carried out in a number of ways. Two techniques which will be used in the next section are:

(i) Subdivision of the data into sets of low, medium, and high coverage runs, followed by estimation of the parameters using Eqs. (1) and (3), then testing whether variations in the parameters with coverage are significant; and

(ii) A comparison of the fit achieved by using Eqs. (1) and (3) with that achieved by using Eqs. (1) and (7), to determine whether there is a significant improvement when allowance for a heterogeneous surface is made when fitting the rate model.

Before discussing the application of these two techniques to the oxidation rate data, there are two points to be made. First, we also considered the analogy to the Freundlich isotherm, for which the energy of activation of adsorption increases exponentially as θ increases. The relative density of site energies is then given by

$$S(E_a) = \alpha_1 \exp(\alpha_2 E_a) \quad \text{for } E_{a,\min} < E_a < E_{a,\max}.$$

Substitution into Eq. (5) leads to an expression for θ which cannot be integrated analytically but which can of course be integrated numerically. We feel that this additional mathematical complexity makes the use of the Freundlich assumption unwarranted unless application of the two techniques referred to above shows that the homogeneous surface assumption is not valid. In such a case it would be useful to compare the result of the Temkin assumption with that of the Freundlich assumption.

The second point is to answer the question: why are we using the Temkin assumption when Stanislaus *et al.* (*1*) judged their correlation to be "inconsistent with the theoretical basis of the Temkin isotherm"? It should be noted that Stanislaus *et al.* used the simplified form of the Temkin isotherm, and this form is appropriate only in the middle of the range of surface coverage, i.e., at θ approximately equal to 0.5. As θ approaches zero or unity the term which is eliminated in deriving the simplified Temkin equation cannot be ignored. Estimation of θ for the three temperature data sets used by Stanislaus *et al.* reveals some values of θ greater than 0.94 at each temperature, and values as high as 0.98 in the 325°C set. It appears likely that the inconsistency noted by Stanislaus *et al.* is due to using an inappropriate simplified form of the isotherm. Our derivation of Eq. (7) is valid for the full range of θ values.

RESULTS AND DISCUSSION

Technique I: Subdivision of the Data into Sets of Low, Medium, and High Coverage Runs

Initial rate studies of the vanadium oxide catalyzed oxidation of naphthalene (*3*), toluene (*4*), benzene (*5*), and *o*-xylene (*6, 7*) show that the SSAM provides an adequate representation of the rate data for these reactions. This was confirmed by a reexamination of the data by Pritchard and Bacon

(*8*). In these analyses it was assumed that the surface was homogeneous, and this is the assumption we now wish to test.

The data from the toluene and *o*-xylene investigations were divided into roughly equal numbers of runs at low, medium, and high coverages. The coverage values used for this division were calculated using Eq. (3) with parameter estimates obtained from the fits which assumed a homogeneous surface. The rate constants were written in the Arrhenius form and the model was fitted to the data to estimate parameters E_a (low θ), E_a (medium θ), and E_a (high θ). These estimates are presented in Table 1.

The question for the analyst at this stage is not whether the surface is heterogeneous, but whether a more complicated model representing a heterogeneous surface is necessary. This is the manner in which the validity of the assumption of a homogeneous surface is tested. If the surface is heterogeneous then E_a should increase with increasing surface coverage.

The differences among the estimates of E_a in Table 1 are not significant at the 5% level. Therefore the assumption of a homogeneous surface is considered to be valid.

High conversion data were reported by Boag *et al.* (*2*) for *o*-xylene oxidation in a gradientless reactor and reexamined by Pritchard (*9*). These data were divided into runs at low and high coverage and k_a estimates were made for the different coverages. Again the difference (1%) was not significant at the 5% level. In passing it may be of interest to note that data from a high conversion isothermal plug flow reactor were also examined (*10*). Once again, no evidence of a heterogeneous surface was found. However, the plug flow reactor analysis requires additional assumptions involving axial variations of θ and therefore this reactor is not really suitable for this type of analysis.

TABLE 1

Estimates of E_a with Approximate 95% Confidence Intervals Obtained from Fitting SSAM to Data Corresponding to Different Catalyst Coverages

Hydrocarbon	E_a (kcal/g mole)	θ
Toluene	34 ± 2	High 0.72–0.85
	34 ± 2	Medium 0.50–0.72
	34 ± 2	Low 0.15–0.50
o-Xylene (Catalyst No. 1)	27 ± 7	High 0.35–0.65
	27 ± 7	Medium 0.20–0.35
	27 ± 7	Low 0.05–0.20
o-Xylene (Catalyst No. 2)	35 ± 3	High 0.40–0.65
	38 ± 3	Medium 0.20–0.40
	40 ± 3	Low 0.05–0.20

Technique II: A Comparison of the Fit Achieved by a Homogeneous Surface Model and a Temkin-type Heterogeneous Surface Model

Boag's data for *o*-xylene oxidation (*11*) were fitted by a multiresponse SSAM (9) using Eqs. (1) and (2) which assume a homogeneous surface. In this application the SSAM involved 13 parameters, the oxygen adsorption rate constant k_a plus specific rate constants for each of the 12 steps in the proposed reaction network. The SSAM was then refitted in the form which uses the Temkin assumption that the energy of activation increases linearly with θ, i.e., by a multiresponse model using Eq. (1) and the isothermal form of Eq. (7). This model required one extra parameter, k_a being replaced by $k_{a,\min}$ and $k_{a,\max}$.

Both models gave satisfactory fits. For the homogeneous surface model [Eqs. (1) and (2)] the maximum likelihood estimate of k_a, with approximate 95% confidence interval, is 8.74×10^{-5} ($\pm$ 0.20×10^{-5}). For the heterogeneous surface model [Eqs. (1) and (7)] the maximum likelihood estimates of $k_{a,\max}$ and $k_{a,\min}$, with approximate 95% confidence intervals, are 8.88×10^{-5} ($\pm 1.15 \times 10^{-2}$) and 8.69×10^{-5} ($\pm 1.13 \times 10^{-2}$), respectively. Because the estimates of $k_{a,\max}$ and $k_{a,\min}$ are not nearly equal and because there is a negative correlation between these estimates in excess of -0.9995, the denominator expression in Eq. (7) caused severe numerical convergence problems during the estimation. One result of the extremely high correlation between the parameter estimates is the very large confidence interval for both $k_{a,max}$ and $k_{a,min}$ relative to that obtained for k_a in the homogeneous surface model.

It can be seen that the estimates of $k_{a,max}$ and $k_{a,min}$ in the heterogeneous surface model fall within the approximate 95% confidence interval for k_a in the homogeneous surface model. Therefore extension of the reaction rate model to account for a heterogeneous surface is not warranted.

CONCLUSION

Two techniques for testing the validity of the assumption that the catalyst surface is homogeneous have been presented. Data from the vanadium oxide catalyzed oxidation of toluene and *o*-xylene have been used to illustrate the techniques. The assumption of a homogeneous catalyst surface has been found to be adequate for these data.

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