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Kinetic Modeling for the Catalytic Oxidation of Benzo(a)pyrene

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A microcatalytic flow reactor system was used to elucidate the kinetics of benzo(a)pyrene (BAP) oxidation over a mixed vanadium pentoxide–molybdenum oxide catalyst. Experimental conditions covered the following ranges: reaction temperature 275–345°C; BAP concentration 0.002–0.05 g mol/m³; and oxygen concentration 4.0–26.0 g mol/m³. Current statistical methodology was utilized in conjunction with the data obtained to discriminate among rival kinetic models, as well as to provide model parameter estimates. Results show that the oxidation reaction follows a classical redox mechanism.

INTRODUCTION

Considerable attention has been given to the kinetics of the heterogeneously catalyzed oxidation of numerous polynuclear aromatic hydrocarbons (PAH's). Most notably, reviews on some of the earlier work with naphthalene, anthracene, and phenanthrene have appeared (*3, 12*), which suggest that a common kinetic model exists for PAH oxidation over transition metal oxide catalysts. The definitive work of Mars and van Krevelen (*8*) and that of Shelstad *et al.* (*13*) postulate a redox type mechanism in which the catalyst sites are first oxidized by the gas phase oxygen and later reduced with gas phase PAH.

In addition, the literature yields several papers which deal with PAH oxidation kinetics in conjunction with certain statistical model discrimination procedures. Peterson (*9*) and Kittrell and Mezaki (*6*) discuss the kinetic modeling of naphthalene oxidation and review some of the statistical techniques of benefit to the kineticist. Subramanian and Murthy (*15–17*) apply nonparametric model discrimination procedures but use linear regression methods in their work upon anthracene oxidation.

An important member of the PAH series is the often occurring carcinogen benzo(a)-pyrene (BAP) which is pyrosynthesized during the combustion of many natural organic wastes, as well as meat and tobacco. Trace removal of potentially harmful oxidation products of the PAH type from effluent gas streams may eventually become a commercial necessity. It is the purpose of this paper to report upon the heterogeneous oxidation of BAP over a commercial low-surface-area oxidation catalyst, and also the application of existing statistical methods to these data for selection of an adequate kinetic rate model and determination of model parameters.

EXPERIMENTAL METHODS

Figure 1 shows a schematic of the experimental microreactor system which, except for the gas flow controllers and rotameters, was built within the oven of a Varian 200 series gas chromatograph. BAP vapor was transported from the vaporizer (A) by a constant mass flow controlled

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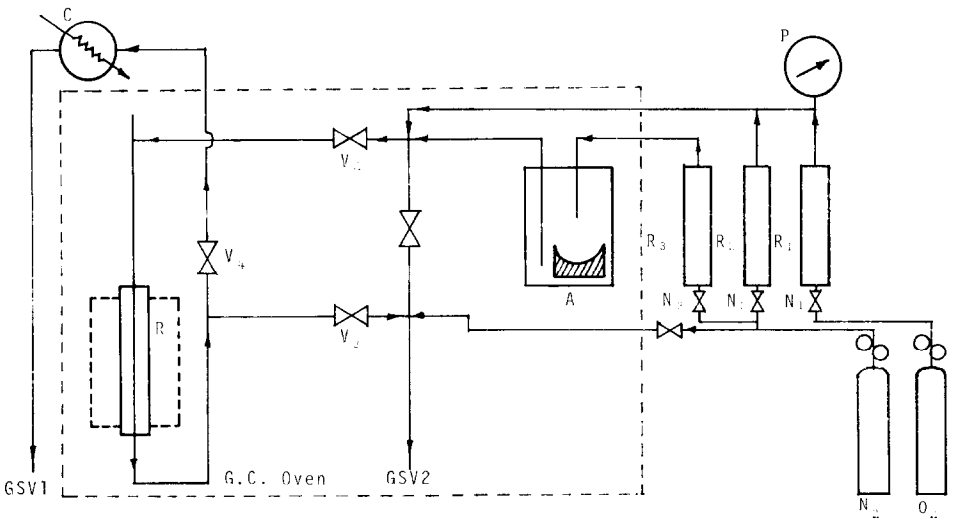

FIG. 1. Experimental system. A, Vaporizer; C, air condenser; GSV1, gas sample valve; GSV2, gas sample valve; N_1, N_2, N_3, mass flow control valves; N_4, needle valve; P, pressure gauge; R_1, R_2, R_3, rotameters; T, type K thermocouple; and V_1–V_4, bellows valves.

nitrogen stream and mixed with an oxygen-containing nitrogen gas stream of known composition before entering the separately heated microcatalytic reactor (R) contained within the oven.

The reactor was constructed from a short length of Pyrex glass tubing (20 × 0.4 cm internal diameter) and contained crushed glass chips upstream from the catalyst bed to enhance both mixing and heat transfer. Axial temperature profiles, previously obtained in the reactor tube completely packed with catalyst, indicated that reasonably isothermal conditions (±2°C) existed in the bed, over the last half of the reactor tube. Consequently, the experimental catalyst bed (1.0–2.5 cm in length) was located within this nearly isothermal region. Reaction temperature was monitored using an internal, type K thermocouple (0.15 cm outer diameter) inserted 0.2 cm axially into the catalyst bed as shown in Fig. 2.

The catalyst (Harshaw V-1002) was a mixture of vanadium pentoxide (6% by weight) and molybdenum oxide (3% by weight) supported upon low surface area (1 m^2/g) α-alumina. Before use, the catalyst was crushed and sized (40/80 mesh) but no additional special pretreat-

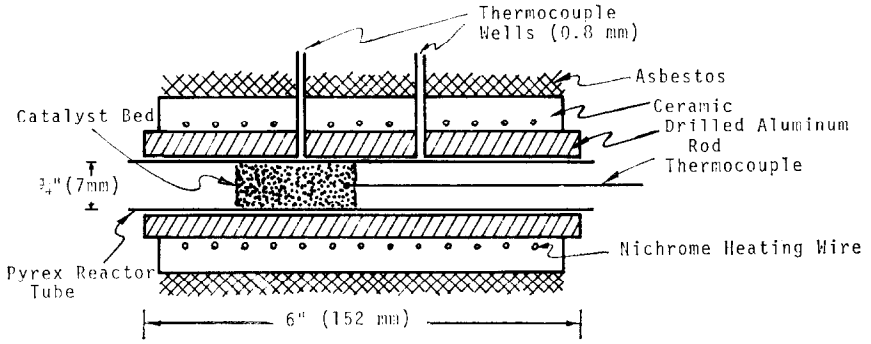

FIG. 2. Detail of reactor and heating element.

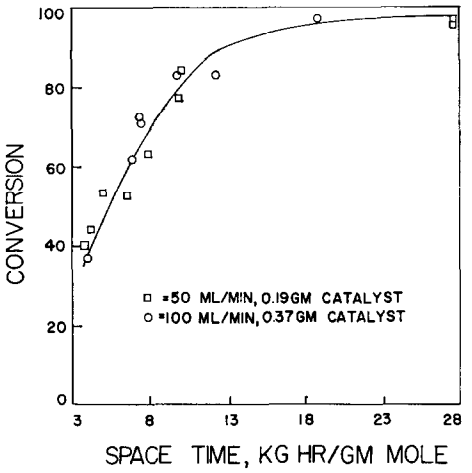

FIG. 3. External diffusion test results.

ment was carried out. During use, no catalyst aging effects were noticed for the duration of the experimental program.

Analyses of either the inlet or outlet gas streams were performed by gas chromatography using either a 5% SE 30 on a Chromosorb-W HP column for hydrocarbons or a 5A molecular sieve column for the carbon oxides. Detection was by flame ionization for which the carbon oxides were catalytically reduced to methane prior to entering the detector. Glass-lined stainless steel tubing was used wherever both BAP vapor and oxygen coexisted, since it had been previously found that type 316 stainless steel will catalyze the oxidation of BAP. Further details of the experimental system are given in an earlier work (*19*).

PROCEDURE

For a typical run series the following procedure was adopted. The vaporizor was charged with approximately 0.2 g of BAP, sufficient for about 20 h of continuous experimentation, and the gas chromatograph oven was allowed to reach 275°C. The reaction conditions (temperature, total flow rate, and reactant concentrations) were set and the inlet stream monitored until a constant inlet BAP concentration was obtained. The flow was then diverted through the catalyst bed and the effluent BAP concentration monitored until a steady state was reached. After recording all necessary data, new reaction conditions could be set and the procedure repeated. In this way it was possible to obtain several data points during a given run series.

PRELIMINARY RESULTS

Homogeneous Runs

The preliminary homogeneous phase of the experimental program consisted of 53 runs made without any catalyst present in the reactor. The majority of these runs were at 440°C since conversions were small and hence difficult to quantify at lower temperatures. The data obtained at 345°C indicated that conversions were small (less than 10%) even at high space times. Consequently, subsequent observations of the heterogeneously catalyzed reaction were confined to temperatures below 345°C where the assumption of negligible contribution from the blank reaction was believed valid.

Catalytic Runs

Preliminary catalytic scouting runs were designed to determine whether mass transfer effects would be rate limiting. Since a low surface area catalyst (1 m^2/g) was used in all runs, pore diffusion limitations were deemed insignificant. This assumption is corroborated using the estimation methods described by Aris (*1*) which show diffusion limitations to be inconsequential. For determining possible external (film) diffusion limitations, the classical test of increasing the superficial velocity while maintaining constant residence time was used. The results of this test are shown in Fig. 3 as a plot of space time against conversion and suggest the absence of external diffusion limitations. These results

TABLE 1

Experimental Conditions

System	Run sequence	Temperature (°C)	Hydrocarbon concentration (mol/std m³)	Oxygen concentration (mol/std m³)
Homogeneous	A	345–440	0.002–0.053	4.16–38.2
V_2O_5/MoO_3	B	350	0.002–0.033	4.16–25.0
V_2O_5/MoO_3	C	275–340	0.003–0.033	4.16–25.0
V_2O_5/MoO_3	D	275–340	0.002–0.034	4.16–25.0

are further substantiated by estimation methods described by Yang and Hougen (*18*) which indicate that both external diffusion limitations and particle temperature gradients are negligible.

At the outset of the program it had been envisioned that the methods of sequential experimental design using posterior probability model discrimination which aid in efficient experimentation would be used. These important but seldom used methods are not discussed in the present paper since several excellent reviews have appeared in the literature (*4, 5, 10, 11*).

Not all the independent variables could be experimentally altered separately, and because it was considerably faster to saturate the experimental space than to iterate between the laboratory and the computer, sequential statistical designs were not followed. However, posterior probability model discrimination was used following preliminary model screening with classical statistical methods. Parameter estimates were obtained using the nonlinear estimation method of Marquardt (*7*).

RESULTS AND DISCUSSION

The major goals of this work were to obtain kinetic data for the heterogeneously catalyzed oxidation of BAP and to find a suitable mechanistic rate model for the reaction. Several empirical rate models were also considered, since this type of model is often useful for interpolative, but not extrapolative, purposes.

Table 1 summarizes the total experimental space observed for the kinetic data. Table 2 represents a summary of the experimental data from run sequences C and D.

Empirical Model

The reactor was assumed to behave as an ideal plug flow integral reactor which is described by

$$\frac{W}{QC_A{}^0} = \int_0^{X_A} \frac{dx_A}{-r_A}. \tag{1}$$

The kinetic data obtained experimentally were used to evaluate parameters in the generalized empirical rate model:

$$-r_A = \phi \exp\left[\frac{-E}{RT}\right] C_A{}^{\alpha} C_0{}^{\beta}. \tag{2}$$

Models of this type are useful for interpolation of kinetic data. However, they are invalid in extrapolation and, of course, do not shed any light on physical understanding of the reaction mechanism. Substituting Eq. (2) into Eq. (1) and performing the integration gives

$$\frac{W}{Q} = \frac{C_A{}^{(1-\alpha)}}{\phi \exp\left\{\dfrac{-E}{RT}\right\} C_0{}^{\beta}} \times [(1 - X_A)^{(1-\alpha)} - 1]. \tag{3}$$

Using the Marquardt method, least-squares

TABLE 2

Summary of Results

Run	C_A (mol/m³)	C_0 (mol/m³)	W (g)	Q (ml/min)	Temperature (°C)	Conversion
C1	0.03289	24.96	0.3704	50	275	0.0410
C2	0.01164	24.96	0.3704	100	340	0.4175
C3	0.01830	24.96	0.3704	100	310	0.1647
C4	0.01459	24.96	0.3704	100	275	0.0966
C5	0.01351	24.96	0.3704	100	275	0.0980
C6	0.00354	24.96	0.3704	100	310	0.2680
C7	0.00366	4.16	0.3704	100	310	0.1673
C8	0.00359	4.16	0.3704	100	275	0.0873
D1	0.02936	8.32	0.4320	100	275	0.0466
D2	0.03398	24.96	0.4320	100	275	0.0465
D3	0.02082	24.96	0.4320	100	310	0.0806
D4	0.00309	24.96	0.4320	100	310	0.2624
D5	0.00287	4.16	0.4320	100	310	0.1622
D6	0.00280	24.96	0.4320	100	275	0.1124
D7	0.00233	24.96	0.4320	100	275	0.1320
D8	0.00240	24.96	0.4320	100	340	0.9590
D9	0.00461	4.16	0.4320	100	340	0.3080
D10	0.00545	24.96	0.4320	100	340	0.9270
D11	0.00664	25.73	0.4320	97	340	0.7480
D12	0.00670	4.24	0.4320	98	340	0.3380
D13	0.00636	25.73	0.4320	97	310	0.2730
D14	0.00611	4.16	0.4320	100	310	0.1140
D15	0.00596	24.96	0.4320	100	275	0.1230
D16	0.00589	4.16	0.4320	100	275	0.1612
D17	0.0080	24.96	0.4320	100	275	0.0870
D18	0.00885	24.96	0.4320	100	310	0.1490
D19	0.00904	24.96	0.4320	100	340	0.5760

estimates were obtained for the apparent reaction orders α and β and the Arrhenius parameters together with their respective approximate 97.5% confidence intervals. These values are shown in Table 3. Positive fractional orders (0.20 ± 0.03 for BAP, and 0.60 ± 0.05 for oxygen) were obtained for both reactants and a relatively large value was obtained for the apparent activation energy (31.9 ± 4.3 kcal/mol).

Mechanistic Models

Historically, the catalytic oxidation data for the few PAH that have been studied favor a single mechanism. This mechanism, which results in the redox model, was first proposed by Mars and van Krevelen (*8*), while a mathematically equivalent mechanism was outlined by Shelstad (*13*). The redox model suggests that the gas phase hydrocarbon reacts rapidly with an oxidized catalyst site to form the reaction products

TABLE 3

Parameter Estimates and Approximate 97.5% Confidence Intervals for $-r_A = \phi \exp\{-E/RT\} C_A{}^{\alpha} C_0{}^{\beta}$ [=] g mol/kg h

Parameter	Estimate
ϕ	$8.3 \pm 1.4 \times 10^9$
E	31.9 ± 4.3 kcal/mol
α	0.20 ± 0.03
β	0.60 ± 0.05

TABLE 4

Kinetic Models

Model	Rate expression	Integrated PFR equation	Comments
M1	$-r_A = kC_0^{\beta}$	$\frac{W}{Q} = C_A^0 X_A / kC_0^{\beta}$	Empirical model Zero order wrt hydrocarbon Empirical order wrt oxygen
M2	$-r_A = kC_A$	$\frac{W}{Q} = -\frac{1}{k}\ln(1 - X_A)$	Empirical model First order wrt hydrocarbon Zero order wrt oxygen
M3	$-r_A = kC_A^{\alpha}$	$\frac{W}{Q} = \frac{C_A^{0(1-\alpha)}}{k(1-\alpha)}\{(1 - X_A)^{(1-\alpha)} - 1\}$	Empirical model Empirical order wrt hydrocarbon Zero order wrt oxygen
M4	$-r_A = kC_A^{\alpha}C_0^{\beta}$	$\frac{W}{Q} = \frac{C_A^{0(1-\alpha)}}{k(1-\alpha)C_0^{\beta}}\{(1 - X_A)^{(1-\alpha)} - 1\}$	Empirical model Empirical order wrt hydrocarbon Empirical order wrt oxygen
M5	$-r_A = kC_AC_0^{\beta}$	$\frac{W}{Q} = -\frac{1}{kC_0^{\beta}}\ln(1 - X_A)$	Empirical model First order wrt hydrocarbon Empirical order wrt oxygen
M6	$-r_A = \frac{k_1C_Ak_2C_0}{Nk_1C_A + k_2C_0}$	$\frac{W}{Q} = \frac{C_A^0 X_A}{(k_2/N)C_0} - \frac{1}{k_1}\ln(1 - X_A)$	Redox model Oxygen adsorbs irreversibly onto catalyst surface Gas phase hydrocarbon reacts with adsorbed oxygen Oxygen adsorption is the rate-controlling step

TABLE 4—*Continued*

Model	Rate expression	Integrated PFR equation	Comments
M7	$-r_A = \dfrac{k_1C_Ak_2C_0}{[k_2C_0 + (k_1k_2/k_3)C_AC_0 + k_1C_A]}$	$\dfrac{W}{Q} = C_A{}^0X_A\left(\dfrac{1}{k_3} + \dfrac{1}{k_2C_0}\right) - \dfrac{1}{k_1}\ln(1 - X_A)$	[*S*–] + oxygen → [*S*–0][a] [*S*–0] + hydrocarbon → [hyd.–*S*–0] [hyd.–*S*–0] → [*S*–] + products
M8	$-r_A = \dfrac{kC_A}{1 + kC_A}$	$\dfrac{W}{Q} = C_A{}^0X_A - \dfrac{1}{k_1}\ln(1 - X_A)$	Langmuir adsorption model Assuming hydrocarbon reversibly adsorbs on catalyst surface Rate is proportional to surface fraction covered Independent of oxygen concentration
M9	$-r_A = \dfrac{k_1C_Ak_2C_0{}^\beta}{(1 + k_1C_A)}$	$\dfrac{W}{Q} = \dfrac{1}{k_2C_0{}^\beta}\left\{C_A{}^0X_A - \dfrac{1}{k_1}\ln(1 - X_A)\right\}$	Langmuir adsorption model as above but assuming empirical gas phase oxygen dependence
M10	$-r_A = \dfrac{k_1k_2C_AC_0}{(k_3 + k_1C_A + k_2C_0)}$	$\dfrac{W}{Q} = \dfrac{C_A{}^0X_A}{k_2C_0} - \left(\dfrac{k_3 + k_2C_0}{k_1k_2C_0}\right)\ln(1 - X_A)$	Redox model assuming reversible oxygen adsorption
M11	$-r_A = \dfrac{k_1C_Ak_2C_0{}^{\frac{1}{2}}}{Nk_1C_A + k_2C_0{}^{\frac{1}{2}}}$	$\dfrac{W}{Q} = \dfrac{C_A{}^0X_A}{(k_2/N)C_0{}^{\frac{1}{2}}} - \dfrac{1}{k_1}\ln(1 - X_A)$	Redox model assuming rate of oxygen adsorption is ½ order wrt oxygen
M12	$-r_A = \dfrac{k_1k_2k_3C_AC_0}{(1 + k_2C_A + k_3C_0)^2}$	$\dfrac{W}{Q} = \dfrac{2C_A{}^0}{k_1k_3C_0} \times \left\{\left(1 + k_3C_0 + \dfrac{1}{2}k_2C_A{}^0\right)X_A - \dfrac{1}{4}k_2C_A{}^0X_A{}^2 - \dfrac{(1 + k_3C_0)^2}{2k_2C_A{}^0}\ln(1 - X_A)\right\}$	Langmuir–Hinshelwood dual-site model assuming both reactants adsorbed on catalyst surface with reaction occurring between adsorbed species
M13	$-r_A = \dfrac{k_1k_2C_AC_0}{1 + k_2C_0}$	$\dfrac{W}{Q} = \dfrac{1}{k_1}\left(1 + \dfrac{1}{k_2C_0}\right)\ln(1 - X_A)$	Langmuir–Rideal model assuming equilibrium oxygen adsorption and reaction with gas phase hydrocarbon molecule

[a] *S*, site; O, oxygen; hyd., hydrocarbon.

and that additional gas phase oxygen then slowly adsorbs onto the reduced site (S).

$$\text{Hydrocarbon} + [S\text{–}0] \xrightarrow[\text{fast}]{r_1} \text{Products} + [S\text{–}] \quad (4)$$

$$[S\text{–}] + \text{oxygen} \xrightarrow[\text{slow}]{r_2} [S\text{–}0] \quad (5)$$

From the above mechanism, if it is assumed that N moles of oxygen are required per mole of hydrocarbon for the oxidation reaction, it can be shown that

$$-r_A = \frac{k_1 C_A k_2 C_0{}^{\alpha}}{N k_1 C_A + k_2 C_0{}^{\alpha}}. \quad (6)$$

Sampson and Shooter (*12*) have suggested that the catalyst reoxidation could occur from oxygen present either in the monatomic or molecular states: for the monatomic process $\alpha = \frac{1}{2}$; for the molecular process $\alpha = 1$. To date, the majority of studies have favored model adequacy when $\alpha = 1$.

In the present study the 12 additional models shown in Table 4 were also evaluated, many of which were considered by Subramanian and Murthy (*16*) in their work an anthracene oxidation. Many of these equations are implicit in the true response variable (X_A) and consequently a half-section search routine was incorporated into the Marquardt routine. For each of these models, best estimates (least-squares) of the parameters were obtained, and the classical statistical model discrimination techniques of variance ratio and residual bias were applied (*2*). The results of this procedure are given in Table 5. Only Models 1, 4, 6, and 7 remained statistically viable after this preliminary discrimination procedure. Models 1 and 4 are empirical, while Model 6 is the redox model with $\alpha = 1$, and Model 7 is a redox-type model with the additional assumption that the hydrocarbon adsorbs onto the activated site before reaction products can be formed. Table 5 shows that among these four models the general empirical model (Model 4) had the lowest residual sum of squares (0.052), while the two-stage redox model (Model 6) had the highest residual sum of squares (0.074). Since it was the primary intention of the present study to determine the best mechanistic model, Models 1 and 4 were eliminated from further evaluation, and a posterior probability discrimination (*2*) was carried out on the two remaining mechanistic models.

After 27 runs, the posterior probability in favor of the classical redox model (Model 6) was found to be 0.935. Thus,

TABLE 5

Preliminary Model Discrimination

Model	SSQ	Bias	s_R	s_R^2/s_e^2	$F_{0.025}$
M1	0.061	—	0.062	1.54	4.08
M2	0.468	All	0.166	11.02	4.06
M3	0.372	All	0.152	9.24	4.08
M4	0.052	—	0.059	1.39	4.10
M5	0.177	All	0.105	4.41	4.08
M6	0.074	—	0.070	1.96	4.10
M7	0.053	—	0.064	1.64	4.17
M8	0.461	All	0.165	10.89	4.06
M9	0.171	All	0.112	5.02	4.13
M10	0.074	C_0	0.075	2.25	4.17
M11	0.467	All	0.177	12.53	4.10
M12	0.169	All	0.114	5.10	4.17
M13	0.173	All	0.108	4.67	4.17

TABLE 6

Parameter Estimates and Approximate 97.5% Confidence Intervals for $-r_A = [(\exp\{\ln \phi_2^* - E_2/R(1/T - 1/T')\})^{-1} + (\exp\{\ln \phi_1^* - E_1/R \times (1/T - 1/T')\})^{-1}]^{-1}$

Parameters	Estimates
$\phi_1^* = \phi_1 \exp\left(\frac{-E_1}{RT'}\right)$	2.21 ± 0.30
E_1	39 ± 12 kcal/mol
$\phi_2^* = \frac{\phi_2}{N} \exp\left(\frac{-E_2}{RT'}\right)$	-6.21 ± 0.35
E_2	21 ± 8 kcal/mol
T'	583°K

this model with a molecular oxygen adsorption process appears to be mechanistically heavily favored for the oxidation of BAP over the mixed vanadia–molybdena catalyst.

For estimation of the Arrhenius parameters in the redox model the rate constants were reparameterized according to

$$k = \phi \exp\left\{\frac{-E}{RT}\right\}$$

$$= \exp\left\{\ln \phi^* - E/R\left(\frac{1}{T} - \frac{1}{T'}\right)\right\}. \quad (7)$$

Table 6 shows the values obtained for the parameter estimates together with the confidence intervals. It was not possible to determine the stoichiometric coefficient, N, since the spectrum of oxidation products was not totally determined. Hence, a lumped parameter, ϕ_2/N, the Arrhenius pre-exponential factor for the oxygen adsorption step, was obtained.

The numerical value of 21 kcal/mol obtained in this study for E_2 (the activation energy for the oxygen adsorption process involved in the catalytic oxidation of BAP) compares favorably with the value of 22 kcal/mol obtained by Mars and van Krevelan (*8*) when they used the redox model to explain oxidation kinetics of several aromatic hydrocarbons over a mixed vanadia–molybdena catalyst. Furthermore, Stanislaus *et al.* (*14*) studied the chemisorption of oxygen on a commercial vanadium pentoxide catalyst and obtained an activation energy for the process of 21 kcal/mol, again in agreement with present results.

CONCLUSIONS

Experimental data for the oxidation of benzo(*a*)pyrene (BAP) over a mixed vanadia–molybdena catalyst are adequately correlated by the redox mechanistic model which implies oxygen adsorption as the limiting process. This observation is in good agreement with previous investigations of aromatic hydrocarbon oxidation over vanadia–molybdena type catalysts.

NOTATION

C	Reactant concentration
E	Activation energy
k	Rate constant
N	Stoichiometric coefficient
Q	Flow rate
r	Reaction rate
R	Gas law constant
$[S-]$	Catalyst site in reduced state
$[S-0]$	Catalyst site in oxidized state
T	Absolute temperature
W	Weight of catalyst
X	Fractional conversion
α, β	Reaction order
ϕ	Arrhenius pre-exponential factor

Subscripts

A	Aromatic hydrocarbon
0	Oxygen
1, 2, 3	Reaction mechanism steps

Superscripts

0	Initial values
*	Reparameterized
′	Reference value

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