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Combustion of Carbonaceous Deposits within Porous Catalyst Particles I. Diffusion-Controlled Kinetics

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At a sufficiently high temperature, dependent on particle size, the rate of combustion of carbonaceous fuel within a porous catalyst particle becomes controlled solely by a diffusion process. Here the curve of burnoff vs. time, as well as a characteristic time for total burnoff are fully determined by: initial carbon content, particle size, diffusivity, and oxygen partial pressure. The behavior is totally independent of composition of the catalyst, as well as of the nature of the "coke." Quantitative relationships are given involving all variables, and the dependencies on each variable are demonstrated with experimental examples.

INTRODUCTION

This paper deals with the kinetic processes of combustion, with oxygen, of carbonaceous matter contained within the pores of granules of a porous refractory solid. In the practice of catalysis, we encounter this circumstance in catalyst "regeneration," i.e., in the process of removal by combustion of carbonaceous deposits ("coke") accumulated during catalytic operation with hydrocarbon or other organic reactants. Sometimes porous adsorbents are similarly "regenerated."

An understanding of the mechanisms involved in this particular type of rate process is not only of technological interest, but it evolves kinetic models which are instructive and exemplary of a broader scope of rate processes.

The phenomena involved have been subjected to systematic study, and can be classified into major topical categories, of which this study represents one: The combustion-rate dependencies of all major fundamental variables and phenomena under *diffusion-controlled* conditions. These prevail for sufficiently high temperature and sufficiently large particle size.

This study deals with the behavior of the individual solid particle. All experimental information is based on measurements using individual near-spherical solid granules under "differential reactor" conditions, i.e., where reactant (oxygen) is supplied at sufficient flow rate so that its concentration is depleted by less than 2%, and is thus well defined.

The carbonaceous material, or "fuel," to be burned is presumed to be solid, immobile, and essentially evenly distributed throughout the radius of the porous particle, at the outset of the combustion process. The oxygen-containing gas phase diffuses into the porous structure of the solid particle.

The system differs from that involved in the burning of porous carbons in that the physical, structural framework through which gaseous oxygen must move, remains substantially unaltered as the combustion process proceeds.

Some studies have been published which deal with limited aspects of the reaction behavior of this process.

Haggerhammer and Lee (*1*) studied the combustion of coke on silica-alumina cracking catalyst beads in a moving catalyst bed, and attempted empirical correlations of performance with various operating vari-

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ables of the system. Dart, Savage, and Kirkbride (*2*) studied the air regeneration of coked clay catalyst pellets in a static bed, with little indication of intraparticle diffusional effects on combustion behavior under their conditions of operation. Panchenkov and Golovanov (*3*), using pelleted silica-alumina granules, have demonstrated qualitatively the existence of operating regions wherein internal diffusion effects will or will not modify reaction behavior. Dobyehin and Klibanova (*4*) studied combustion on silica-alumina, and interpreted data in terms of carbon located within and outside the granules, a phenomenon for which we have no evidence in our work. Haldeman and Botty (*5*) have studied details of the nature of the carbon deposits, including rates of burnoff under conditions of negligible mass transport effects.

EXPERIMENTAL TECHNIQUES

Apparatus

Combustion rate data are obtained on individual granules of the catalyst weighing from 50 to 200 mg, at a known temperature, oxygen partial pressure, and at an air flow rate approximately two orders of magnitude greater than the rate of oxygen consumption in the reacting sample. Using apparatus, method, and typical data plots as described previously by Goodwin (*6*), we obtain a pen record of cumulative amount of carbon dioxide produced vs. time, after any carbon monoxide is further converted to carbon dioxide.

The data are advantageously evaluated in terms of fractional amount of carbon burned (or remaining) vs. time. In view of the asymptotic nature of the final burnoff, the total amount of carbon is ascertained by raising sample temperature to achieve a definite end point.

Porous Solids Used

Most extensive studies have been made on silica-alumina cracking catalyst particles in near-spherical bead form. These materials, and procedures for obtaining extensive variations in porosity properties, have been previously described by Weisz and Schwartz (*7*). Laboratory samples of catalysts as well as fresh commercial production cracking catalyst, and catalyst withdrawn from refinery cracking units have been used. In addition, spherical chromia-alumina catalyst particles [see ref. (*7*)] have been examined. Appropriate detail will be mentioned in the course of discussion.

Deposition of Carbonaceous Material

Two methods of deposition of carbonaceous matter were employed, involving thermal or catalytic formation of deposits from a hydrocarbon atmosphere:

(a) Passing a light East Texas gas oil over the catalyst at a rate of about 1 g/hr/g catalyst at 470°C, at atmospheric pressure.

(b) Passing a petroleum naphtha of 90° to 200°C distillation range over the catalyst at a rate of about 1 g/hr/g catalyst at 510°C, and atmospheric pressure.

The carbonaceous material deposited by such thermal or catalytic hydrocarbon decomposition is usually termed "coke." It is known to contain some hydrogen, to an amount represented by the empirical formula CH_n, where $0.5 < n < 1.0$. However, we will have occasion below to point out the virtually complete insensitivity of the particular burning behavior studied in this paper to the nature of the carbonaceous material. The only requirement to be satisfied is that of a radially uniform deposit. To obtain this, the conditions for the carbon deposition by hydrocarbon cracking were chosen to satisfy the general criteria (*8, 9*) for negligible diffusional effects for the deposition reaction.

GENERAL REGIONS OF REACTION BEHAVIOR

For the carbon combustion process in a granule of given physical properties, we should be able to predict the magnitude of reaction rate admissible without noticeable influence of mass transport phenomena, or conversely which must lead to considerable influences from such phenomena, by the use of the magnitude criterion discussed by Weisz (*8, 9*).

For a typical and conventional cracking catalyst bead, we have $R = 0.2$ cm radius, and an effective diffusivity (for oxygen at combustion temperature) of $D \sim 5 \times 10^{-3}$

cm^2/sec [see Weisz, ref. (*8*)]. With oxygen concentration at atmospheric combustion conditions being about $C \sim 3 \times 10^{-6}$ moles/cm^3, the criterion *8* gives

$$dN/dt < CD/R^2 = 4 \times 10^{-7} \text{moles/cm}^3 \text{ sec} \quad (1)$$

for the magnitude of combustion rate per unit catalyst volume, dN/dt, below which we may expect to observe no appreciable mass transport effects.

In Fig. 1 are reproduced measurements for the burning rate (average rate for 85% of total burnoff) of such beads, bearing an initial amount of 3.4 wt % of carbon, as a function of temperature, drawn in the manner of an Arrhenius plot (dashed curve). The above calculation indicates that above 470°C burning kinetics should be strongly modified by mass transport. Indeed, when the same measurements are repeated with coked beads from the same lot but ground to fine particles of $R = 0.01$ cm, the straight-line Arrhenius behavior is obtained.

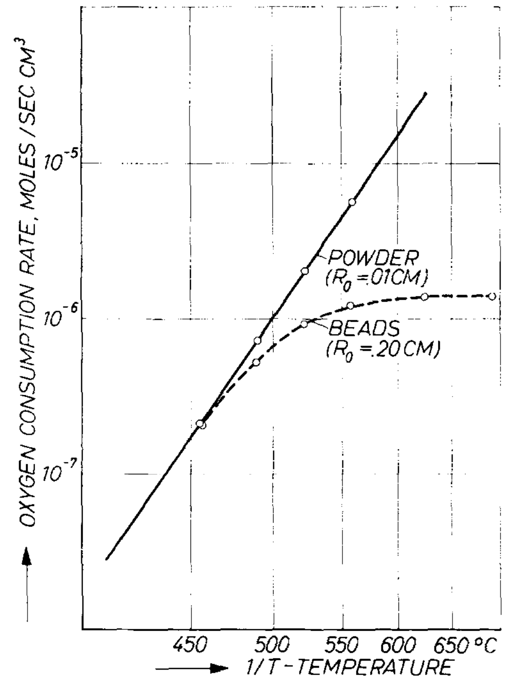

Fig. 1. Average observed burning rates of conventional silica-alumina cracking catalyst. Initial carbon contents, 3.4 wt %. Beads (dashed line), and ground up catalyst (full curve).

Silica-alumina beads are rendered transparent by immersion in a liquid, preferably one of high refractive index, e.g. carbon tetrachloride. In this manner beads can be inspected for the presence, and to some extent for the density of coke deposits. Figure 2 (top) shows beads that had an initial carbon content of 1 wt %, and which were subjected to *partial* carbon removal (a) at 450°C, (b) at 515°C, and (c) at 625°C. In spite of the difference in appearance, beads (a) and (c) have been burned to the same fractional amount remaining, namely about 0.15 of initial carbon content. Spotting the three temperatures on Fig. 1, we find that (a) corresponds to the straight-line Arrhenius portion, (b) is in the transition range, and (c) is in the "flat" mass-transport–dominated region of operation.

On the basis of this information, we recognize two distinct limiting models for the burnoff mechanism: The "intrinsic" region of chemical kinetics, with combustion rate at any one time substantially equal at all points of the bead radius [case (a)]; and the totally mass-transport–controlled region [case (c)]. The latter is characterized by a shell-progressive burnoff. The time progression in radial carbon concentration for the two cases is illustrated by (a) and (c) of the lower portion of Fig. 2. Case (b) represents the intermediate case where both intrinsic activity and diffusion phenomena contribute to over-all behavior.

In this paper, we shall examine the burning behavior in the latter region, case (c). In this realm of mass-transport–controlled activity we need not be concerned about questions involving the chemical nature of the "coke," or structural changes during burnoff.

The "Shell-Progressive" Region of Kinetics

This mode of behavior, case (c) above, can be interpreted in terms of the profile of the oxygen concentration within the particle pictured in Fig. 3. Oxygen diffusing into the structure is totally consumed upon initial contact with carbonaceous fuel. Thus

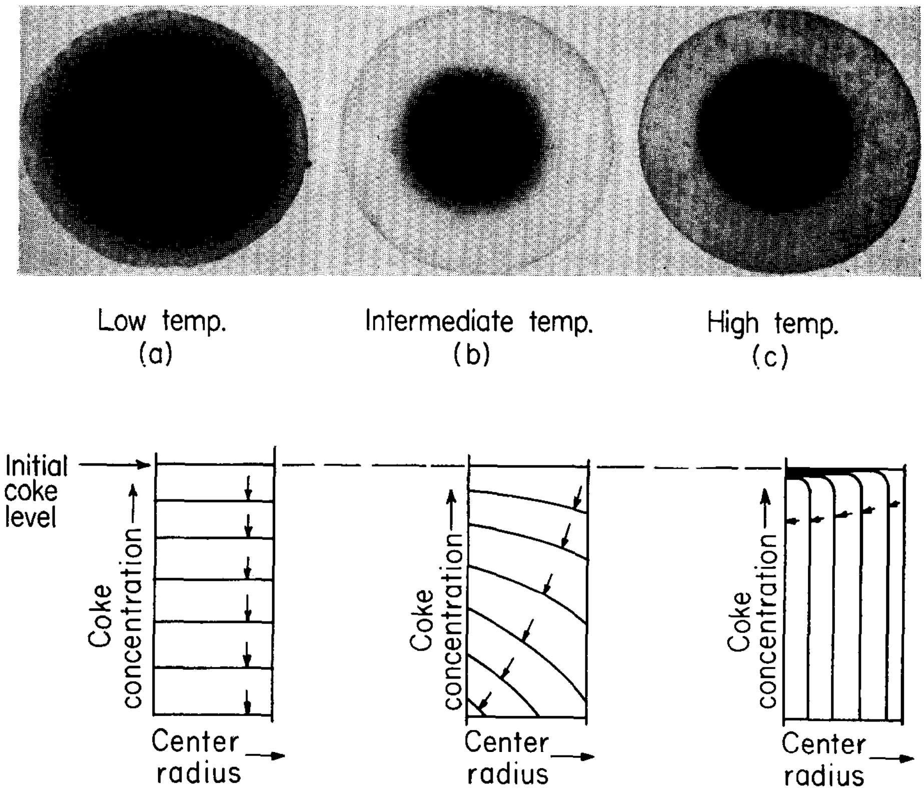

FIG. 2. Appearance after partial burnoff (above), and coke concentration vs. radius in beads for successive stages of burnoff (below), for three temperature regions.

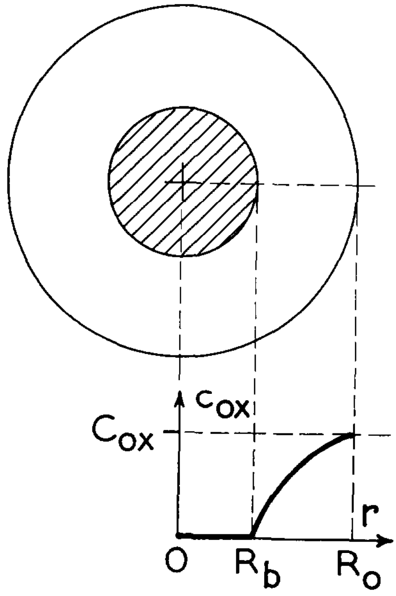

FIG. 3. Model of shell progressive combustion.

at any finite time interval after onset of reaction, the surface of the remaining coke shell at R_b will react as fast as oxygen can diffuse to it through the space $R_0 - R_b$. For this space the oxygen concentration C_{ox} must satisfy the diffusion equation $D\nabla^2 C_{\mathrm{ox}} = 0$, with the boundary condition $C_{\mathrm{ox}} = C_{\mathrm{ox}}$ at $r = R_0$, and $C_{\mathrm{ox}} = 0$ at $r = R_b$. For the sphere we have

$$d^2C_{\mathrm{ox}}/dr^2 + 2dC_{\mathrm{ox}}/rdr = 0 \qquad (2)$$

We can solve this equation for the oxygen gradient at the surface $(dC_{\mathrm{ox}}/dr)r = R_0$, and with it we can obtain the rate of oxygen consumption from

$$dN_{\mathrm{ox}}/dt = D4\pi R_0^2(dC_{\mathrm{ox}}/dr)_{r=R_0} \qquad (3)$$

where D is the effective diffusivity of the porous granule for oxygen. With a knowledge of the stoichiometric ratio n of carbon burned per molecule of oxygen consumed, we obtain the carbon removal rate, dN_c/dt, from

$$dN_c/dt = ndN_{ox}/dt \tag{4}$$

or we can introduce the variable y = fraction of initial carbon remaining

$$y = N_c/N_{c,0} = (R_b/R_0)^3 \tag{5}$$

with $N_{c,0}$ the initial amount of carbon on the solid.

Using (2) to (5), the solution yields,

$$1/2(1 - y^{2/3}) - 1/3(1 - y) = Kt \tag{6}$$
$$K \equiv nDC_{ox}/R_0^2C_c$$

where C_c is the initial molar carbon concentration on the solid granule.

The time course of burnoff $y(t)$ should be described by Eq. (6). Figure 4 reproduces experimental burnoff measurements at 700°C with y data plotted in terms of the left-hand side expression in Eq. (6) as the ordinate for three individual silica-alumina beads of 350 m^2/g surface area, differing only in initial coke content and in diameter. Experimental behavior is in agreement with the model in that the plots are linear through the origin. The slope should be representative of the combination of property constants K. The burnoff rate is most conveniently characterized by the time required for a given amount of fractional burnoff. Thus by setting $y = 0$ or $y = 0.15$ in formula (6) we find the characteristic total burnoff time:

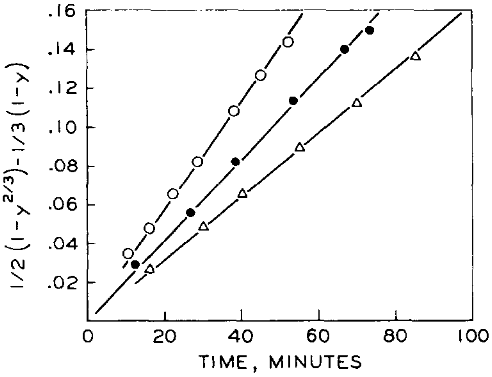

FIG. 4. Burnoff function vs. time on three different beads (y = fractional amount carbon remaining).

$$T_{100} = 0.167\,K = 0.167\,R_0^2C_c/nDC_{ox} \tag{7a}$$

or the 85% burnoff time:

$$T_{85} = 0.076\,K = 0.076\,R_0^2C_c/nDC_{ox} \tag{7b}$$

with the numerical constant so calculated that the time scale is in minutes. Since burnoff rates are progressively slower towards the end, finding the exact end point, i.e. T_{100}, is relatively difficult, and we have found it most convenient to use the 85% burnoff time, T_{85} as a practical measure of the burnoff character.

Dependence on initial carbon concentration, C_0, of the burnoff time, should follow a direct proportionality. Individual silica-alumina cracking catalyst beads from a single type of material coked to various levels between about 1 wt % and 5 wt % carbon were burned in air, the total coke content, and T_{85} burning time determined. The material represented a commercial silica-alumina catalyst (10 wt % Al_2O_3, 0.15 wt % Cr_2O_3) of 1.2 g/cm^3 particle density and 0.4 cm^3/g pore volume, coked by the gas oil cracking procedure; variation of coke level was achieved by sampling catalyst at various axial depths in the bed. Beads were screened and hand-picked for uniformity in size, of 0.4 cm diameter. Combustion was carried out for each bead at 705°C. The expected linear relationship is well confirmed in the data plotted in Fig. 5.

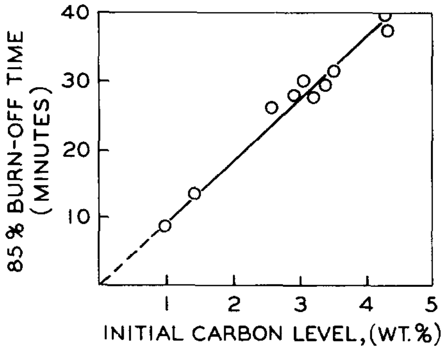

FIG. 5. Dependence of burnoff time on initial carbon level, for diffusion controlled combustion (silica-alumina cracking catalyst, 700°C).

Dependence on particle size, R_0, was tested, using catalyst beads from the same coked batch, by comparing results of individual experiments on beads of various size but for which the coke level was found to be constant 3.0 ± 0.2 wt %. In Fig. 6 the burning

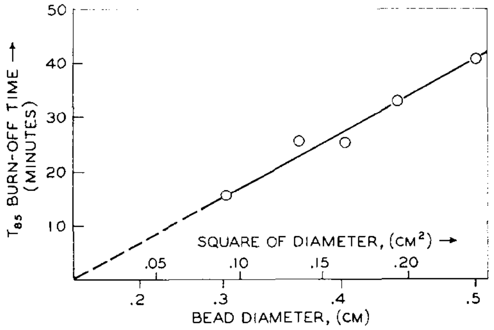

FIG. 6. Dependence of burnoff time on bead size for diffusion-controlled combustion.

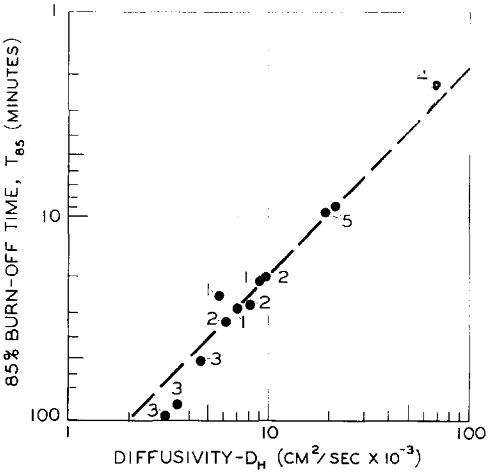

FIG. 7. Dependence of burnoff time on structural diffusivity, of various types of spherical particles, for diffusion-controlled combustion region.

time is plotted against the square of bead diameter on the abscissa. The results are in good agreement with prediction by formula (7b).

Dependence on diffusivity was tested, making use of materials of widely different pore structure. A total spread in available diffusivity of nearly two orders of magnitude was available to us. Samples were handpicked for uniform size of $R = 0.4$ cm. Diffusivity was measured by the hydrogen through-flow method discussed by Weisz (*8*). The variation of diffusivity of diverse materials such as used here was described by Weisz and Schwartz (*7*). Variations in initial carbon content C_c were taken into account by correcting T_{85} by the required proportionality correction for each individual carbon content to correspond to a standard reference carbon concentration of 3.0 wt % on silica-alumina. Since oxygen diffusivity at a given combustion temperature should be in constant proportion to hydrogen diffusivity at the fixed temperature of the diffusivity test, we have plotted our T_{85} data in Fig. 7, directly against the experimentally measured hydrogen diffusivity, D_H. There is generally good agreement of experimental data with the linear relationship between time of burnoff and diffusivity, represented by the dashed line of unit slope. This agreement, over a span of nearly two orders of magnitude in the variables involved, is particularly significant in that we have included beads which differ in pore structure as well as in chemical composition as follows:

Beads marked (1) are laboratory preparations of silica-alumina cracking catalysts with surface areas between 270 and 400 m^2/g. Those marked (2) are commercial preparations containing 0.15 wt % of chromia, which have seen extensive cracking duty in refinery cracking units; (3) are similar cracking catalyst beads withdrawn from a commercial cracking plant in which, however, some thermal catalyst damage had occurred. Beads (4) are of high-diffusivity silica-alumina, obtained by introducing a dispersion of dried silica-alumina powder into the forming solution before formation and drying of the spherical particle; by this method a bimodal pore-size distribution due to a superimposed set of macro pores is achieved [see ref. (*7*)]. Beads (5) are chromia-alumina [see ref. (*7*)]; this material possesses an intrinsic coke-combustion activity which is several orders of magnitude greater than that of the silica-alumina materials. The compatibility of these with the rest of the data constitutes a particularly striking demonstration of the independence of diffusion-controlled combustion process from intrinsic, chemical combustion activity.

Dependence on oxygen partial pressure should be such that the rate of the diffusion-controlled process is proportional to the oxygen partial pressure, and burnoff time should be inversely proportional, as per formula (7b). The burnoff was compared for 0.21 atm of oxygen (air) as used in the case of all data reported so far above, and for 1 atm of oxygen. Table 1 below summarizes data on two types of catalyst beads. The results are seen to be in excellent agreement with expectation.

TABLE 1
COMPARISON OF BURNOFF TIMES IN AIR AND OXYGEN

Catalyst	Air			Oxygen			
	C_c (%)	T_{85} (min)	T_{85} corr. (min)	C_c (%)	T_{85} (min)	T_{85} corr. (min)	Ratio T_{ox}/T_{air}
Silica-alumina (lab. prep.)							
R = 0.24 cm, temp. 630°C	4.0	45	45	4.6	10.5	9.1	—
T_{85} corrected to							
C_c = 4.8%, wt	3.7	48	52	4.1	10.6	10.3	—
Average			48.5			9.7	0.20
Silica-alumina (0.15% Cr_2O_3, commercial)							
R = 0.19 cm, temp. 690°C	3.03	30	29.7	3.35	6.3	5.55	—
T_{85} corrected to	3.40	29	25.6	—	—	—	—
C_c = 3%, wt	3.21	27	25.2	—	—	—	—
Average			26.6			5.55	0.21

DISCUSSION

At a sufficiently high temperature the combustion process in a porous granule assumes a shell-progressive character. This behavior is satisfactorily described by formula (6) as regards the course of burnoff with time, and by the formulae (6) and (7) as regards its dependence on all significant property parameters.

The onset of shell-progressive reaction depends on the relative magnitude of the reaction *rate*, and the size and diffusivity of the solid granule at hand, and can be appraised by use of the criterion (1). At what *temperature* this condition will prevail depends on the course of intrinsic reactivity with the temperature. Figure 1 demonstrates the particular behavior of silica-alumina.

The physical model of the shell-progressive reaction is significantly insensitive to many phenomena which may otherwise be critical. Since the rate is controlled by the diffusion process, details of chemical or physical texture and intrinsic reactivity of the carbonaceous fuel are of no consequence, as long as it remains "sufficiently" reactive. Also, another phenomenon potentially disturbing to kinetic behavior, namely a possible internal positive temperature gradient due to the exothermic reaction process, would remain of no consequence, since the intrinsic reactivity which is increased, is no longer capable of exerting any kinetic influence even before its further elevation. While diffusivity D, and also gaseous concentration C_{ox}, are actually slow functions of (absolute) temperature, the effects would be outside of the scope of precision justifiable in this investigation. It may be useful to mention that, actually, intraparticle gradients cannot be large in these materials as has been demonstrated by Prater (*12*).

It is of interest that the shell-progressive rate mechanism should have considerable general applicability in a large variety of phenomena. Similar processes have been encountered in solid-gas reactions such as in the reduction of oxides (*10*), and in the oxidation of pyrite (*11*). Analogous models apply to adsorption and chromatographic, phase transition, and other phenomena.

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