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# Diffusion-limited reaction kinetics in nanofabricated porous model catalysts

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Electron beam lithography makes it possible to fabricate ideal, representative models of supported, porous catalysts (with pore and particle dimensions and separations of $\sim$ 10 nm and up). This allows systematic exploration of various scientifically and technically important phenomena associated with porous, supported catalysts. In the present work, we have derived general equations describing the reaction kinetics on such model catalysts in combination with mass-transport corrections. Depending on the geometrical parameters and boundary conditions the reaction rate may be limited by bulk or Knudsen diffusion of reactants inside pores or by diffusion in the regions near or far from the support surface. All these regimes are treated in detail. The results will help both to guide and interpret experiments with nanofabricated catalysts.

**Keywords:** nanometer catalysts, support, pores, bulk diffusion, Knudsen diffusion

The rate of catalytic reactions in porous catalysts is kinetically controlled only at low temperatures while it is limited by internal or external diffusion of reacting species at high temperatures. Models describing the interplay between reaction and diffusion are numerous (see the classical textbooks by Satterfield [1] and Aris [2] and references in recent studies [3,4]). The results obtained there are, however, not directly applicable to the new class of model catalysts produced by modern nanofabrication methods and specifically by electron beam lithography [5,6]. This technique allows [6] the preparation of supported catalysts consisting of controlled size noble-metal particles (down to 10 nm or less in diameter, height and separation) located at the bottom of cylindrical pores (of similar sizes) as schematically shown in figure 1. The height of pores can be varied from zero (no pores) up to many pore diameters. This type of structures – still in the early stage of manufacturing – will be ideal to study various phenomena associated with supported, porous catalysts. Various limits can be systematically explored by independent variations of relevant dimensions.

The goal of this Letter is to treat the role of diffusion limitations in reactions on such catalysts. We want to develop a theoretical tool that can both guide and help to analyze experiments with systematically varied model structures like the one shown in figure 1. Our attention is focused on the first-order reaction, occurring only on the active particles at the bottom of pores (figure 1) under steady-state conditions. This case makes it possible to understand all the essential aspects of the problem under consideration and can easily be generalized to more complex reaction kinetics.

To describe reactant diffusion in the gas phase to the active catalyst, we need to formulate the boundary conditions far from the support surface. In general, these conditions depend on the spatial distribution of the macroscopic gas flux. We consider that the experiment is arranged so that the reactant concentration is fixed, at $c = c_0$, at the distance $H$ from the support surface. In this region (i.e., at $0 \leqslant z \leqslant H$, where $z$ is the coordinate perpendicular to the support surface) and also inside the pore space, the macroscopic gas motion by flow is assumed to be negligible and the spatial reactant concentration is considered to be described by the diffusion equation (the reactive gas mixture is assumed to be diluted so that the reactant diffusion is not affected by counter diffusion of the reaction product).

The diffusion transport is known to depend on the relationship between the pore radius, $R$, and the mean free path of the gas molecules, $l \propto P^{-1}$ ($P$ is pressure). Bulk diffusion occurs at relatively high pressures, where $l < R$. As the pressure or the pore radius are reduced, a change occurs in the diffusion behaviour at $l \simeq R$, from normal bulk diffusion to the Knudsen regime. Expressions for the coefficients of bulk and Knudsen diffusion are available in textbooks (e.g., ref. [1]). To understand the results presented below, we only need to recall that the scale of these coefficients is $D \simeq vl$ for $l < R$, and $D_K \simeq vR$ for $l > R$, where $v \propto T^{1/2}$ is the average thermal velocity of molecules. In addition, one should bear in mind that sometimes diffusion in pores is affected by reactant adsorption on the pore walls. In our treatment, this effect is ignored (if necessary, it can easily be incorporated into the analysis).

For the geometry under consideration (figure 1), an accurate analytical solution to the diffusion equation is hardly possible. But, employing relevant simplifications

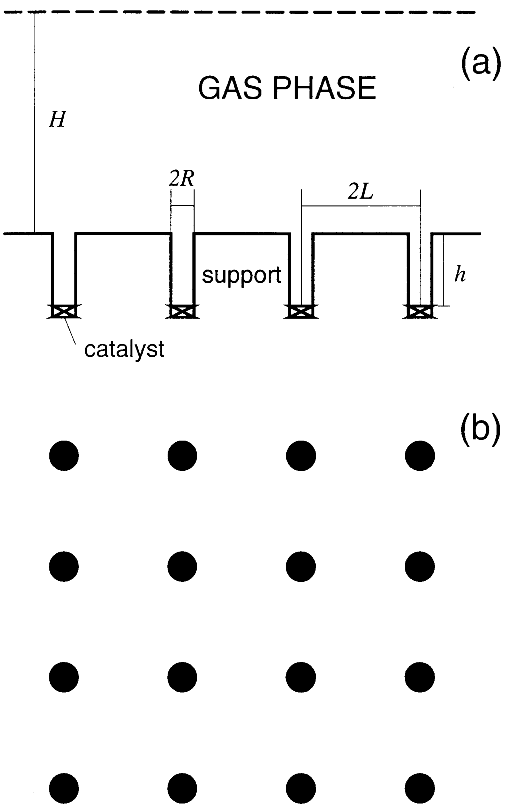

Figure 1. Structure of a model supported catalyst made by nanofabrication. Panels (a) and (b) show the side and top views of the catalyst, respectively. $R$ and $h$ are the pore radius and length. $2L$ is the distance between pores. The gas concentration is fixed at the inlet gas composition at the distance $H$ from the support surface.

in different regions, one can construct approximate solutions incorporating all the interesting features of the problem. This approach is used below for the limits $l < R$ and $l > R$, respectively. In both cases, the distance $H$ is assumed to be macroscopic and large compared to all other distances, i.e. $H > \max(L, h, R, l)$, where $2L$ is the spacing between pores, and $h$ the pore height. For example, for a monolith type of geometry, it could represent the thickness of the (stagnant) boundary layer.

If diffusion occurs via *the bulk mechanism* both outside and inside pores (i.e., $l < R$), the behaviour of the solution to the diffusion equation is qualitatively different in the following three regions.

(i) Far from the pores (at $L \leqslant z \leqslant H$), the perturbations of the gas concentration, created by reaction in different pores, are strongly overlapping. Physically, it is clear that in this region the effect of the details of the pore structure on the type of the solution to the diffusion equation is negligible, i.e., the gas concentration should depend only on $z$,

$$c(z) \simeq c_1 + (c_0 - c_1)(z - L)/(H - L)\,, \tag{1}$$

where $c_1$ is the concentration at $z = L$ ($c_1$ and the concentrations $c_2$ and $c_3$ introduced below will eventually be eliminated to obtain explicit expressions for the reaction rate via $c_0$, $D$ and the known dimensions $H$, $L$, $R$ and $h$). The diffusion flux (per one pore, i.e., per cross section area $4L^2$) is in this case given by

$$J_1 = 4L^2 D(c_0 - c_1)/(H - L) \simeq 4L^2 D(c_0 - c_1)/H\,. \tag{2}$$

(ii) Near the pores (at $0 \leqslant z \leqslant L$), the gas concentration at a particular point in space depends first of all on the reaction in the nearest pore(s). In this case, we can construct half-spheres with radii $R$ and $L$ above every pore (see the left pore in figure 1). To a first approximation, the solution to the diffusion equation in these regions is spherically symmetric, i.e., it depends only on the distance $r$ ($R \leqslant r \leqslant L$) between a given point and center of the entrance of the pore,

$$c(r) \simeq \frac{c_1 L - c_2 R}{L - R} - \frac{RL(c_1 - c_2)}{r(L - R)}\,. \tag{3}$$

This expression has been constructed so that $c(L) = c_1$ and $c(R) = c_2$, where $c_2$ is the concentration near the pore entrance. The diffusion flux (per one pore) is accordingly represented as

$$J_2 = 2\pi RL(c_1 - c_2)/(L - R)\,. \tag{4}$$

In reality, the solution of the diffusion equation in the region under consideration depends of course not only on $r$ but also on the polar angles. The deviations from spherical symmetry are, however, expected to be minor. For this reason, we have ignored such deviations. The latter allows to produce a transparent solution given by eq. (3), to calculate the diffusion flux (4), and afterwards to get analytical expressions for the reaction rate.

(iii) Inside the pores (at $-h \leqslant z \leqslant 0$), the gas concentration again depends primarily on $z$,

$$c(z) \simeq c_3 + (c_2 - c_3)(z + h)/h\,, \tag{5}$$

and the diffusion flux (per one pore) is given by

$$J_3 = \pi R^2 D(c_2 - c_3)/h\,, \tag{6}$$

where $c_3$ is the concentration near the catalyst (at $z = -h$). In addition, we have the equation for the reaction rate (per one pore)

$$W = \pi R^2 k_{\mathrm{r}} c_3\,, \tag{7}$$

where $k_{\mathrm{r}}$ is the reaction rate constant.

The balance equations for the diffusion fluxes are

$$J_1 = J_2\,, \quad J_2 = J_3\,, \quad J_3 = W\,. \tag{8}$$

Substituting (2), (4), (6) and (7) into (8) yields

$$c_0 - c_1 = X(c_1 - c_2)\,, \tag{9}$$

$$c_1 - c_2 = Y(c_2 - c_3)\,, \tag{10}$$

$$c_2 - c_3 = Zc_3\,, \tag{11}$$

where $X = \pi RH/[2L(L - R)]$, $Y = R(L - R)/(2Lh)$, and $Z = hk_{\mathrm{r}}/D$.

From eqs. (9)–(11), one can easily find that the reaction rate, expressed via the known gas concentration far from the pores, is given by

$$W = \pi R^2 k_r c_0 / (1 + Z + YZ + XYZ)\,. \tag{12}$$

Inserting the explicit expressions for $X$, $Y$ and $Z$ into eq. (12) yields

$$W = \pi R^2 k_r c_0 \Big/ \left[1 + \frac{hk_r}{D} + \frac{R(L-R)k_r}{2LD} + \frac{\pi R^2 H k_r}{4L^2 D}\right]. \tag{13}$$

The three terms in the square brackets in this equation describe, respectively, the diffusive resistance in regions (i), (ii) and (iii). The total diffusive resistance is significant if the sum of these terms is of the order of unity or larger. Diffusion in one of the regions limits the reaction rate alone if the corresponding term is much larger than unity and much larger than the other two terms.

In particular, the reaction rate, limited by diffusion inside pores,

$$W \simeq \pi R^2 D c_0 / h\,, \tag{14}$$

is as expected increased by an increasing pore width and a decreasing pore depth. If the reaction is limited by diffusion in the region near the support surface, the reaction rate depends first of all on the pore radius,

$$W \simeq 2\pi RLD c_0 / (L - R)\,. \tag{15}$$

When diffusion far from the support is the limiting factor, the reaction rate,

$$W \simeq 4L^2 D c_0 / H\,, \tag{16}$$

is entirely determined by the surface area per pore and the position of $H$.

If the mean free path of the gas molecules is larger than the pore radius ($l > R$), diffusion inside pores occurs via *the Knudsen mechanism*. In this case, the analysis of the reaction kinetics is basically the same as for $l < R$. The details of the treatment are slightly different in the situations when $l < L$ and $l > L$, respectively.

If $l < L$, we can again analyze diffusion in the regions (i), (ii) and (iii) as described above. The only new two points are that (a) the smaller half-spheres, constructed near the pores (region (ii)), should be of the radius $l$ instead of $R$ (because application of the diffusion equation at $r < l$ is senseless) and (b) $D$ in the equations for region (iii) should be replaced by $D_K$. Then we again have eqs. (9)–(10) for the concentrations $c_1$, $c_2$ and $c_3$ and eq. (12) for the reaction rate, but now with $X = \pi l H / [2L(L - l)]$, $Y = R^2(L - l)D_K/(2LlhD)$, and $Z = hk_r/D_K$. Substituting these expressions into eq. (12) yields

$$W = \pi R^2 k_r c_0 \Big/ \left[1 + \frac{hk_r}{D_K} + \frac{R^2(L-l)k_r}{2lLD} + \frac{\pi R^2 H k_r}{4L^2 D}\right]. \tag{17}$$

Taking into account that $R < l$, $l < L$, $D \simeq vl$, and $k_r \leqslant v$, we conclude that the second diffusive term in the square brackets in this equation is in fact negligible, i.e. region (ii) does not contribute to the diffusive resistance. Omitting this term, we have

$$W = \pi R^2 k_r c_0 \Big/ \left[1 + \frac{hk_r}{D_K} + \frac{\pi R^2 H k_r}{4L^2 D}\right]. \tag{18}$$

This equation can be simplified in two limits corresponding to the diffusive resistance occurring primarily inside and outside pores, respectively. In the former case, the reaction rate, $W \simeq \pi R^2 D_K c_0 / h$, is the same as eq. (14) but with $D$ replaced by $D_K$. In the latter case, we again have eq. (16).

For $L < l \ll H$, one can omit region (ii) from the analysis entirely, because application of the diffusion equation near the support surface at distances less than $l$ is senseless. The reaction rate is then given by eq. (18).

The results obtained above for the first-order reaction can easily be generalized to *more complex reaction schemes*. If for example the reaction involves $n$ reactants, we have $n$ concentrations $c^i(z)$ ($i \leqslant n$) with the condition that $c^i(H) = c^i_0$, where $c^i_0$ is the concentration of reactant $i$ at $z = H$. Then, we introduce the concentrations $c^i_1$, $c^i_2$ and $c^i_3$ defined in analogy with those ($c_1$, $c_2$ and $c_3$) used in secs. 2 and 3. The consumption rate (per one pore) of reactant $i$ is given by (cf. eq. (7))

$$W_i = \pi R^2 k^i_{\mathrm{ef}} c^i_3\,, \tag{19}$$

where $k^i_{\mathrm{ef}}$ is the *effective* adsorption rate constant dependent on surface coverage and defined so that $k^i_{\mathrm{ef}} c^i_3$ is the *net* adsorption rate (per unit area) of reactant $i$. Employing the equation derived above ((13) or (18)), we can express $c^i_3$ in eq. (19) via $c^i_0$. Then, eq. (19) should be solved self-consistently with the kinetic equations for reactant coverages, i.e., with the equations describing elementary reaction steps in the adsorbed overlayer.

In summary, we have derived general equations showing how diffusion limitations come into play in reactions occurring on model supported catalysts that can be fabricated by electron beam lithography. The results obtained can be used to estimate when the diffusive resistance is important in real reactions, and in that case, in which regions of the catalyst the diffusive resistance is highest.

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