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Mathematical aspects of deactivation processes of rough catalytic surfaces

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Abstract

The progressive deactivation of catalytic surfaces, either by parallel or serial fouling, is a key problem in heterogeneous catalysis. A mathematical model of the deactivation of a catalytic reactor is presented. It is shown that this dynamical model can be turned into the study of the steady-state non-linear response of the same system but for a virtual species. This mapping of the problem permits to obtain analytical results such as the duration of the reactor or its total production. As an example, one shows how a fractal surface would respond in such a deactivation process. Finally, a way to control the time dependency of the reactor production is suggested.

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Keywords: Catalysis; Diffusion; Fractal; Non-linear

The understanding of heterogeneous catalysis represents today an important economic and scientific challenge [1–6]. In this paper, we consider a catalytic interface slowly deactivated due to a fouling mechanism, and address the following question: what role does the geometrical irregularity of the catalytic surface play on the dynamics of the deactivation process? Furthermore, how do the geometry and the deactivation process interplay to affect the overall performance and duration of the catalytic activity? The aim of the present study is to give some preliminary answers to these questions. The

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most important result of our theoretical work suggests a new way to control the time dependency of the catalytic production in a slowly deactivated catalyst. For a first order reaction, our results show that *the knowledge of a single time response function of the system provides a means to control the production process under a broad range of operational conditions. Moreover, we show that this general result can be applied to a catalyst of unknown deactivation dynamics and arbitrary geometry.*

1. Theoretical model

We first introduce the model describing the slow deactivation of an irregular catalytic surface in the Eley–Rideal situation. In such a system, the reactant A diffuses from a source at a given concentration C_A^{src} (which may be time dependent) towards a catalytic surface. The bulk diffusion is characterized by Fick's law, $\vec{J}_A = -D\vec{\nabla}C_A$, C_A being the concentration of A and D its diffusion coefficient. When encountering the surface, a molecule A can react in two different ways. First, it can react with the catalyst X according to the desired catalytic reaction that creates a new species A^*, $A + X \rightarrow A^* + X$. On the other hand, it also can react according to another reaction, called *parallel fouling*, $A + X \rightarrow (AX)_c$, that creates a complex species $(AX)_c$ no longer active as a catalytic site.

As shown in the left part of Fig. 1, we are concerned with the steady-state regime of the system where the concentration C_A in the bulk of the diffusion–reaction cell obeys the Laplace equation, $\nabla^2 C_A = 0$. On the catalytic surface, the local flux of disappearance of species A is given by $j = k_1 C_X C_A + k_2 C_X C_A = K C_X C_A$, where C_X is the surface concentration of active sites, k_1 and $k_2 \ll k_1$ are the rate coefficients respectively for the catalytic and the deactivation reactions, and $K = k_1 + k_2$. While the boundary condition at the catalytic surface is given by $D\,\frac{\partial C_A}{\partial n} = K C_X C_A$, the local rate of decrease of catalyst concentration C_X, due to the parallel fouling, is $\frac{dC_X}{dt} = -k_2 C_X C_A$. The dynamics of the

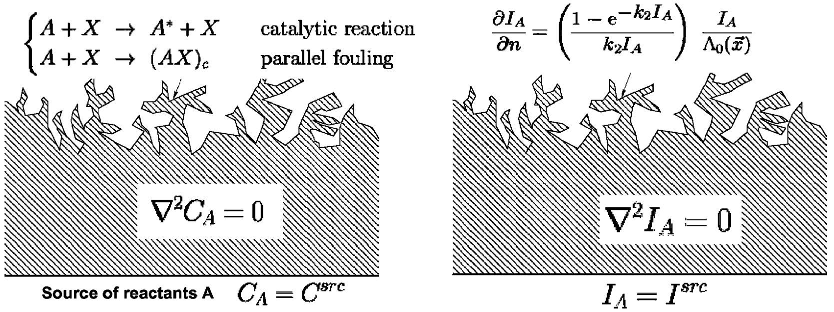

Fig. 1. (left) Schematic of the chemical reactions involved in parallel fouling, (right) Scheme of the static time integrated non-linear problem.

species A and X are thus described by the following set of equations:

$$\begin{aligned}
&C_A = C_A^{src}(t) \quad \text{at the source (a)}\,,\\
&\nabla^2 C_A = 0 \quad \text{in the bulk (b)}\,,\\
&\frac{\partial C_A}{\partial n} = \frac{K}{D} C_X(\vec{x},t) C_A(\vec{x},t) \quad \text{at the surface (c)}\,,\\
&\frac{\mathrm{d}C_X}{\mathrm{d}t} = -k_2 C_X(\vec{x},t) C_A(\vec{x},t) \quad \text{at the surface (d)}\,.
\end{aligned} \tag{1}$$

In the particular case of a constant concentration of A at the source, the evolution of $C_A(\vec{x},t)$ is solely due to the variation of the concentration of active catalyst on the surface. Eq. (1) represents a non-linear system with two unknowns, C_A and C_X, which has in general no analytical solution.

One now introduces the time integrated concentration $I(\vec{x},t) \equiv \int_0^t C_A(\vec{x},\tau)\mathrm{d}\tau$. This quantity obviously also obeys the Laplace equation. Furthermore, Eq. (1d) can be integrated with respect to time, giving:

$$C_X(\vec{x},t) = C_X^0(\vec{x})\mathrm{e}^{-k_2 I(\vec{x},t)}\,,$$

where $C_X^0(\vec{x})$ is the initial distribution of active sites on the surface at time $t = 0$. The boundary condition for I at the catalytic surface is then obtained from the time integrated combination of Eqs. (1c) and (1d)

$$\frac{\partial I}{\partial n} = \int_0^t \frac{\partial C_A(\vec{x},\tau)}{\partial n}\,\mathrm{d}\tau = -\int_0^t \frac{K}{Dk_2}\frac{\mathrm{d}C_X}{\mathrm{d}t}\,\mathrm{d}\tau = \frac{KC_X^0(\vec{x})}{Dk_2}[1-\mathrm{e}^{-k_2 I}]\,. \tag{2}$$

As a result, the deactivation problem can be formulated by means of the new set of equations:

$$\begin{aligned}
&I = I^{src} = \int_0^t C_A^{src}(\tau)\mathrm{d}\tau \quad \text{at the source (a)}\,,\\
&\nabla^2 I = 0 \quad \text{in the bulk (b)}\,,\\
&\frac{\partial I}{\partial n} = \frac{1-\mathrm{e}^{-k_2 I}}{k_2 \Lambda_0(\vec{x})} \quad \text{at the source (c)}\,.
\end{aligned} \tag{3}$$

$\Lambda_0(\vec{x}) \equiv D/KC_X^0(\vec{x})$ can be interpreted as the perimeter of a part of the catalytic interface that works uniformly at the beginning of the reaction [7–9]. The diffusion–reaction system is thus described only in terms of the new variable I in which the time appears now as a dummy variable in the boundary condition at the source. For a fixed value of I^{src}, this set of equations represents a non-linear steady-state system. Given the solution of this system, the evolution of the dynamical system can be obtained in the following way: let $\Phi(I^{src})$ be the response of the non-linear system (3)

$$\Phi(I^{src}) = -D \int_{surf.} \frac{\partial I}{\partial n} \, \mathrm{d}s \; . \tag{4}$$

The time dependent flux of A species that can be written as

$$\phi_A(t) = -D \int_{surf.} \frac{\partial C_A}{\partial n} \, \mathrm{d}s = -D \int_{surf.} \frac{\partial}{\partial n} \frac{\partial I}{\partial t} \, \mathrm{d}s = \frac{\mathrm{d}I^{src}}{\mathrm{d}t} \frac{\mathrm{d}\Phi(I^{src})}{\mathrm{d}I^{src}} \; . \tag{5}$$

The resulting Eq. (5) expresses mathematically the fact that, if the solution $\Phi(I^{src})$ is known for any I^{src}, one can predict the dynamic response of the system for any arbitrary, and even time dependent, input concentration $C_A^{src}(t)$. One therefore can call the function $\Phi(I^{src})$ the "*master curve*" of the system. It is important to stress that this curve also gives the cumulative production at time t. This result is valid whatever the dynamics of the source concentration.

2. General results

In the case of a constant concentration at the source C_A^{src}, the flux of A through the catalytic surface becomes

$$\phi_A(t) = C_A^{src} \left. \frac{\mathrm{d}\Phi}{\mathrm{d}I^{src}} \right|_{(I^{src} = C_A^{src}.t)} \; . \tag{6}$$

This equation indicates that the time dependency of the production provides a direct way to determine the function $\mathrm{d}\Phi/\mathrm{d}I^{src}$ of a catalytic system that, in general, is not known a priori. This single function gathers the signatures of the geometrical as well as the physico-chemical characteristics of the catalytic system (i.e., the internal geometry of the interface, the distribution of active sites, the diffusivity, and both the reaction and fouling kinetics).

The total catalytic production can be written as $N = \int_0^{+\infty} \phi_A(t)\mathrm{d}t$, which is also the flux of I when $t \to +\infty$. In this limit, I increases everywhere and the boundary condition (2) saturates at the value $\left(\frac{KC_X^0(\vec{x})}{k_2 D}\right)$. This leads to $N = \frac{k_1}{k_2} \int_{surf.} C_X^0(\vec{x})\mathrm{d}s = \left(\frac{k_1 \langle C_X^0 \rangle_{surf.}}{k_2}\right) S_{tot}$, where S_{tot} is the total developed surface of the catalyst. The total production of A^* molecules is then directly determined by the total amount of available catalytic surface *independently of the interface morphology and the existence of diffusion limitations.*

For sufficiently large diffusivity or, equivalently, small enough systems, the concentration of A is uniform everywhere and equal to C_A^{src}. In this situation,

$$C_X(\vec{x},t) = C_X^0(\vec{x})\mathrm{e}^{-t/\tau_0} \quad \text{and} \quad \phi_A(t) = (KC_X^0 C_A^{src})\mathrm{e}^{-t/\tau_0} \; , \tag{7}$$

where $\tau_0 \equiv (k_2 C_A^{src})^{-1}$. τ_0 is thus the *intrinsic characteristic time of the deactivation process*. It can be determined experimentally by monitoring the deactivation of a sufficiently small catalyst pellet.

On the other hand, the influence of a small diffusivity (or large access impedance) can be investigated in the case of a flat interface. In this case, the problem can be treated in one dimension. Let I^{su} be the value of I at the surface and h the height of the cell. The flux of I through the bulk is simply given by Fick's law, $S_{tot}D\left(\frac{I^{src}-I^{su}}{h}\right)$, while the flux at the catalytic surface determined by Eq. (3c). The conservation of the flux thus yields the following relation:

$$S_{tot}\left(\frac{KC_X^0}{k_2}\right)[1-\mathrm{e}^{-k_2I^{su}}]=\frac{S_{tot}D}{h}\left(I^{src}-I^{su}\right)\,. \tag{8}$$

The crossover between the early (non-deactivated) and late (deactivated) regimes is determined by the condition $k_2I^{su}\approx 1$. As long as $k_2I^{su}\ll 1$, Eq. (8) can be solved at first order, which yields: $I^{su}\approx\frac{I^{src}}{1+\frac{h}{\Lambda_0}}$.

The crossover condition thus corresponds to: $t\approx\tau_0\left(1+\frac{h}{\Lambda_0}\right)\equiv\tau_1$.

This new time τ_1 is the *characteristic time of the deactivation process in the entire cell*, taking into account both the diffusion process through the cell of height h and the deactivation process on the catalytic surface.

In summary, the flux of reactants A through a cell with a flat catalytic surface remains constant (at a value $DS_{tot}C_A^{src}/(h+\Lambda_0)$) until $t=\tau_1$. After this time, the flux then decreases exponentially with a characteristic time τ_0. In the case of an irregular interface, there exists a distribution of distances between the source and the different regions of the surface, and thus a distribution of the corresponding different deactivation times.

In order to investigate the influence of the interface morphology on the production of slowly deactivated catalytic system, the responses of six different geometries have been numerically computed. As shown in the left part of Fig. 2, these morphologies correspond to the first six generations of the triangular Von Koch curve. Each of these diffusion–reaction cells has been discretized in triangular elements, and the solution of the non-linear Eq. (3) has been computed through finite element techniques. The right part of Fig. 2 presents the "master curves" of the different cells. The increase of their

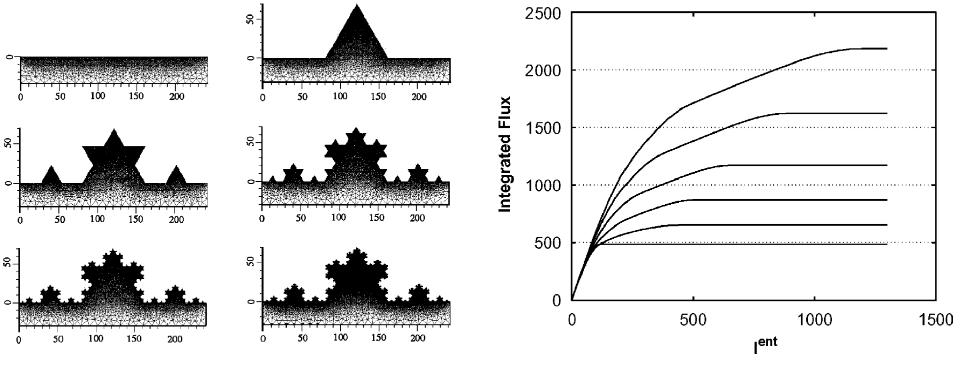

Fig. 2. (left) Finite element meshings for the six prefractal interfaces. (right) Flux of I^{src} versus input concentration I^{src} for the six different interfaces. For each interface, the corresponding curve is the master curve from which can be deduced the response of the cell for *any* input concentration $C^{src}(t)$.

saturation values (i.e., total production) by a factor $\frac{4}{3}$ at each generation corresponds to the increasing lengths of the prefractal perimeters.

3. Controlling the time production of an unknown catalyst

As previously demonstrated, the catalytic production under deactivation is fully determined by the function $\mathrm{d}\Phi/\mathrm{d}I^{src}$, i.e., the derivative of the master curve. Moreover, we have also shown that, even if the geometry of the system and the active sites distribution are unknown, this curve can be experimentally obtained from constant source concentration measurements. But Eq. (5) also provides a way to obtain an arbitrary time-dependent flux $\phi_A(t)$ by imposing an appropriate (variable) input concentration $C_A^{src}(t)$. In order to do so, this concentration must verify, from Eq. (5): $C_A^{src}(t)\frac{\mathrm{d}\Phi}{\mathrm{d}I^{src}}|_{I^{src}(t)}=\phi_A(t)$. A time integration of this equation yields: $\Phi(I^{src}(t))=\int_0^t \phi_A(\tau)\mathrm{d}\tau \equiv F(t)$. Introducing Ψ as the inverse function of Φ, one can express what is the dynamics of the source concentration that will give the reactant flux $\phi_A(t)$:

$$C_A^{src}(t)=\frac{\mathrm{d}}{\mathrm{d}t}[\Psi(F(t))]=\phi_A(t)\left[\left.\frac{\mathrm{d}\Phi}{\mathrm{d}I^{src}}\right|_{I^{src}=\Psi(F(t))}\right]^{-1} . \tag{9}$$

For practical purposes, the only requirement is to know $\mathrm{d}\Phi/\mathrm{d}I^{src}$, from which Φ and Ψ can be deduced. But, as we have shown above, this can be deduced from the experimental determination of the behavior of the flux for a constant concentration (or partial pressure) at the source of the system. An important practical problem is to determine how to operate a diffusion–reaction system that is progressively deactivated, in order to obtain a constant flux of product. In mathematical terms, it corresponds to find the corresponding time dependent source concentration $C_A^{src}(t)$ that would result in a constant output flux ϕ_A. Applying Eq. (9) in the case of a constant flux ϕ_A gives after some algebra:

$$C_A^{src}(t)=\phi_A\left[\left.\frac{\mathrm{d}\Phi(I^{src})}{\mathrm{d}I^{src}}\right|_{I^{src}=\Psi(\phi_A\times t)}\right]^{-1}=\frac{\phi_A}{\Phi'[\Psi(\phi_A\times t)]} . \tag{10}$$

Knowing that the function Φ, which is the flux of species I, saturates at the value $\Phi_{sat.}=(KC_X^0 S_{tot.})/k_2$, the product $\phi_A\times t$ cannot exceed this value. It is thus possible to maintain a constant flux ϕ_A of reactants only until a time t_{end} such that:

$$t_{end}=\frac{KC_X^0}{\phi_A k_2}S_{tot} .$$

In summary, the dynamics of deactivation through parallel fouling of an irregular catalytic interface operating under diffusion-limited conditions has been investigated. We have been able to develop a general analytical approach that can be applied to any arbitrary interface geometry with any distribution of active sites. The main result here is that the behavior of the system, whatever the input concentration and time dependency, can be deduced from the knowledge of a “master curve” which is the solution of a non-linear problem. This curve represents the time integrated production as a function of the time integrated input concentration. It remarkably retains the complete characterization of the catalytic system in terms of its morphology, its diffusional limitations and the chemical reaction kinetics at the surface.

In practical cases where neither the geometry nor the active sites are known, the method developed here provides a means to obtain the "master curve" from a single experiment, namely, the measure of the time production for a fixed concentration at the input. Once obtained, this curve can be used to determine the dynamics of the system subjected to more complex boundary conditions. Finally, our approach also gives some hints on the way to design a catalytic geometry that is proper to a specific chemical process. Although the final total production depends only on the total catalytic surface, we showed here that, as described, the deactivation dynamics can be adequately modulated to perform some required operational task (e.g., production at a constant flux).

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