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When the Final Catalyst Activity Profile Depends Only on the Total Amount of Admitted Substance: Theoretical Proof

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Significance

It is shown, based on pulse-response experiments, that under special conditions the activity profile of a prepared catalytic system depends only on the total amount of admitted substance. This property, previously found computationally, is here established mathematically for porous and nonporous catalysts in different pulse reactors. This result can be used as a theoretical guidance for the design of systems or materials with an optimal activity profile, in particular a catalyst bed or a catalyst particle. Consequently, it can be used for understanding and developing the different diffusion-reaction processes, e.g., wet impregnation, deactivation of active materials, and so forth.

Keywords: catalyst preparation, catalyst activity profile, temporal analysis of products, pulse-response experiment, mathematical model

The optimal or controlled design of catalytic systems at all scales, that is, active site, catalyst pellet or membrane, and catalytic reactor, remains one of the most important problems in chemical technology.[1,2] Now it is evident that special, in general nonuniform distributions of the active sites within the catalytic unit (pellet, membrane, reactor, etc.) may bring many advantages in terms of controlling selectivity or lifetime.[1–6]

Recently, in computational pulse-response adsorption experiments,[7] a very interesting phenomenon was found: the calculated profiles of catalytic active sites were identical if the number of molecules pulsed during the adsorption procedure was the same. Whether 10 “small” pulses containing 10^{13} molecules each or one “large” pulse of 10^{14} molecules

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are injected, the calculated profiles of sorbates, and hence of the final active sites, are identical. Phanawadee et al.[7] analyzed the model of temporal analysis of products (TAP) response gas-solid experiments. Details on the latter technique can be found elsewhere.[8–10] This property was found for several different cases studied in the TAP-setup: (a) for nonporous and for porous catalysts; (b) for different configurations of the TAP reactor, that is, one-zone, thin-zone, and three-zone.

A one-zone reactor is a bed filled by catalyst pellets. In a three-zone reactor, the catalyst bed is sandwiched between two beds packed with nonporous inert particles (quartz). A thin-zone reactor is a three-zone reactor in which the middle, catalytic, zone is thin enough to be considered longitudinally uniform regarding the catalytic active site distribution. The goal of this article is to provide a rigorous theoretical explanation of the computational result,[7] and hence also clues for the development of a new paradigm of design of catalytic units with a controlled profile of catalytic active sites.

The TAP-experiment is performed in the Knudsen diffusion regime, in which the diffusion coefficient does not depend on the chemical mixture composition, or on the total pressure. However, this property can be fulfilled even in a domain somewhat wider than the Knudsen diffusion domain, and not only for gas-solid processes. In the modeling by Phanawadee et al.,[7] it was assumed that the adsorption process is irreversible and monomolecular. We would like to stress that irreversible monomolecular adsorption in a TAP reactor can be considered as the simplest process representing impregnation of supports for catalyst preparation. Our analytical results will be obtained specifically for this process and hold equally for an irreversible reaction involving the formation of gas-phase products; however, the same analysis can be applied to many processes of material preparation with a controlled profile of active substances, for example, preparation of materials via wet impregnation and optimization of the catalyst profile during the deactivation process.

From the beginning of this article, we would like to distinguish the following characteristics of catalytic units: (1) the profile: longitudinal, in our case corresponding to the reactor scale; or radial, in our case corresponding to the catalytic support scale; (2) the integral amount of gas by which the catalyst is treated at the given position (longitudinal or radial) during all preparation procedures. This integral amount can be found as the area under the concentration curve vs. time and can be interpreted as the total gas exposure over time. For nonporous catalysts, identical longitudinal properties were obtained across the bed. For porous catalytic systems, two types of identical profiles were found, at two length scales: (1) longitudinal profiles across the reactor; (2) radial profiles within the catalyst pellet. In all mentioned cases, the profiles calculated computationally[7] were functions of the total amount of pulsed molecules only, not of any other parameters of the pulse procedure, such as the number of pulses and the number of molecules per pulse.

First, we are going to formulate two principles of uniqueness, starting from which the phenomenon can be explained theoretically both from the physicochemical and mathematical viewpoint.

1. At any position (longitudinal or radial) of the catalytic unit, the final catalyst composition is uniquely defined by the integral amount of gas substance concentrations related to the given position. This statement reflects a chemical feature, that is, the irreversible interaction between the fluid ingredients, say the active site precursor, and the solid phase, for example, the catalyst support. It is completely independent of the fluid dynamics.
2. The integral amount of gas substance concentrations related to the given position is uniquely defined by the total amount of molecules admitted to the chemical reactor. This statement reflects a specific hydrodynamic feature of our device, viz. the type of transport, boundary conditions, and so forth.

The following five cases have been analyzed, and similar results have been obtained: (1) nonporous catalyst, single-zone TAP reactor; (2) nonporous catalyst, three-zone TAP reactor; (3) nonporous catalyst, thin-zone TAP reactor (TZTR); (4) porous catalyst, three-zone TAP reactor; (5) porous catalyst, TZTR.

Within this article, being limited by space, only two cases can be presented:

1. Three-zone TAP reactor (nonporous catalyst). Its particular modifications are the single-zone TAP reactor and TZTR with the nonporous catalyst, respectively.
2. TZTR with the porous catalyst

Three-Zone Bed Reactor, Nonporous Catalyst

If the three zones have lengths L_1, L_2, and L_3, and the first and third are inert but the second is reactive, the equations in the three-zone nonporous reactor are:

- The diffusion or diffusion/reaction equations for the gas concentration C

$$\epsilon_1 \frac{\partial C(x,t)}{\partial t} = D_1 \frac{\partial^2 C(x,t)}{\partial x^2}, \quad 0 \le x < L_1, \quad 0 \le t < +\infty \tag{1}$$

$$\epsilon_2 \frac{\partial C(x,t)}{\partial t} = D_2 \frac{\partial^2 C(x,t)}{\partial x^2} - \rho_s (1-\epsilon_2) k C(x,t)(1-\theta(x,t)), \quad L_1 < x < L_1+L_2, \quad 0 \le t < +\infty \tag{2}$$

$$\epsilon_3 \frac{\partial C(x,t)}{\partial t} = D_3 \frac{\partial^2 C(x,t)}{\partial x^2}, \quad L_1+L_2 < x < L_1+L_2+L_3, \quad 0 \le t < +\infty \tag{3}$$

where the $\epsilon_{1,2,3}$ are the void ratios of the zones, the $D_{1,2,3}$ their diffusivities, ρ_s the number of moles of active sites per volume of catalyst pellet, and k the adsorption rate constant;

- The interface equations for the concentration C at the boundaries between zones, expressing continuity of concentration

$$C(L_1^-,t) = C(L_1^+,t), \quad C(L_1+L_2^-,t) = C(L_1+L_2^+,t), \quad 0 \le t < +\infty \tag{4}$$

and of flux

$$-D_1 \frac{\partial C}{\partial x}(L_1^-,t) = -D_2 \frac{\partial C}{\partial x}(L_1^+,t), \quad 0 \le t < +\infty \tag{5}$$

$$-D_2 \frac{\partial C}{\partial x}(L_1+L_2^-,t) = -D_3 \frac{\partial C}{\partial x} C(L_1+L_2^+,t), \quad 0 \le t < +\infty \tag{6}$$

- The reaction equation for the coverage θ in the second zone

$$\frac{\partial \theta(x,t)}{\partial t} = kC(x,t)(1-\theta(x,t)), \quad L_1 < x < L_1+L_2, \quad 0 \le t < +\infty \tag{7}$$

- The boundary condition on C at the reactor inlet (i.e., $x=0$)

$$-D_1 \frac{\partial C}{\partial x}(0,t) = \frac{N_p}{A} I(t), \quad 0 \le t < +\infty \tag{8}$$

where A is the cross-sectional area of the bed, N_p the number of moles of the reactant gas in the inlet flow, and $I(t)$ the unit-area normalized distribution of inlet flux intensity with respect to time;

- The boundary condition on C at the reactor outlet (where $x=L_1+L_2+L_3$)

$$C(L_1+L_2+L_3,t)=0, \quad 0 \le t < +\infty \tag{9}$$

- The initial condition on C (empty reactor)

$$C(x,0)=0, \quad 0 \le x \le L_1+L_2+L_3 \tag{10}$$

- the initial coverage θ_0

$$\theta(x,0)=\theta_0(x), \quad L_1 < x < L_1+L_2 \tag{11}$$

Despite the nonlinearity of the system (1)–(11), its special properties do allow an integration over time, as follows. Rewriting (7) as

$$\frac{1}{1-\theta(x,t)} \frac{\partial \theta(x,t)}{\partial t} = kC(x,t), \quad L_1 < x < L_1+L_2, \quad 0 \le t < +\infty \tag{12}$$

both sides can be integrated from $t=0$ to $+\infty$, yielding

$$\ln \frac{1-\theta_0(x)}{1-\theta_{+\infty}(x)} = kM(x) \tag{13}$$

where by $\theta_{+\infty}(x) = \lim_{t\to\infty} \theta(x,t)$, we denote the final coverage, and by $M(x)=\int_0^{+\infty} C(x,t)dt$, the zeroth moment of $C(x, t)$. This $M(x)$ is, therefore, the total concentration exposure. Solving (13) for $\theta_{+\infty}(t)$, we find that

$$\theta_{+\infty}(x) = 1-(1-\theta_0(x))\exp(-kM(x)) \tag{14}$$

The expression $kM(x)$, which is dimensionless, characterizes the efficiency of exposure, and will be denoted by $\tilde{M}$. By substitution of the reaction term in (2), we then obtain

$$\epsilon_2 \frac{\partial C(x,t)}{\partial t} = D_2 \frac{\partial^2 C(x,t)}{\partial x^2} - \rho_s(1-\epsilon_2)\frac{\partial \theta(x,t)}{\partial t}, \quad L_1 < x < L_1+L_2 \tag{15}$$

which can be integrated over $0 \le t < +\infty$ to produce

$$0 = D_2 \frac{d^2 M(x)}{dx^2} - \rho_s(1-\epsilon_2)(1-\theta_0(x))\exp(-kM(x)), \quad L_1 < x < L_1+L_2 \tag{16}$$

The interface conditions (4) imply that $M(x)$ is a continuous function at $x=L_1$ and $x=L_1+L_2$, and (5) and (6) imply that

$$\begin{aligned} -D_1 \frac{dM}{dx}(L_1^-) &= -D_2 \frac{dM}{dx}(L_1^+), \\ -D_2 \frac{dM}{dx}(L_1+L_2^-) &= -D_3 \frac{dM}{dx}(L_1+L_2^+) \end{aligned} \tag{17}$$

The inlet boundary condition (8) integrates to

$$-D_1 \frac{dM}{dx}(0) = \frac{N_p}{A}\int_0^{+\infty} I(t)dt \tag{18}$$

and the outlet boundary condition (9) integrates to

$$M(L_1+L_2+L_3)=0 \tag{19}$$

Now the system consisting of (16)–(19) is a second-order ordinary differential equation with fully specified boundary conditions, defining uniquely the solution $M(x)$; and the inlet pulse $(N_p/A)I(t)$ only occurs under the form of the total inlet pulse, its integral $(N_p/A)\int_0^{+\infty} I(t)dt$. The solution $M(x)$ determines the final coverage profile $\theta_{+\infty}$ in the second zone uniquely via (13). Therefore, both uniqueness Principles (I) and (II) hold, and the final coverage is a function only of the total amount pulsed in, and does not depend on any other properties of the distribution $I(t)$ over time.

If the initial coverage $\theta_0(x)$ is zero, a semianalytical solution can be found as follows:

- In the first zone, (1) is readily integrated using the fact that the gas concentration C tends to zero when $t \to +\infty$, giving $0=D_1 \frac{d^2M}{dx^2}$, so that $M(x)=a+bx$ for $0 \le x < L_1$, for some constants a and b. The constant b is directly obtained from the inlet condition (18), $-D_1 b = \frac{N_p}{A}\int_0^{+\infty} I(t)dt$. To determine the constant a, we write M_l for $M(L_1)$, the value at the left of the reactive zone. Then $M_l=a+bL_1$ determines a from b and M_l.
- Similarly, integrating (3) leads to $M(x)=a'+b'x$ when $L_1+L_2 < x < L_1+L_2+L_3$, with a' and b' other constants. If we write M_r for $M(L_1+L_2)$, the value at the right of the reactive zone, $M_r=a'+b'(L_1+L_2)$ and the outlet boundary condition (19) implies $0=a'+b'(L_1+L_2+L_3)$, so that a' and b' are uniquely determined by two independent linear equations.
- Now the analysis concentrates on the second zone, introducing the dimensionless coordinate $\xi=(x-L_1)/L_2$ so that $0 < \xi < 1$, and the dimensionless concentration moment $\tilde{M}=kM$. We introduce the following dimensionless groups: the Damköhler number $\mathrm{Da}=\frac{k\rho_s(1-\epsilon_2)L_2^2}{D_2}$, the dimensionless pulse size $\tilde{p}=\frac{N_p \mathrm{Da}}{\rho_s(1-\epsilon_2)AL}\int_0^{+\infty} I(t)dt$, and the aspect ratio of Zones 3 and 2, $\tilde{\alpha}=\frac{L_3/D_3}{L_2/D_2}$.

Let $\tilde{V}$ denote $d\tilde{M}/d\xi$, then $d^2\tilde{M}/d\xi^2=\tilde{V}(d\tilde{V}/d\tilde{M})$ and $\tilde{V}(d\tilde{V}/d\tilde{M})=\mathrm{Da}(1-\exp(-\tilde{M}))$, which is a separable ordinary differential equation that integrates to $\frac{1}{2}(\tilde{p}^2-\tilde{V}^2)= \mathrm{Da}(\tilde{M}_l-\tilde{M}+\exp(-\tilde{M}_l)-\exp(-\tilde{M}))$. Defining the dimensionless auxiliary functions $\tilde{\psi}(x,y)=(\tilde{p}^2-2\mathrm{Da}(x-y+\exp(-x)-\exp(-y)))^{1/2}$ and $\tilde{\phi}(a,b)=\int_a^b d\tilde{M}/\tilde{\psi}(b,\tilde{M})$, we then obtain a system of equations for $\tilde{M}_l$ and $\tilde{M}_r$: $\tilde{\phi}(\tilde{M}_r,\tilde{M}_l)=1$ and $\tilde{\alpha}\tilde{\psi}(\tilde{M}_l,\tilde{M}_r)=\tilde{M}_r$. Using these, the solution is defined implicitly as $\tilde{\phi}(\tilde{M}(\xi),\tilde{M}_l)=\xi$, from which the final coverage follows by $\theta_{+\infty}=1-\exp(-\tilde{M}(\xi))$.

Thin-Zone Bed Reactor, Porous Catalyst

The superscript p is used to indicate properties of the pores; these have radius R and the external surface area of the pellet per unit volume of the pellet is denoted λ. We assume that the initial coverage is zero, $\theta_0^p(y)=0$. Writing M_z for the moment of concentration in the thin-zone and $M^p(y)$ for the moment of concentration inside the pellet, as a function of the internal variable y, $0 \leq y \leq R$, we introduce the dimensionless internal variable $\zeta = y/R$ and the dimensionless moments $\tilde{M}_z = kM_z, \tilde{M}^p(\zeta) = kM^p(y)$. Using the two Damköhler numbers $\mathrm{Da} = \frac{k\rho_s(1-\epsilon_2)L_2L_3}{D_3}$ and $\mathrm{Da}^p = \frac{k\rho_s R^2}{D_p}$, a similar time integration of the diffusion-reaction equation leads to

$$\frac{d^2\tilde{M}^p}{d\zeta^2} = \mathrm{Da}^p\left(1-\exp\left(-\tilde{M}^p(\zeta)\right)\right) \tag{20}$$

with boundary conditions $d\tilde{M}^p/d\zeta = 0$ at $\zeta = 0$ and $\tilde{M}^p(1) = \tilde{M}_z$. We limit our analysis to the case $d = 1$, one-dimensional pores, as opposed to $d = 2$ or $d = 3$ because only then does this equation not include explicitly the independent variable ζ, which makes it amenable to solution in terms of quadratures.

Writing $\tilde{M}^p(0) = \tilde{M}_l^p$ for the moment at the inside of the pellet,

$$\int_{\tilde{M}_l^p}^{\tilde{M}^p(\zeta)} \frac{d\tilde{M}^p}{\sqrt{2\mathrm{Da}^p\left(\tilde{M}^p - \tilde{M}_l^p + \exp\left(-\tilde{M}^p\right) - \exp\left(-\tilde{M}_l^p\right)\right)}} = \zeta \tag{21}$$

is the semianalytic, implicit solution for the moment along the pellet profile, from which the final coverage follows as before from $\theta_{+\infty}^p(y) = 1-\exp\left(-\tilde{M}^p(\zeta)\right)$. To determine $\tilde{M}_l^p$ in this formula, we compute the jump over the thin-zone

$$\tilde{p} - \tilde{M}_z = R\lambda \frac{\mathrm{Da}}{\mathrm{Da}^p} \sqrt{2\mathrm{Da}^p\left(\tilde{M}_z - \tilde{M}_l^p + \exp\left(-\tilde{M}_z\right) - \exp\left(-\tilde{M}_l^p\right)\right)} \tag{22}$$

and state that at $\zeta = 1$, $\tilde{M}_z = \tilde{M}^p(1)$ due to the absence of external transport limitations, so that (21) specializes to

$$\int_{\tilde{M}_l^p}^{\tilde{M}_z} \frac{d\tilde{M}^p}{\sqrt{2\mathrm{Da}^p\left(\tilde{M}^p - \tilde{M}_l^p + \exp\left(-\tilde{M}^p\right) - \exp\left(-\tilde{M}_l^p\right)\right)}} = 1 \tag{23}$$

Consequently, (22) and (23) form a system of two equations defining $\tilde{M}_l^p$ and $\tilde{M}_z$; when the former is known, (21) gives the profile. Once again, its dependence on the total amount of injected gas flux is established and both uniqueness principles (I) and (II) apply.

Conclusions

A remarkable phenomenon described and explained here, that is, that the final catalytic profile depends only on the total amount of substance admitted to the reactor, can be a prototype of precise preparation procedures for materials with desired active component profiles. It can be applied in the area of catalysis and even far beyond the catalytic technology in processes in which the active material distribution plays a significant role (impregnation processes, processes with activation and deactivation, etc.). In subsequent work, we will extend the developed theory into the domain of elevated pressures, intending to cover an area of industrial catalysis.

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