Influence of Site Energy Distribution on Catalytic Rates with Multicomponent Chemisorption

Without using the assumption of constancy of mole fractions in adsorption space, dual-component adsorption accompanied by catalytic reaction on a heterogeneous surface is modeled. A simple parallel reaction scheme which is supposed to idealize key steps in cracking and disproportionation reactions is studied. Quantities of interest in catalytic kinetics such as mean surface coverage, mean squared surface coverage, and others are calculated as statistical averages over the bivariate analogs of four well-known monovariate distributions, with the assumption of realistic heats of adsorption. Using a variant of the Mellin transform method proposed earlier, explicit expressions for the rates are given as functions of partial pressure ratio and the parameters characterizing the site energy distribution. Methods are proposed to determine the characteristic ratio of partial pressures at which a desired selectivity pattern is realized. Lastly, two reaction schemes which outline key steps in platforming and reforming reactions and which occur on bifunctional catalysts are analyzed and methods for determining the characteristic pressure ratio are suggested.

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SCOPE

In many industrially important catalytic reactions surface concentrations of more than one species have to be accounted for in determining the kinetics. While many studies have been carried out in the realm of physical adsorption (Tompkins and Young, 1951; Jaroniec et al., 1978), there exist only a few studies in multicomponent chemisorption. In addition, nonidealities in adsorption such as the influence of site energy distribution on the kinetics of the overall reaction have not been considered in sufficient detail. A previous study in mixed gas adsorption on hetrogeneous surfaces assumed constancy of mole fractions in the adsorption space for the two components. While such an assumption may be justified in the case of physical adsorption, it is invalid in chemisorption where the heats of adsorption of the two components vary widely. Nevertheless, the assumption has the advantage of simplifying the mathematics of the problem (Temkin, 1979).

In the present study two-component adsorption is studied, and bivariate distributions which are analogous to the well studied one-component distributions are proposed to describe two-component adsorption. The fractional coverages for the entire surface are then expressed as statistical averages over the bivariate distributions.

Using the randomly distributed patch model of the catalyst surface, a Langmuir type isotherm (denoted as local isotherm) is assumed to describe adsorption on each of the patches. Interaction effects between each of the components are assumed to contribute only negligibly to the heats of chemisorption.

Often, for mathematical convenience and also to make the resulting isotherms independent of the limits chosen, the assumption of 0 and ∞ as the limits of heat of adsorption is made. In the present study, however, finite limits are chosen which are representative of and in conformity with experimentally observed differential heat values.

First a relatively simple reaction scheme on a monofunctional catalyst is analyzed. Although the reaction scheme is hypothetical, it is believed that it could represent key steps in cracking and disproportionation reactions. The principal parameter used in the analysis is the characteristic ratio of partial pressures at which a desired selectivity is achieved. This is related to the parameters of the bivariate analogs of four well-known monovariate site energy distributions: (1) positive exponential distribution, (2) constant distribution, (3) negative exponential distribution, and (4) skewed Gaussian distribution.

In the industrially important catalytic reforming reaction the catalyst often consists of two different functions, namely an acid function for effecting isomerization and a hydrogenation/dehydrogenation function. Two such reaction schemes which occur on a bifunctional catalyst are analyzed. In one scheme, sequences of irreversible second-order reactions are considered; in the other a first-order series reaction with both irreversible and reversible steps is analyzed. The theory is illustrated for the same distributions mentioned earlier. Since in actual practice not more than two surface concentrations enter into the kinetic expressions, it is hoped that the theory developed here will find application in a variety of situations encountered in industrial practice. As far as possible, explicit expressions for the rates are derived as functions of pressures and the parameters characterizing the distributions.

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CONCLUSIONS AND SIGNIFICANCE

The influence of site energy distribution on catalytic rates and selectivity is investigated for the case of dual-component chemisorption. Without the restrictive assumption of constancy of mole fractions in the adsorption space, quantities which are of immediate importance in kinetic expressions such as mean surface coverages, mean squared surface coverages, and others are calculated as statistical averages over four bivariate distributions. A variant of the Mellin transform method which was proposed earlier is used to derive expressions for the rates and selectivities. A simple parallel reaction scheme which idealizes key steps in cracking and disproportionation reactions has been modeled. Wherever possible, explicit expressions for the rates and selectivity are derived as functions of the parameters characterizing the site energy distribution and the partial pressure ratio γ. Methods are suggested to determine the characteristic ratio of partial pressures at which a desired selectivity pattern is realized.

The positive exponential distribution predicts the lowest and the negative exponential predicts the largest γ values. Since the parameter defining the differential heat at zero coverage (Q_M) can easily be determined from a few differential heat measurements, the selectivity pattern over a wide range of partial pressure ratios γ can easily be predicted. Further the reaction rate for a bimolecular step rises steeply over a narrow range of γ values for the homogeneous surface compared to the heterogeneous surface. A table of γ values calculated for the uniform and heterogeneous surfaces (which show good divergence) is presented. We get maximal values of the surface rate by operating at these γ values.

Two industrially important reactions, namely reforming and platforming (schemes II and III), have been modeled. The selectivity behavior of the dual-function catalysts with an isomerization function and a hydrogenation/dehydrogenation function has been studied. Explicit expressions for the rates are given as a hypergeometric series in the partial pressure ratio and the parameters defining the site energy distributions.

For reaction scheme II, which involves X and Y groups of sites, one of the products R is preferentially obtained at lower γ values. A slight shift in the ratio of surface kinetic constants causes a remarkable change in the γ values required for equal selectivities. The divergence between the site energy distributions is maximum at higher γ values.

For reaction scheme III the intermediate product B is preferentially obtained at higher γ values. For this model also divergence between the positive and negative exponential distribution is maximum. Further, γ is a strong function of the ratio of surface reaction kinetic constants.

One surprising feature of the present work is that two functionally different distributions are shown to exhibit nearly identical selectivity behavior. This is illustrated by the constant and skewed Gaussian distributions. This fact highlights the difficulties involved in uniquely determining the site energy distribution from experimental data.

In practice, as not more than two surface concentrations enter into the kinetic expressions for the steady state rates, it is hoped that the theory developed herein will find a variety of applications in modeling catalytic reaction sequences on heterogeneous surfaces.

INTRODUCTION

Quantitative description of multicomponent adsorption on energetically heterogeneous surfaces is an exceedingly difficult problem. The random patch model of the surface has found considerable utility in describing one-component adsorption (Halsey and Taylor, 1947; Rudnitsky and Alexeyev, 1975; Temkin, 1967; Prasad and Doraiswamy, 1977, 1983a,b), and to a limited extent this has been applied to two-component adsorption as well (Jaroniec et al., 1978).

In the random patch model the surface is assumed to consist of a collection of homottatic (energically uniform) patches randomly distributed. Adsorption equilibrium is assumed to prevail on each of the patches and a local isotherm relates the local surface coverage on the patch to pressure and temperature. The mean surface coverage is then calculated as a statistical average over the site energy distribution function, after making reasonable assumptions about the nature of site energy distributions, local isotherms, and the limits of heat of adsorption.

A rigorous calculation of statistical averages, which are required in the kinetic expressions for fractional surface coverages, would involve multivariate distributions. In an earlier study of two-component adsorption, constancy of mole fractions in the adsorption space was presupposed (Temkin, 1979). This assumption, which results in considerable simplification of the problem (bivariate distribution becomes monovariate), can be justified only in physisorption. In chemisorption, where the heats of adsorption of both components vary widely, the assumption becomes too restrictive. But this assumption makes the mathematics of the problem simpler, as we are essentially dealing with monovariate distributions (Temkin, 1979) and closed analytical expressions are possible with the assumption of an infinite upper limit of heat of adsorption.

Temkin's assumption of constancy of mole fractions is advantageous in treating tricomponent or multicomponent chemisorption, as trivariate or multivariate distributions have to be postulated for the statistical treatment. However in most catalytic kinetic studies not more than two surface concentrations enter into the rate expressions. Besides, it is useful to explore the functional relationships between selectivity and the site energy distributions. In the supplementary material it is shown that approximate analytical expressions are possible for the bivariate distribution, a prerequisite for the quantitative treatment (see note at the end of this paper).

We propose bivariate analogs of the four site energy distributions:

1. Positive exponential distribution (Temkin, 1967; Rudnitsky and Alexeyev, 1975)

$$\delta(Q_A,Q_b) = \frac{\exp(Q_A/Q_M)\exp(Q_B/Q_M)}{Q_M^2[\exp(Q_{A2}/Q_M) - \exp(Q_{A1}/Q_M)][\exp(Q_{B2}/Q_M) - \exp(Q_{B1}/Q_M)]} \tag{1}$$

2. Constant distribution (Temkin and Pyzev, 1940)

$$\delta(Q_A,Q_B) = \frac{1}{(Q_{A2} - Q_{A1})(Q_{B2} - Q_{B1})} \tag{2}$$

3. Negative exponential distribution (Rudnitsky and Alexeyev, 1975)

$$\delta(Q_A,Q_B) = \frac{\exp(-Q_A/Q_M)\exp[-Q_B/Q_M]}{Q_M^2[\exp(-Q_{A1}/Q_M) - \exp(-Q_{A2}/Q_M)][\exp(-Q_{B1}/Q_M) - \exp(-Q_{B2}/Q_M)]} \quad (3)$$

4. Skewed Gaussian distribution (Sparnaay, 1968; Misra, 1969; Jaroniec, 1975)

$$\delta(Q_A,Q_B) = \frac{Q_A Q_B[\exp(-Q_A^2/2Q_M^2)][\exp(-Q_B^2/2Q_M^2)]}{Q_M^4[\exp(-Q_{A1}^2/2Q_M^2) - \exp(-Q_{A2}^2/2Q_M^2)][\exp(-Q_{B1}^2/2Q_M^2) - \exp(-Q_{B2}^2/2Q_M^2)]} \quad (4)$$

All these distributions have been extensively used for studying one-component adsorption on heterogeneous surfaces.

THEORETICAL BASIS

The statistical averages such as mean fractional coverage are easily related to the bivariate site energy distribution:

$$\bar{\theta}_A = \int_{Q_{A1}}^{Q_{A2}} \int_{Q_{B1}}^{Q_{B2}} \theta_{1i}^A(Q_A,Q_B)\delta(Q_A,Q_B)dQ_A dQ_B \quad (5)$$

where $\theta_{1i}^A(Q_A,Q_B)$ denotes the fractional coverage of A on the ith patch which is a function of temperature and pressure; $\delta(Q_A,Q_B)$ is the bivariate site energy distribution function; Q_{A1}, Q_{A2} and Q_{B1}, Q_{B2} are the lower and upper heats of adsorption for species A and B respectively.

The ideal Langmuir model for two-component adsorption will be assumed. This implies negligible interaction between the adsorbed molecules, an assumption which can be justified for many experimental systems (de Boer, 1953). We thus have

$$\theta_{1i}^A(Q_A,Q_B) = \frac{1}{1 + (b_{oA}/p_A)\exp(-Q_A/RT)[1 + (p_B/b_{oB})\exp(Q_B/RT)]} \quad (6)$$

We further make the simplifying assumption that $b_{oA} = b_{oB}$, i.e., entropy change factors (referred to the standard state of $\theta_A = 0.5$), are the same for both components and the variation of b_o with heat of adsorption is negligible. The latter assumption has been shown to be correct for one-component adsorption (Hoory and Prausnitz, 1967).

An examination of the site energy distributions from Eqs. 1–4 shows that they can be represented as

$$\delta(Q_A,Q_B) = \delta_A(Q_A)\delta_B(Q_B) \quad (7)$$

In other words, statistical independence of Q_A,Q_B is assumed for all the patches. This assumption makes the mathematical analysis simpler.

APPLICATION TO A BIMOLECULAR REACTION ON A MONOFUNCTIONAL CATALYST

We now analyze a relatively simple reaction scheme to illustrate the influence of site energy distribution.

Scheme I

$$A_g \underset{k_{dA}}{\overset{k_{aA}}{\rightleftharpoons}} A_s \quad B_g \underset{k_{dB}}{\overset{k_{aB}}{\rightleftharpoons}} B_s$$

$$A_s + B_s \xrightarrow{k_{r1}} P_1$$

$$A_s + A_s \xrightarrow{k_{r2}} P_2$$

It is assumed that on each of the patches surface reactions are controlling and adsorption equilibrium prevails between gas and surface species for the molecules A and B. Further, molecules P_1 and P_2 are desorbed so rapidly as to make their surface concentrations effectively zero.

Before we pursue the question of selectivity, in order to illustrate the difference between homogeneous and heterogeneous surfaces, let us assume $k_{r2} = 0$ in scheme I. We are thus essentially dealing with a simple reaction. Then it is required to find the partial pressure ratio $\gamma = p_B/p_A$ such that r_{P1} is maximum. For a uniform surface we have

$$r_{P1}^u = k_{r1}\theta_A^u\theta_B^u \quad (8)$$

$$\theta_A^u = \{1 + (b_{oA}/p_A)\exp(-\bar{Q}_A/RT)[1 + (p_B/b_{oB}) \times \exp(\bar{Q}_B/RT)]\}^{-1} \quad (9)$$

$$\theta_B^u = \{1 + (b_{oB}/p_B)\exp(-\bar{Q}_B/RT) \times [1 + (p_A/b_{oA})\exp(\bar{Q}_A/RT)]\}^{-1} \quad (10)$$

where the superscript u denotes a uniform surface.

For the heats Q_A^u, Q_B^u of the uniform surface, we choose $\bar{Q}_A,\bar{Q}_B$ calculated as statistical averages over Eq. 7. (In principle, we could choose any value $Q_{A1} \leqslant Q_A^u \leqslant Q_{A2}$, $Q_{B1} \leqslant Q_B^u \leqslant Q_{B2}$ for comparison purposes.) It is possible to have for Q_A^u and Q_B^u common values for the uniform surface instead of the statistical averages calculated using Eq. 7. If statistical average is used, as in the present work, then the negative exponential distribution has the lowest average heat and hence the highest γ value.

Since the maximum surface coverage possible is 0.5 for θ_A^u or θ_B^u, the optimal value of the partial pressure ratio γ such that $\theta_A^u = \theta_B^u = 0.5$ is given by

$$\gamma^u = \frac{p_B}{p_A} = \frac{K_A^u}{K_B^u} = \frac{b_{oB}\exp(\bar{Q}_B/RT)}{b_{oA}\exp(\bar{Q}_A/RT)} \quad (11)$$

On the other hand, if we write the rate r_{P1} in terms of the mean surface concentration for a heterogeneous surface, we have

$$r_{P1} = k_{r1}\bar{\theta}_A\bar{\theta}_B \quad (12)$$

where we calculate $\bar{\theta}_A$, $\bar{\theta}_B$ using equations similar to Eq. 5. (Customarily we write the kinetic expressions in terms of $\bar{\theta}_A$, $\bar{\theta}_B$. If methods are available for the direct measurement of surface concentrations, then they constitute an independent check on the kinetic model. However this is seldom possible in an actual experiment and hence the importance of adsorption isotherms relating the gas and surface concentrations. It is understood that for a het-

TABLE 1. COMPARISON OF γ OF DIFFERENT DISTRIBUTIONS FOR HETEROGENEOUS AND HOMOGENEOUS SURFACES AT p = 266.64 Pa

Distribution Type	γ for Heterogeneous Surface	γ for Homogeneous Surface
Temkin	0.25	0.49
Freundlich	2.50	2.00
Temkin-Pyzev	0.87	1.00
Dubinin-Radushkevich	0.84	0.96

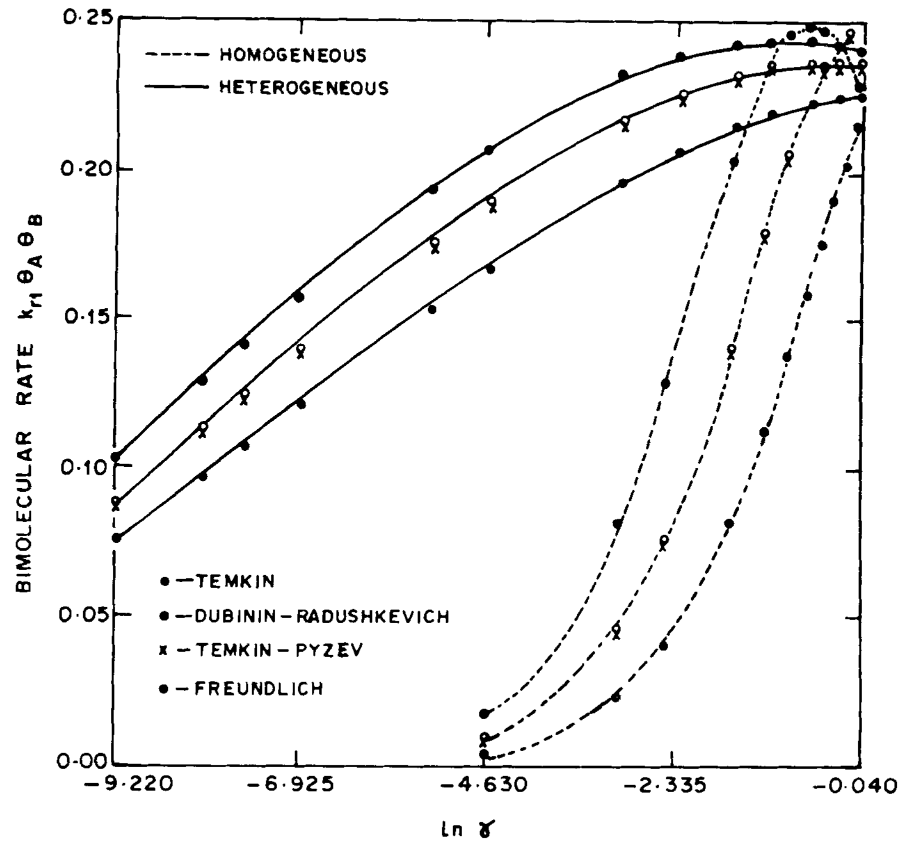


Figure 1. Bimolecular rate (arbitrary units) vs. lnγ for four distributions and comparison of homogeneous and heterogeneous surfaces. For the equivalent heats $\bar{Q}_A, \bar{Q}_B$ of the homogeneous surface heat values averaged over the site energy distribution used:

$Q_{A1} = 17 \quad Q_{A2} = 31 \quad Q_M = 24 \quad Q_{B1} = 14 \quad Q_{B2} = 34 \quad k_{r1} = 1 \quad P = 266.64$ Pa $\quad b_{oA} = 1E8 \times 133.32$ Pa

erogeneous surface the isotherms relate the mean surface coverages and the partial pressures of the individual components.) Closed form analytical expressions are possible for predicting the selectivity in the case of the homogeneous surface, while such expressions are possible only in a narrow range of pressures for the heterogeneous surface. An approximate analytical representation of the double integral is possible. The details are worked out in the supplementary material. Also, for the various pressure ranges of $\underline{p}_A$ different analytical expressions are needed for expressing $\bar{\theta}_A$, $\bar{\theta}_B$. The hypergeometric series and its analytical continuation formulae are given in the supplementary material.

The statistical averages $\bar{\theta}_A$, $\bar{\theta}_B$ can also be computed by straightforward numerical integration. The integrations are performed with a precision of 1 in 10^6. Integration over one dimension can easily be effected analytically, then over the second dimension the computation can be done numerically. This itself results in considerable saving of computer time. Table 1 gives the values of γ for a heterogeneous surface compared to a homogeneous surface with $p = 266.64$ Pa, which is a typical value for many rate studies. Even though this may be a sufficiently low value in comparison with the actual values of pressures employed in industrial practice, for the choice of the limits of heats of adsorption for the two components A,B, adopted in the present work, $\bar{\theta}_A + \bar{\theta}_B \cong 1$. Hence any further increase in γ or total pressure would not affect the total surface coverage to any appreciable extent.

For the values of limits of heat of adsorption chosen, the negative exponential distribution gives the largest value of γ and the positive exponential distribution the lowest. It is easily seen that at the value of total pressure chosen the difference between the γ values can be used to discriminate between the different candidate distributions. Also the divergence between γ values is maximum for the positive exponential distribution. In Figure 1 the bimolecular rate r_{P1} is plotted against lnγ for the four distributions. The constant and skewed Gaussian distributions display almost identical pressure dependence. The behavior of the uniform surface is also illustrated. The homogeneous surface shows a steep rise in the values of the bimolecular rates in a narrow range of γ values compared to the heterogeneous surface. Consequently the pressure derivatives of the rates are higher for the homogeneous surface in contrast to the heterogeneous.

The Q_M values in the distributions are chosen such that the differential heat at zero coverage approaches the upper limit of heat of adsorption when we consider only one-component adsorption. In general, $Q_M \geq 15$ is necessary especially for the negative exponential distribution. For comparison purposes the other distributions are also assumed to have the same Q_M values. In Figure 2 the averages $\bar{\theta}_A$, $\bar{\theta}_B$ are plotted against lnγ for various values of Q_M. For larger Q_M values ($Q_M \gg 23$) the selectivity patterns are almost identical. It is as if a wrong choice of the site energy distribution would not matter at all.

We now pursue the case for $k_{r2} \neq 0$. If we refer to reaction scheme I, we have the selectivities for P_1,P_2 (denoted by S_1,S_2 respectively) expressed as

$$S_1 = k_{r1}\bar{\theta}_A\bar{\theta}_B/[k_{r1}\bar{\theta}_A\bar{\theta}_B + k_{r2}\bar{\theta}_A{}^2] \tag{12}$$

$$S_2 = k_{r2}\bar{\theta}_A{}^2/[k_{r1}\bar{\theta}_A\bar{\theta}_B + k_{r2}\bar{\theta}_A{}^2] \tag{13}$$

In order to illustrate further the theory and also the difference

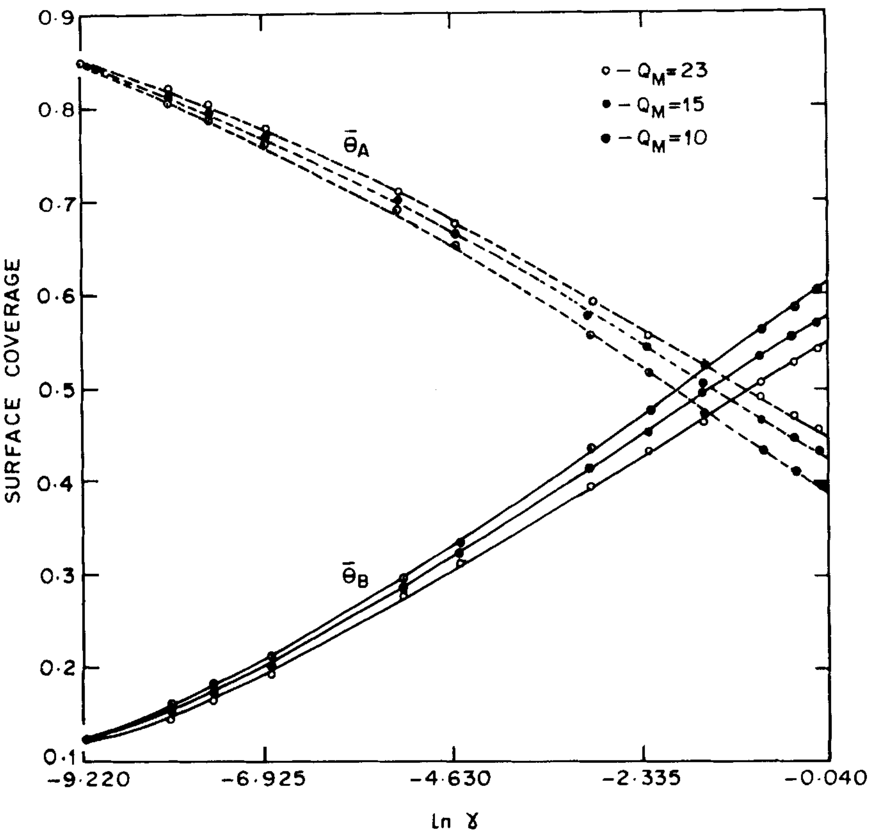


Figure 2. Mean fractional surface coverage vs. lnγ for the Temkin distribution for three Q_M values.

between the behavior of homogeneous and heterogeneous surfaces we arbitrarily choose $S_1 = LS_2$ as the desired pattern to be realized, for $0 < L \leq 1$. For the case of $S_1 = S_2$ we have

$$\bar{\theta}_B/\bar{\theta}_A = k_{r2}/k_{r1} \tag{14}$$

For a pressure $p_A \geq 266.64$ Pa (which is typical of many catalytic experiments) we can approximate $\bar{\theta}_A + \bar{\theta}_B \cong 1$ (in our numerical experiments this value is greater than 0.98). So Eq. 14 can be rewritten as

$$\bar{\theta}_A \cong k_{r1}/(k_{r1} + k_{r2}) \tag{15}$$

For this chosen value of (k_{r1}/k_{r2}), γ can be found by the crossover point of the S_1, S_2 plots. A similar expression for θ_A^u can be readily written from which the value of γ can be calculated for the homogeneous surface as

$$\gamma^u = (k_{r2}/k_{r1})(b_{0B}/b_{0A})\exp[(\bar{Q}_B - \bar{Q}_A)/RT] \tag{16}$$

In Figures 3 and 4 we plot S_1 and S_2 against ln γ at a total pressure of 266.64 Pa, for k_{r1}/k_{r2} ratios of 0.5 and 0.8. The characteristic pressure values for which $S_1 = S_2$ can be easily read from the abscissa. Even with two bimolecular reactions, the characteristic ratio of partial pressures shows appreciable divergence as reflected in the γ values measured at the abscissa of the crossover points of the S_1, S_2 curves (Figure 3). The steep fall in the S_1 curves in a narrow range of values may be noted.

If we compare the characteristic γ's for the uniform and heterogeneous surfaces, as before the divergence between these values is maximum for the positive exponential distribution, minimum for the negative exponential distribution, with constant and the skewed Gaussian distributions showing intermediate values.

If we consider a single-reaction example and consider the γ needed for maximum rates and the case of two parallel bimolecular reactions (as reflected in the γ values needed to realize a desired selectivity), a few interesting observations can be made. Thus for the single reaction case the difference in γ values between the homogeneous and heterogeneous surfaces can be as much as a factor of 2. In contrast to this, for the two-reaction example (Figure 3) for the positive exponential distribution, γ can be affected by a factor of 80 (as measured for the $S_1 = S_2$ criterion). Thus, by approximate choice of the selectivity criterion the effects of surface heterogeneity can readily be examined in an experimental program.

If we compare Figures 3 and 4, for $k_{r1}/k_{r2} = 0.5$ we have $\gamma_{\text{het}}/\gamma_{\text{hom}} = 80$, while for $k_{r1}/k_{r2} = 0.8$ $\gamma_{\text{het}}/\gamma_{\text{hom}} = 7.2$, illustrating the drastic dependence of the characteristic γ on the ratio of the kinetic constants.

Similar results can easily be observed by keeping γ constant and increasing the total pressure. Hence we do not present results for the variation of total pressure p_o at constant γ.

ADSORPTION BEHAVIOR OF DUAL FUNCTION CATALYSTS

In this section we analyze two complex reaction schemes (II and III) to study the effects of multicomponent chemisorption on dual function catalysts. Schemes II and III are complementary in forming a complete picture of reforming.

It may be noted that reforming is a rather general term where any metal function of the VIIIth group (Ru, Os, Rh, Ir, Pd, etc.) may be used. It is impossible to model the entire reaction sequences involved in platforming or reforming. But we believe that at least some of the key steps involved therein can be modeled. Thus re-

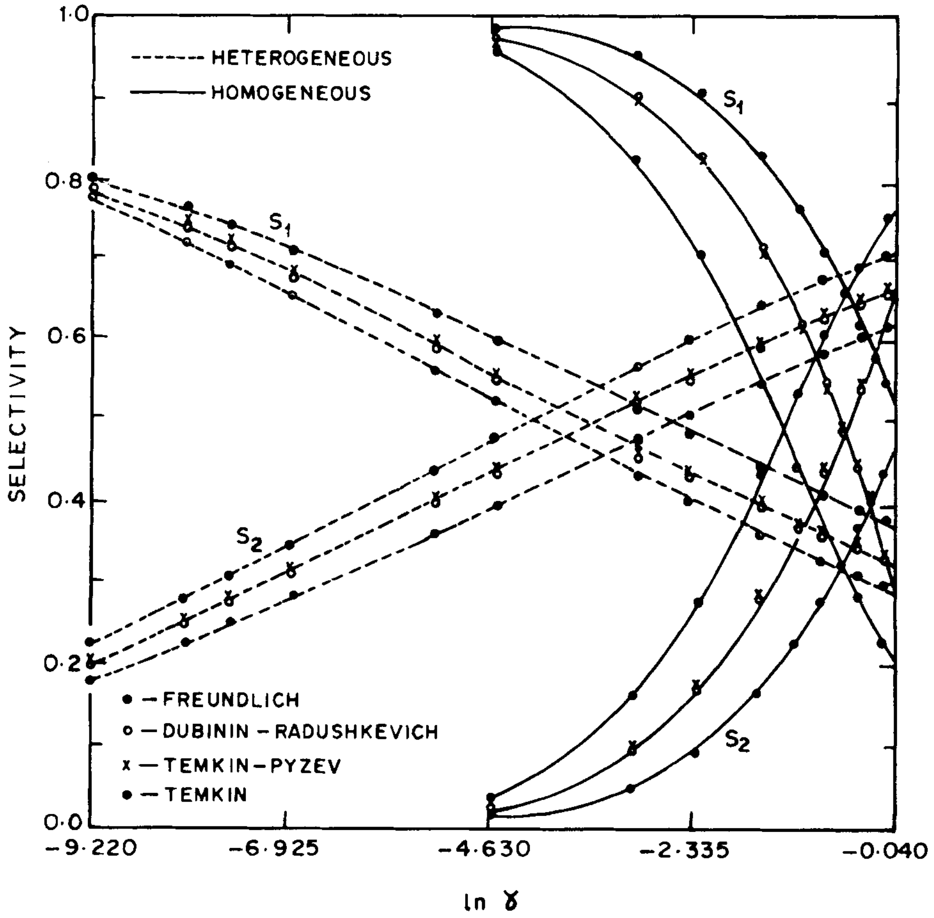


Figure 3. Selectivity for products P_1 and P_2 against lnγ for both homogeneous and heterogeneous surfaces.
Q_{A1} = 17 Q_{A2} = 31 Q_M = 24 Q_{B1} = 14 Q_{B2} = 34 P = 266.64 Pa k_{r1}/k_{r2} = 0.5 $b_{oA} = b_{oB}$ = 1E8 × 133.32 Pa

action schemes II and III can be thought of as complementary in forming a complete picture of reforming.

Scheme II: Skeletal Isomerization; Disproportionation and Alkylation

X sites

$$A_g \underset{k_{dA}}{\overset{k_{aA}}{\rightleftharpoons}} A_s$$

$$B_g \underset{k_{dB}}{\overset{k_{aB}}{\rightleftharpoons}} B_s$$

$$B_s \xrightarrow{k_{2X}} C_g$$

Y sites

$$B_g \underset{k'_{dB}}{\overset{k'_{aB}}{\rightleftharpoons}} B_s$$

$$C_g \xrightarrow{k'_{aC}} C_s$$

$$B_s + B_s \xrightarrow{k_{1Y}} R$$

$$B_s + C_s \xrightarrow{k_{2Y}} P$$

The overall reactions are

$$B \rightarrow C$$

$$2B \rightarrow R$$

$$B + C \rightarrow P$$

It is difficult to give a ready example for illustrating reaction scheme II which is essentially hypothetical. $B \rightarrow C$ can be thought of as occurring by a skeletal isomerization of the aromatics by the metal on the X group of sites and disproportionation and alkylation by the acidic Y group of sites. It is possible to account for cracking on Y group of sites by adding a first-order term in surface concentration.

Adsorption equilibrium is assumed to prevail in each group of patches (either X or Y type patches), for both reactants and A and B are assumed to be in adsorption equilibrium. Surface processes are assumed to be slow compared to the adsorption-desorption rates. We assume that the species C_g is transported through the gas phase from X group to Y group of sites. We neglect the role of diffusion in this transport process.

At steady state we have for C_g, C_s the following equations:

$$\frac{dC_g}{dt} = k_{2X}\bar{\theta}_{BX} - k'_{aC}C_g = 0 \tag{17a}$$

$$\frac{dC_s}{dt} = k'_{aC}C_g - k_{2Y}\bar{\theta}_{BY}\bar{\theta}_{CY} = 0 \tag{17b}$$

The prime represents adsorption coefficients on the second group of Y sites and the overbar denotes an averaging within the framework of scheme II. We can write the overall rates of formation r_R and r_P as

$$r_R = k_{1Y}\bar{\theta}^2_{BY} \tag{18}$$

$$r_P = k_{2X}\bar{\theta}_{BX} \tag{19}$$

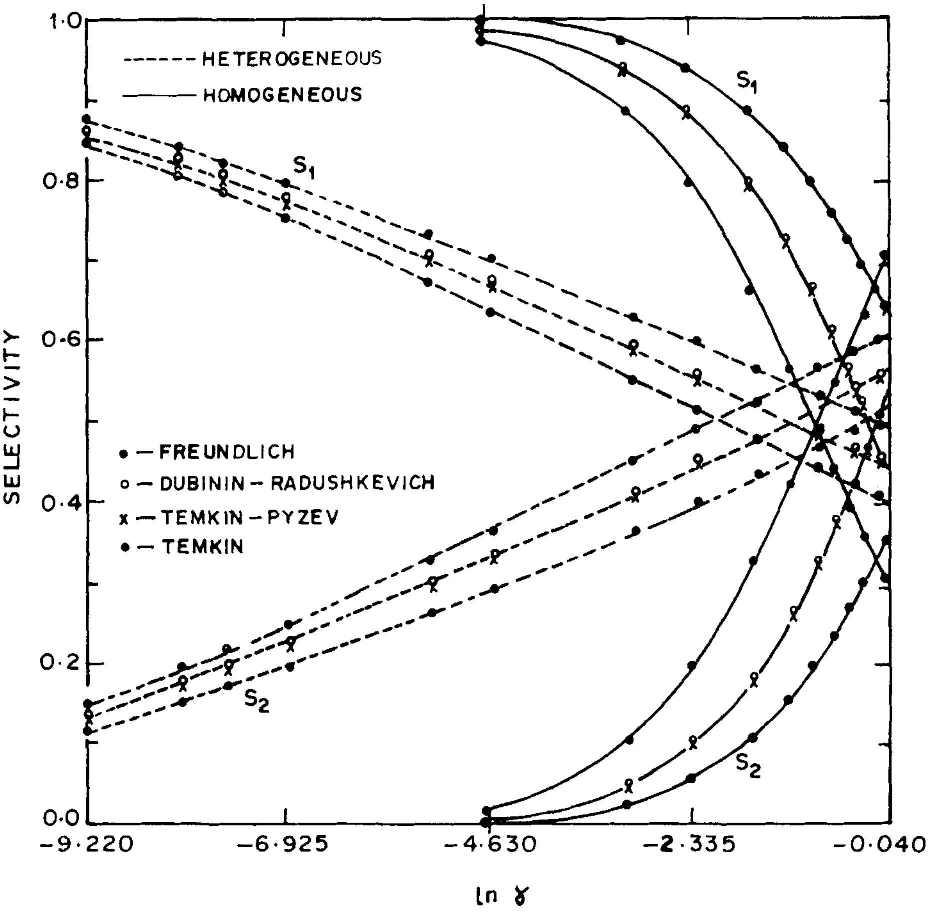


Figure 4. Selectivity for products P_1 and P_2 against lnγ for both homogeneous and heterogeneous surfaces.
$Q_{A1} = 17$ $Q_{A2} = 31$ $Q_M = 24$ $Q_{B1} = 14$ $Q_{B2} = 34$ $P = 266.64$ Pa $k_{r1}/k_{r2} = 0.8$ $b_{oA} = b_{oB} = 1E8 \times 133.32$ Pa

where mean concentration is indicated by a bar. In Eqs. 18 and 19 we assume second- and first-order kinetics respectively. The main feature of the reaction scheme is that at steady state the rate of production of P in the Y type patches can be represented in terms of fractional coverages in the X type patches.

It is to be noted that in X group patches the molecule A is a mere diluent and only competes for sites with molecule B. Also in the Y group, the effective concentration of C molecules C_s is so small as to be neglected in the expression for fractional coverage. Consequently, in calculating a statistical average such as mean square coverage $\overline{\theta^2_{BY}}$ on the Y group of patches, we use essentially methods of one-component adsorption. On the contrary, for calculating the statistic $\overline{\theta}_{BX}$, we need averages over the bivariate distribution functions using Eqs. 1 to 4.

Under these assumptions we have:

$$r_R = k_{1Y}\int_{Q'_{B1}}^{Q'_{B2}}[1 + (b'_{oB}/p_B)\exp(-Q'_B/RT)]^{-2}\delta_B(Q'_B)dQ'_B \tag{20}$$

where Q'_{B1}, Q'_{B2} denote respectively the lower and upper limits of heat of adsorption, and b'_{oB} is the entropy factor for the Y group of patches for molecule B. Eq. 20 can be readily expressed in terms of hypergeometric series both for the positive exponential distribution represented by Eq. 1 and the negative exponential distribution represented by Eq. 3. The details are given in the supplementary material.

Originally, a Mellin transform method was proposed (Rudnitsky and Alexeyev, 1975) to calculate the mean surface coverage and mean squared surface coverage as a function of pressure. We extend this method to deal with first- and second-order surface reactions both for positive and negative exponential distributions. We substitute $(b_o/p)\exp(-Q/RT) = x$; $\mu/RT = 1/Q_M$; $b_o \exp(-Q'_{B1}/RT) = p'_1$; $b_o \exp(-Q'_{B2}/RT) = p'_2$; $x_1 = (b_o/p)\exp(-Q'_{B1}/RT)$; $x_2 = (b_o/p)\exp(-Q'_{B2}/RT)$ and derive the analytical expressions.

For the negative exponential distribution represented by Eq. 3 we can readily express r_R as a function of p_B for various pressure ranges. Thus we have:

For $p < p'_2$

$$r_R = k_{1Y}(p/b_o)^{\mu}[RT/(\mu - 2)]C_1[x_1^{\mu-2}F(2,2-\mu;3-\mu;-1/x_1) - x_2^{\mu-2}F(2,2-\mu;3-\mu;-1/x_2)] \tag{21}$$

For $p'_2 < p < p'_1$

$$r_R = k_{1Y}(p/b_o)^{\mu}(RT/\mu)C_1\{(\mu/\mu - 2)x_1^{\mu-2}F(2,2-\mu; 3-\mu;-1/x_1) + \mu(1-\mu)[\Pi/\sin(\mu\Pi)] - x_2^{\mu}F(2,\mu;\mu+1;-x_2)\} \tag{22}$$

And for $p > p'_1$

$$r_R = k_{1Y}(p/b_0)^{\mu}(RT/\mu)C_1[x_1^{\mu}F(2,\mu;\mu+1;-x_1) - x_2^{\mu}F(2,\mu;\mu+1;-x_2)] \tag{23}$$

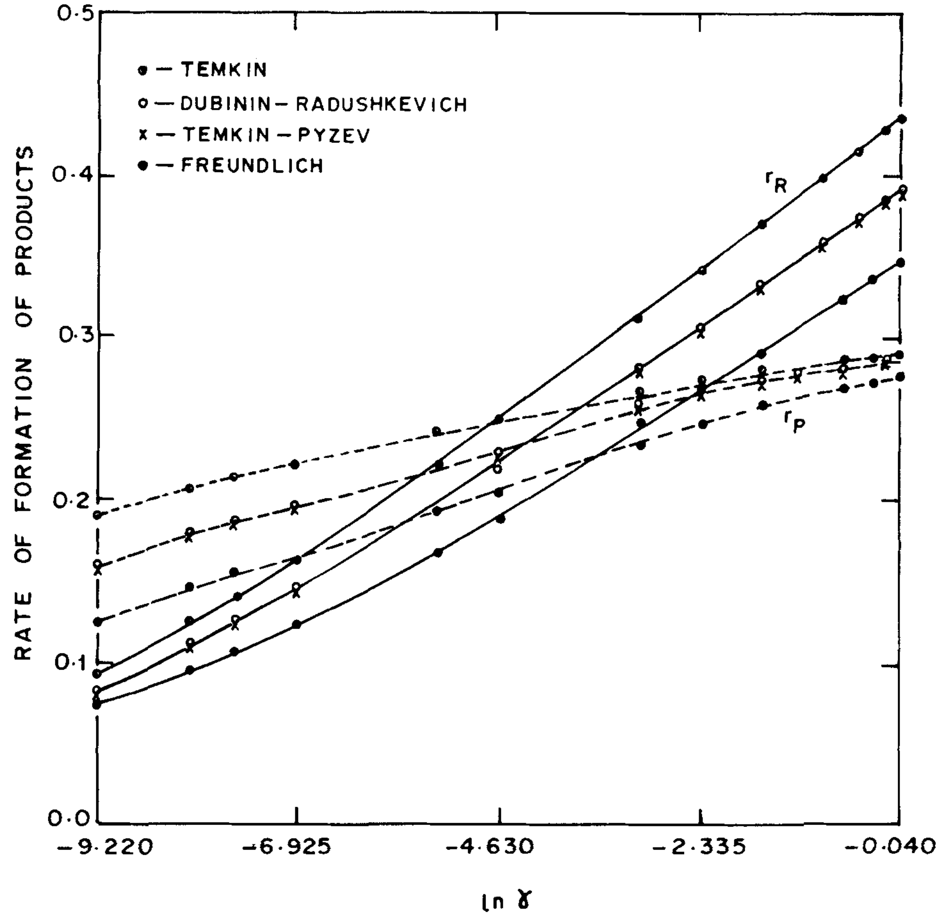


Figure 5. Rate of production of products R and P (arbitrary units) against lnγ for the four distributions.
$k_{1Y} = 0.8$ $k_{2X} = 0.3$ $Q_{A1} = 17$ $Q_{A2} = 31$ $Q_M = 24$ $Q_{B1} = 14$ $Q_{B2} = 34$ $Q'_{B1} = 14$ $Q'_{B2} = 34$ $b_{oA} = b_{oB} = 1E8 \times 133.32$ Pa $P = 266.64$ Pa $b'_{oB} = 1E6 \times 133.32$ Pa

where the hypergeometric series $F(2,2-\mu;3-\mu;-x_1^{-1})$,$F(2,\mu;\mu+1;-x_1)$ can be expanded as

$$F(2,2-\mu;3-\mu;-x_1^{-1}) = \sum_{n=0}^{n=\infty}(-x_1^{-1})^n[(2-\mu)/(n+2-\mu)](n+1) \quad (24)$$

$$F(2,\mu;\mu+1;-x_1) = \sum_{n=0}^{n=\infty}(-x_1)^n(n+1)[\mu/(\mu+n)] \quad (25)$$

Similarly, for the positive exponential distribution defined by Eq. 1, we can write three expressions for the different pressure ranges as
For $p < p'_2$

$$r_R = k_{1Y}C_2[RT/(\mu+2)](b_o/p)^\mu[x_2^{-(2+\mu)}F(2,\mu+2;\mu+3;-1/x_2) - x_1^{-(2+\mu)}F(2,\mu+2;\mu+3;-x_1^{-1})] \quad (26)$$

For $p'_2 < p < p'_1$

$$r_R = k_{1Y}C_2(RT/\mu)(b_o/p)^\mu[F(2,-\mu;1-\mu;-x_2)x_2^{-\mu} - x_1^{-(2+\mu)}[\mu/(\mu+2)]F(2,\mu+2;\mu+3;-1/x_1) - (\mu+1)[\mu\Pi/\sin(\mu\Pi)] \quad (27)$$

And for $p > p'_1$

$$r_R = k_{1Y}(b_o/p)^\mu C_2(RT/\mu)[F(2,-\mu;1-\mu;-x_2)x_2^{-\mu} - F(1,-\mu;1-\mu;-x_1)x_1^{-\mu}] \quad (28)$$

with the following expansions for the hypergeometric series:

$$F(2,\mu+2;\mu+3;-x_1^{-1}) = \sum_{n=0}^{n=\infty}(-x_1)^{-n}(2+\mu)(n+1)/(n+2+\mu) \quad (29)$$

$$F(2,-\mu;1-\mu;-x_1) = \sum_{n=0}^{n=\infty}(-x_1)^n\mu(n+1)/(\mu-n) \quad (30)$$

For the constant distribution represented by Eq. 2, straightforward integration gives a simple expression for r_R:

$$r_R = [k_{1Y}/(Q'_{B2}-Q'_{B1})]RT\{\ln[(\mu'_2+\lambda)/(\mu'_1+\lambda)] + \lambda[(\mu'_2+\lambda)^{-1} - (\mu'_1+\lambda)^{-1}]\} \quad (31)$$

where

$$\mu'_1 = \exp(Q'_{B1}/RT); \quad \mu'_2 = \exp(Q'_{B2}/RT); \quad \lambda = \frac{b'_oB}{p_B}$$

For the skewed Gaussian distribution defined by Eq. 4, no analytical expressions for r_R are possible and hence recourse to numerical methods is necessary.

To calculate r_P we notice that since two surface concentrations are involved, integration over bivariate distributions defined for the X group of sites is necessary. Using expressions similar to Eqs. 5, 6, and 7 we have,

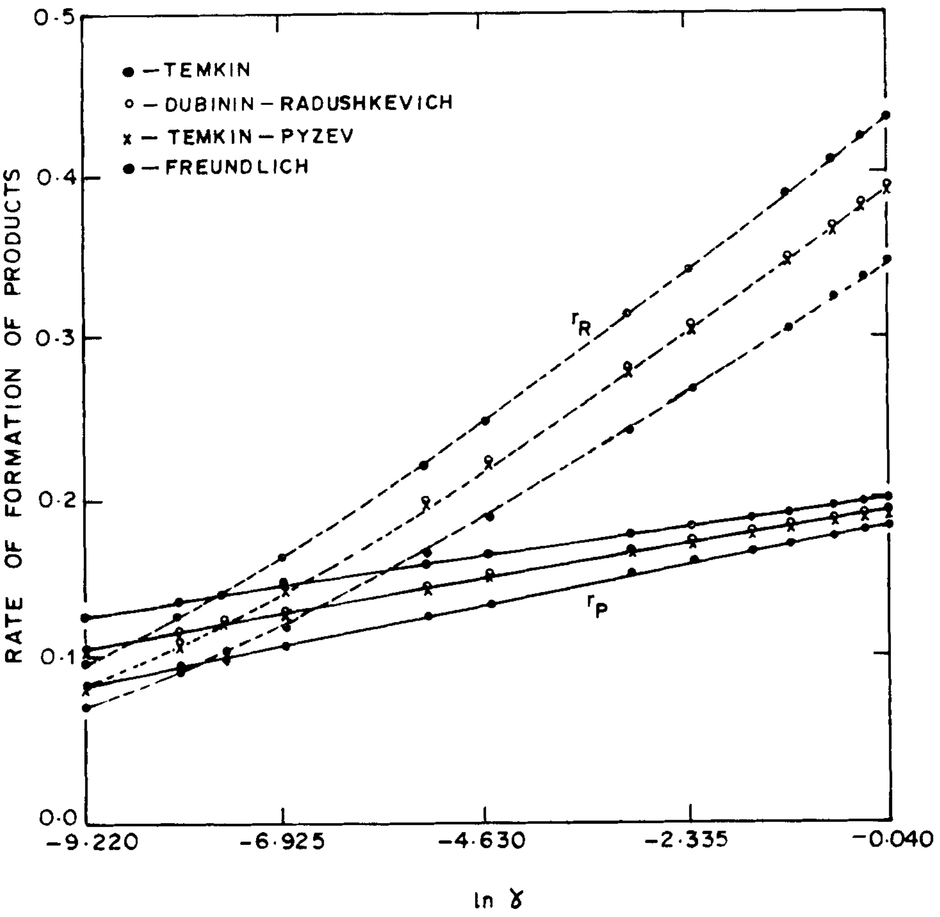


Figure 6. Rate of production of products *R* and *P* (arbitrary units) against lnγ for the four distributions.
$k_{1Y} = 0.8$ $k_{2X} = 0.2$ $Q_{A1} = 17$ $Q_{A2} = 31$ $Q_M = 24$ $Q_{B1} = 14$ $Q_{B2} = 34$ $Q'_{B1} = 14$ $Q'_{B2} = 34$ $P = 266.64$ Pa $b'_{oB} = 1E6 \times 133.32$ Pa $b_{oA} = b_{oB} = 1E8 \times 133.32$ Pa

$$r_P = k_{2X} \int_{Q_{A1}Q_{B1}}^{Q_{A2}} \int^{Q_{B2}} \frac{\delta_A(Q_A)\delta_B(Q_B)dQ_A dQ_B}{1 + (b_{oB}/p_B)\exp(-Q_B/RT)[1 + (p_A/b_{oA})\exp(Q_A/RT)]} \tag{32}$$

where the subscript X denotes that the integration has been carried over the X group of sites for the rate of production of P. We make the assumption of equal entropy change factors b_{oA}, b_{oB}, for the X group of sites. Different entropy factor and heat limits are assumed for the Y group of sites.

In calculating the statistic r_P the same procedure suggested for scheme I (Eq. 12) can be used. As before, for the positive and negative exponential distributions one integration can be performed and the result expressed approximately in terms of the hypergeometric series. For the skewed Gaussian distribution numerical methods are necessary.

Using Eqs. 20 to 32, we can investigate the conditions necessary (in particular, determination of the correct ratio of partial pressures $\gamma = p_B/p_A$) to realize the desired selectivity pattern. As before,

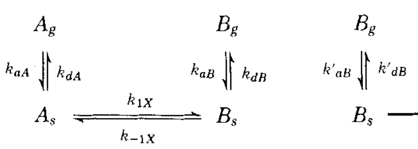
$$S_1 = r_R/[r_R + r_P] \tag{33}$$

$$S_2 = 1 - S_1 \tag{34}$$

In Figures 5 and 6 r_R is plotted against ln γ for various values of the ratio of kinetic constants. At higher γ values a better selectivity to R is obtained. The equal selectivity condition can be realized by operating at the γ vlaues of the crossover points. A slight change in the ratio of kinetic constants causes a remarkable shift in the γ values needed such that $S_1 = S_2$ is attained. In contrast to this, operating at higher γ values P is obtained in predominantly large amounts. The divergence between the behavior of the different distributions is maximum at higher γ values. On the contrary the two qualitatively different distributions, namely the skewed Gaussian and constant distributions, show the same selectivity behavior at all γ values.

Up to this point we have studied an irreversible second-order reaction sequence. Now we consider a first-order series reaction of the type encountered in platforming catalysts, *in which irreversible* and reversible reactions occur.

Scheme III: Isomerization and Dehydrogenation Steps



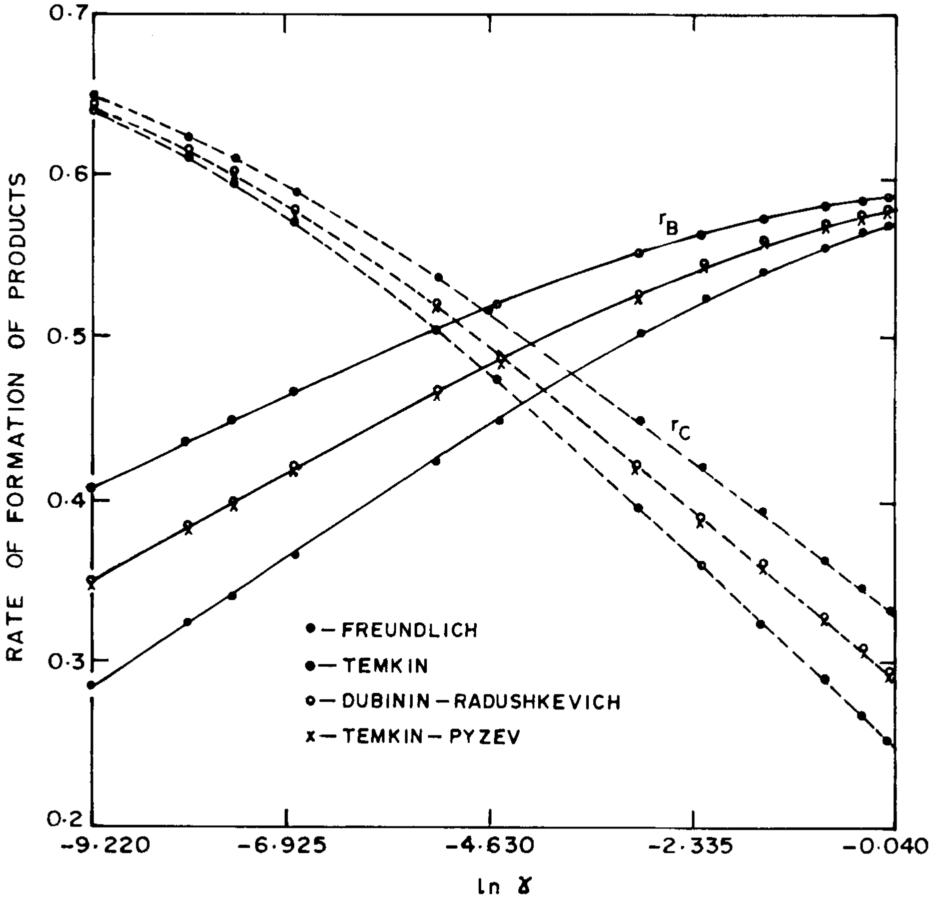


Figure 7. Rate of production of products *B* and *C* (arbitrary units) against lnγ for the four distributions.
$k_{1X} = 0.8$ $k_{-1X} = 0.2$ $k_{2Y} = 0.6$ $Q_{A1} = 17$ $Q_M = 24$ $Q_{B2} = 34$ $Q'_{B1} = 14$ $Q'_{B2} = 34$ $P = 266.64$ Pa
$Q_{A2} = 31$ $Q_{B1} = 14$ $b_{oA} = b_{oB} = 1E8 \times 133.32$ Pa

Most of the reforming catalysts consist of a noble metal like platinum dispersed on an acid support like alumina. The dispersed metal effects hydrogenation/dehydrogenation reactions while the acid function is mainly responsible for skeletal isomerization of hydrocarbons. Sinfelt (1964) has considered several industrial examples of this type of bifunctional catalysts. While the entire reaction sequence cannot be modeled, we idealize the essential features of the reaction network by the above reaction scheme.

So the overall reaction is $A \rightleftharpoons B \rightarrow C$, which is a typical model reaction for bifunctional catalysis. Thus the isomerization reaction $A \rightleftharpoons B$ is effected by the X group of acid sites while the dehydrogenation is done by the Y group of sites. As before, we will assume surface reaction controlling on X,Y group of sites and A,B are in adsorption equiibrium with their respective surface species. Reaction scheme III can be readily illustrated:

Ethyl cyclopentane $\xrightleftharpoons{X \text{ sites}}$ methyl cyclohexane $\xrightarrow{Y \text{ sites}}$ toluene

We assume that the transport of B from X sites to Y sites is through the gas phase. Further, the surface reaction is controlling on the Y group of patches. The species C is desorbed so rapidly as to make the surface concentration essentially zero. Thus fractional coverages on the X group of sites can be averaged over bivariate site energy distributions, while for describing adsorption on Y sites averaging over only monovariate distributions is necessary.

Thus the rate of production r_B can easily be written as

$$r_B = \left[\int_{Q_{A1}}^{Q_{A2}} \int_{Q_{B1}}^{Q_{B2}} (k_{1X}\theta_{AX} - k_{-1X}\theta_{BX})\delta(Q_A)\delta(Q_B)dQ_A dQ_B \right]_X \tag{35a}$$

$$r_B = k_{1X}\bar{\theta}_{AX} - k_{-1X}\bar{\theta}_{BX} \tag{35b}$$

$\bar{\theta}_{AX}, \bar{\theta}_{BX}$ can be calculated using analogous methods employed for the determination of r_P (Eq. 32) in the earlier section.

An analytical expression can be readily written for r_C:

$$r_C = k_{2Y} \int_{Q'_{B1}}^{Q'_{B2}} \theta_{BY}\delta(Q'_B)dQ'_B \tag{36}$$

r_C can be calculated by adopting methods suggested by Prasad and Doraiswamy (1983a,b) (see also *Tables of Integral Transforms*, 1954; *Higher Transcendental Functions*, 1953). Since $B \rightarrow C$ transformation is first order, the procedure is straightforward and one that has been well studied (Rudnitsky and Alexeyev, 1975). In principle the expressions are strictly analogous to Eqs. 21–30, except that in the hypergeometric series the a parameter of $F(a,b,c,z)$ is different, i.e., it is one instead of two. Also we have to use techniques of analytical continuation when the argument of the hypergeometric series become greater than unity (see supplementary material).

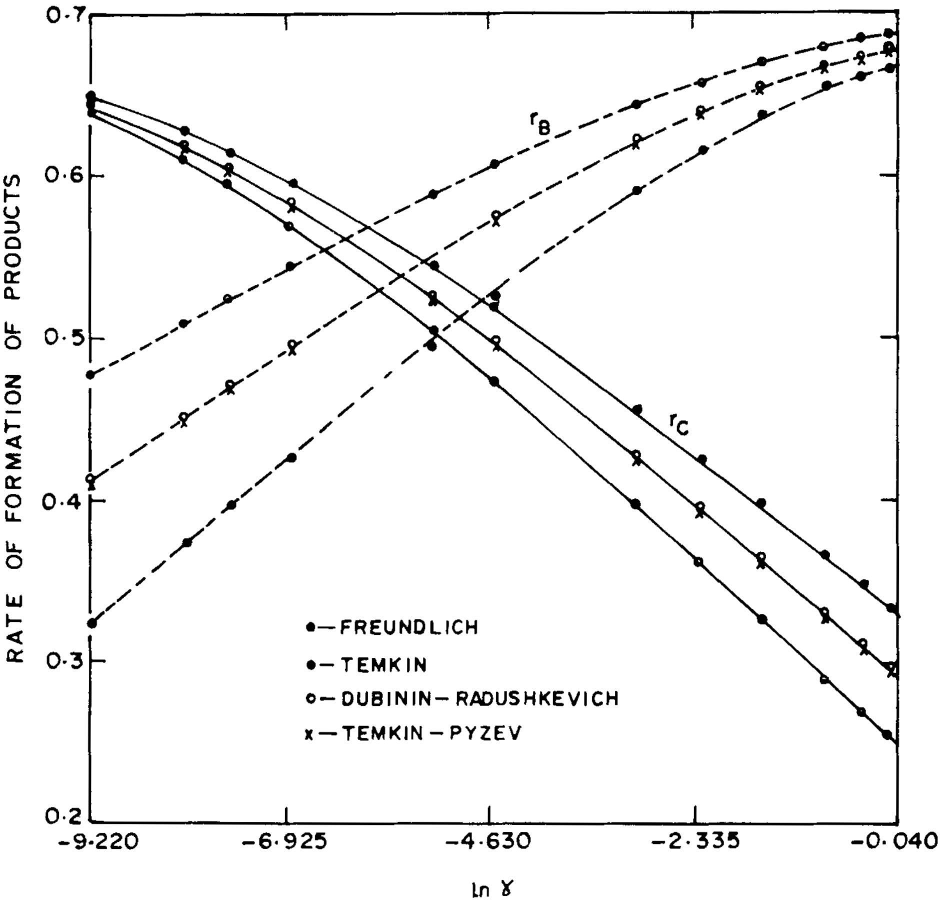


Figure 8. Rate of production of products *B* and *C* (arbitrary units) against lnγ for the four distributions.

$k_{1X} = 0.8$ $k_{-1X} = 0.2$ $k_{2Y} = 0.7$ $Q_{B1} = 14$ $Q_{B2} = 34$ $Q'_{B1} = 14$ $Q'_{B2} = 34$ $P = 266.64$ Pa

$Q_{A1} = 17$ $Q_{A2} = 31$ $Q_M = 24$ $p_{oA} = b_{oB} =$ 1E8 × 133.32 Pa

Now explicit expressions can easily be written for r_C. For the negative exponential distribution given by Eq. 3, we have the expression in three pressure ranges (Prasad and Doraiswamy, 1983a,b). Thus we have:

For $p < p'_2$

$$r_C = k_{2Y}(p/b_o)^{\mu}[RT/(\mu - 1)]C[x_1^{\mu-1}F(1,1-\mu; 2-\mu; -x_1^{-1}) - x_2^{\mu-1}F(1,1-\mu; 2-\mu; -x_2^{-1})] \quad (37)$$

For $p'_2 < p < p'_1$

$$r_C = k_{2Y}(p/b_o)^{\mu}C(RT/\mu)\{[\mu\Pi/\sin(\mu\Pi)] + [\mu/(\mu - 1]x_1^{\mu-1}F(1,1-\mu; 2-\mu; -x_1^{-1}) - F(1,\mu; \mu+1; -x_2)x_2^{\mu}\} \quad (38)$$

And for $p > p'_1$

$$r_C = k_{2Y}(p/b_o)^{\mu}(RT/\mu)C[F(1,\mu; \mu+1; -x_1)x_1^{\mu} - F(1,\mu; \mu+1; -x_2)x_2^{\mu}] \quad (39)$$

where

$$F(1,1-\mu; 2-\mu; -x_1^{-1}) = \sum_{n=0}^{n=\infty} (-x_1)^{-n}[1 - \mu/(n + 1 - \mu)] \quad (40)$$

$$F(1,\mu; \mu+1; -x_1) = \sum_{n=0}^{n=\infty} (-x_1)^{n}[\mu/(\mu + n)] \quad (41)$$

Similarly, for the positive exponential distribution defined by Eq. 1 we can write the solution in three pressure ranges. As before we get:

For $p < p'_2$

$$r_C = k_{2Y}[CRT/(\mu + 1)](b_o/p)^{\mu}[x_2^{-(1+\mu)}F(1,\mu + 1; \mu+2; -x_2^{-1}) - x_1^{-(1+\mu)}F(1, \mu+1; \mu+2; -x_1^{-1})] \quad (42)$$

For $p'_2 < p < p'_1$

$$r_C = k_{2Y}(CRT/\mu)(b_o/p)^{\mu}\{[F(1, -\mu; 1-\mu; -x_2)x_2^{-\mu}] - x_1^{-(1+\mu)}[\mu/(\mu + 1)]F(1, \mu+1; \mu+2; -x_1^{-1}) - [\mu\Pi/\sin(\mu\Pi)]\} \quad (43)$$

And for $p > p'_1$

$$r_C = k_{2Y}(CRT/\mu)(b_o/p)^{\mu}[F(1,-\mu; 1-\mu; -x_2)x_2^{-\mu} - F(1,-\mu; 1-\mu; -x_1)x_1^{-\mu}] \quad (44)$$

where

$$F(1,\mu+1; \mu+2; -x_1^{-1}) = \sum_{n=0}^{n=\infty} (-1)^{n}[(\mu + 1)/(\mu + n + 1)]x_1^{-n} \quad (45)$$

$$F(1,-\mu; 1-\mu; -x_2) = \sum_{n=0}^{n=\infty} [(\mu/(\mu - n)](-x_2)^{n} \quad (46)$$

A very simple expression can be derived for constant distribution represented by Eq. 2, i.e.,

$$r_C = [k_{2Y}/(Q'_{B2} - Q'_{B1})]RT\{\ln[(\mu'_2 + \lambda)/(\mu'_1 + \lambda)]\} \qquad (47)$$

where μ'_2,λ have the same meaning as in Eq. 31.

For the skewed Gaussian distribution represented by Eq. 4, as before no analytical expressions are possible and hence numerical methods are necessary to calculate both r_B and r_C.

Now the problem reduces to finding the γ value such that a desired selectivity is obtained. Figures 7 and 8 give the crossover points ($S_1 = LS_2$, $0 < L \leqslant 1$) when r_B and r_C are plotted as functions of ln γ. Note that as the partial pressure of C has no effect on the overall kinetics, the total pressure p quoted in the figures is the sum of P_A and P_B. The divergence between the different distributions is higher for a higher value of k_{2Y}. The crossing of the two rate curves occurs at a particular value of γ which is characteristic of the distribution. If we operate at this value of the partial pressure ratio γ then we get equal selectivities. The value of γ corresponding to any other selectivity pattern to be realized can be easily read from Figures 7 and 8.

As in the previous reaction schemes, the divergence between the selectivity behavior of the constant and the skewed Gaussian distributions is negligible, highlighting the difficulties exprienced in discriminating between the two distributions. However, experimental studies of the differential heat variation with surface coverage can often supplement the information obtained from reaction rate studies.

Lastly, the limitations of the present analysis should be pointed out. Thus interactions between, and mobility of, the adsorbed species are neglected. In choosing the bivariate distributions $\delta_A(Q_A)$, $\delta_B(Q_B)$ have been chosen with the same functional form. In principle, if we list all permutations, we have 4 × 4 types of bivariate distributions for reaction scheme I. Similarly, in analyzing the multicomponent adsorption behavior on a bifunctional catalyst, we have 4 × 4 × 4 possibilities for schemes II and III. Obviously such an analysis is beyond the scope of the present work.

Some comments are in order as to the choice of limits of heats of adsorption and the Q_M values. These have been chosen such that the differential heats at zero coverages approach the upper limit of heat of adsorption. The unrealistic heat limits assumption of zero and infinity is thus avoided.

NOTATION

A_g = reactant A in gas phase
A_s = reactant A in adsorbed phase
B_g = reactant B in gas phase
B_s = reactant B in adsorbed phase
b_{0A},b_{0B} = entropy change factor at half coverage for reactant A and B, respectively
b'_{0B} = entropy change factor at half coverage for component on Y sites of scheme II
C = intermediate product in scheme III
C_1,C_2 = normalized constants for the monovariate negative and positive exponential distributions for molecule B
$F(a,b,c,z)$ = generalized hypergeometric series for a,b,c,z
K^u_A,K^u_B = adsorption equilibrium constants for species A,B on uniform surface
k_{aA},k_{dA} = adsorption and desorption rate constants for reactant A
K_{aB},k_{dB} = adsorption and desorption rate constants for reactant B
k'_{aC} = adsorption rate constant for component C of scheme II
k_{r1},k_{r2} = rate constants for reactions 1 and 2 of scheme I
k_{1X},k_{-1X} = forward and backward reaction constants for X sites of scheme III
k_{2X} = rate constant for reaction on X site of scheme II
k_{1Y},k_{2Y} = rate constants for reaction 1 and 2 on Y sites of scheme II
P_1,P_2 = products
p = partial pressure of component A in Eqs. 21 to 30
p_A,p_B = partial pressure of A and B
p_o = total pressure
Q_A = heat of adsorption for reactant A
Q_B = heat of adsorption for reactant B
Q_M = parameter defining differential heat at zero coverage
Q_{A2},Q_{A1} = upper and lower limits of heats of adsorption for reactant A
Q_{B2},Q_{B1} = upper and lower limits of heats of adsorption for reactant B
Q'_{B2},Q'_{B1} = upper and lower limits of heat of adsorption for component B on Y sites of scheme II
R = gas constant
R,P = products in scheme II
r_R,r_P = rate of formation of products R and P
r^u_{P1} = rate of formation of product P_1 for uniform surface
S_1,S_2 = selectivities for the two products
T = temperature
X,Y = two types of sites

Greek Letters

γ = characteristic partial pressure ratio
γ^u = characteristic partial pressure ratio for the uniform surface
θ^u_A,θ^u_B = fractional surface coverage of reactant A and B respectively for the uniform surface
$\bar{\theta}_A,\bar{\theta}_B$ = fractional mean surface coverage for reactant A and B
$\bar{\theta}_{BX}$ = fractional mean surface coverage of component B on X sites of scheme II
$\bar{\theta}^2_{BY}$ = fractional mean squared surface coverage of component B on Y sites of scheme II
$\bar{\theta}^A_{1i}(Q_A,Q_B)$ = fractional coverages of A on the ith patch which is a function of temperature and pressure
$\delta(Q_A,Q_B)$ = bivariate site energy distribution
$\delta_A(Q_A)$ = site energy distribution function for reactant A
$\delta_B(Q_B)$ = site energy distribution function for reactant B
$\delta'_B(Q_B)$ = site energy distribution function for component B on Y sites of scheme II
μ = dimensionless parameter relating thermal energy and Q_M

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Manuscript received May 3, 1983; revision received July 24 and accepted July 10, 1984.

Supplementary material has been deposited as Document No. 04316 with the National Auxiliary Publications Service (NAPS), c/o Microfiche Publications, 4 North Pearl Street, Portchester, NY 10573, and may be obtained for $4.00 for microfice or $7.75 for photocopies.