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Theoretical Investigations of the Dynamics of Chemical Reactions on Nanocatalysts with Multiple Active Sites

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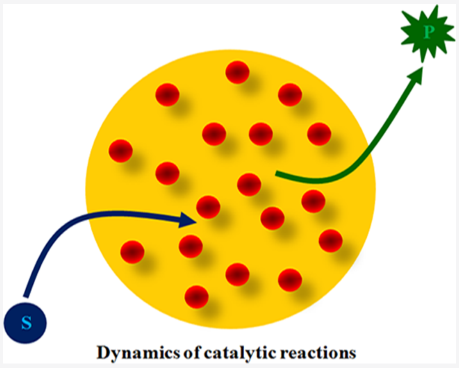
ABSTRACT: Recent synthetic advances led to the development of new catalytic particles with well-defined atomic structures and multiple active sites, which are called nanocatalysts. Experimental studies of processes at nanocatalysts uncovered a variety of surprising effects, but the molecular mechanisms of these phenomena remain not well understood. We propose a theoretical method to investigate the dynamics of chemical reactions on catalytic particles with multiple active sites. It is based on a discrete-state stochastic description that allows us to explicitly evaluate dynamic properties of the system. It is found that for independently occurring chemical reactions, the mean turnover times are inversely proportional to the number of active sites, showing no stochastic effects. However, the molecular details of reactions and the number of active sites influence the higher moments of reaction times. Our theoretical method provides a way to quantify the molecular mechanisms of processes at nanocatalysts.



Dynamics of catalytic reactions

Catalysis remains one of the most important techniques in modern chemical research as well as in multiple industrial applications.[1,2] A huge majority of chemical compounds are currently produced using various methods of heterogeneous catalysis, and new catalysts are constantly developed.[1−4] One of the most promising recent developments is the synthesis of so-called nanocatalysts, which are catalytic particles with well-defined atomic structures and multiple active sites.[4−6] Numerous chemical processes on nanocatalysts have been intensively investigated with high temporal and spatial resolutions, showing that chemical processes at different catalytic sites might interfere with each other,[7−11] but the molecular mechanism of these phenomena remains not well understood.

The intrinsic heterogeneity of nanocatalysts complicates the precise characterization of chemical processes in these systems utilizing only ensemble measurements. Much more detailed information can be obtained by using single-molecule experimental approaches.[7−11] In these experiments, the reactions of transformations of nonfluorescent molecules into the fluorescent products were catalyzed on nanocatalyst particles, and stochastic fluorescent bursts have been monitored with a single-molecule precision. These bursts have been attributed to single catalytic turnovers, and distributions of waiting times before such events have been measured. From these studies, it was found that there is a wide distribution in the rates of product formations and dissociations on nanocatalysts[7,8,12,13] and that the size of nanoparticles is affecting dynamic surface restructuring, leading to temporal dependence of the catalytic activities.[14,15] Also, it was shown that fluctuations in chemical kinetic rates are larger for smaller nanocatalysts. Another surprising observation was that different catalytic sites might influence each other,[10] but the molecular mechanisms of such cooperative communications remain not well quantified.

There is a limited amount of theoretical studies that address the fundamental aspects of processes that are taking place in nanocatalysts. The earliest theoretical attempt to explain the processes on nanocatalysts employed the Langmuir−Hinshelwood approach that assumed that there is one ”effective” catalytic site that represents all active sites.[8] However, this approach has multiple issues. It assumes the binding/unbinding equilibrium between substrates and the catalyst, it cannot explain the experimentally observed size-dependent catalytic activity,[14,15] and it also does not allow us to probe the communication effects between different active sites.[10] Also, this mean-field approach neglects the important stochastic effects due to chemical reactions taking place randomly at each active site, and this prevents the detailed investigations of underlying molecular mechanisms. Later, a more advanced theoretical method to analyze chemical processes on nanocatalysts has been proposed.[16,17] It is based on the first-passage analysis of dynamics, and it partially takes into account the number of active sites and the related stochastic effects.

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However, this approach considers only oversimplified chemical reactions at each catalytic site. The biggest weakness of both current theoretical approaches is that they cannot provide a link between the experimentally measured distributions of reaction times and the molecular mechanisms of underlying processes on nanocatalysts. In this Letter, we present a theoretical study that aims to fill this fundamental gap. Using a discrete-state stochastic model that takes into account the stochasticity of individual chemical reactions at each catalytic site, it is shown how the molecular details of these processes might be related to experimentally measured distributions of reaction times, suggesting explicit procedures of probing the mechanisms of chemical reactions on nanocatalysts.

We consider a system consisting of a single nanocatalyst particle with N identical active sites, as illustrated in Figure 1a.

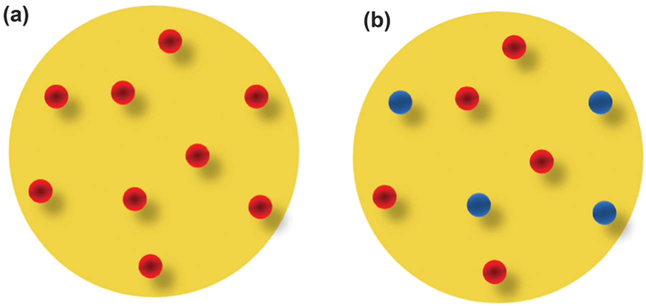

Figure 1. Schematic representation of a nanocatalyst with N (a) identical catalytic sites and (b) two different types of catalytic sites.

It is assumed that all catalytic sites are independent of each other and all of them are equally accessible to the substrate molecules. At each site, the chemical reaction with M ($M = 1, 2, ...$) sequential intermediate states is taking place; see Figure 2a. In this scheme, CS_j describes the intermediate chemical state j ($j = 1, 2, ..., M$) at the given catalytic site. From the state CS_j, the reaction moves forward to the state CS_{j+1} with a rate u_j, whereas the backward transition that leads to the state CS_{j-1} has a rate w_j. The substrate first binds to the catalytic site with a rate proportional to the concentration of substrates, $u_0 = k[S]$, whereas the final transition that creates the product molecule P is assumed to be irreversible, and it has a transition rate u_M (Figure 2a). Just like the experimental measurements, we are calculating the catalytic time distributions and the related statistical quantities associated with the consecutive product formation events where the possibility of one or more product formation from a single or a few sites is considered, and it can be quantified by the number of catalytic sites present in the CS_M state.

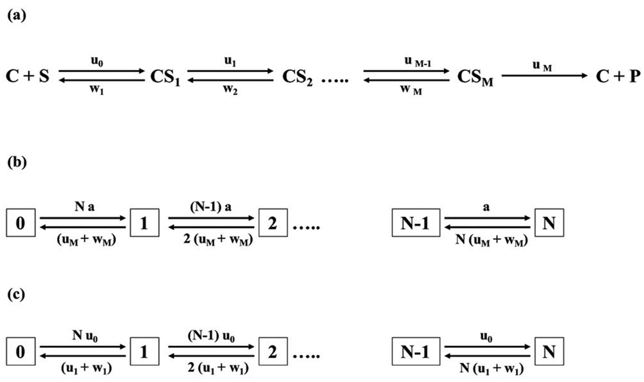

Figure 2. (a) Schematic representation of a chemical reaction taking place at each catalytic site. (b) System with N catalytic sites and with M intermediate states for the reaction at each site. (c) System with one intermediate state, $M = 1$.

Chemical reactions are simultaneously happening at different catalytic sites, and the overall dynamics in the system can be described using a discrete-state stochastic scheme presented in Figure 2b. Here the state n refers to a situation when n active sites are found in the chemical state CS_M just before the product formation is taking place. From the state n, the transition rates to the state $n + 1$ and $n - 1$ are given by $(N - n)a$ and $n(u_M + w_M)$, respectively. The parameter a is the effective rate of reaching the state n from the state $n - 1$, and it can be always explicitly determined in terms of transition rates (u_j, w_j) for any M, as shown later. The physical meaning of the parameter a is as follows. It maps the chemical reaction with M intermediate states at each catalytic site into an effective reaction with only one intermediate state (just before the making the product), and the rate a is the effective rate of reaching this state.

At large times, the dynamics in the system reaches stationary conditions. We define P_n as the steady-state probability of finding the system in the state n, that is, with n sites in the conformation CS_M. Because the number of states in the system is finite, at $t \to \infty$, the discrete-state stochastic model (see Figure 2b) can be viewed to be in effective equilibrium. Then, these probabilities are related to each other via the following relations

$$\begin{aligned} NaP_0 &= (u_M + w_M)P_1 \\ (N-1)aP_1 &= 2(u_M + w_M)P_2 \\ &\dots \\ aP_{N-1} &= N(u_M + w_M)P_N \end{aligned} \tag{1}$$

Taking into account the normalization condition, $\sum_{n=0}^{N} P_n = 1$, these equations can be easily solved to produce

$$P_n = \frac{N!}{(N-n)!n!}\frac{x^n}{(1+x)^N} \tag{2}$$

where $x = \frac{a}{u_M + w_M}$.

We can now estimate the total flux to make the product P under stationary conditions

$$J_N = u_M P_1 + 2u_M P_2 + \dots + Nu_M P_N = N\frac{au_M}{a + u_M + w_M} \tag{3}$$

The reciprocal of the flux gives the mean time between the product release events, $\langle\tau\rangle_N = 1/J_N$, which is also the average reaction time, as measured in single-molecule experiments. Equation 3 implies that

$$\langle\tau\rangle_N = \frac{\langle\tau\rangle_1}{N} \tag{4}$$

That is, the mean reaction times are inversely proportional to the number of active sites. This means that if one considers only the mean reaction times as a measure of the chemical processes occurring at the nanocatalyst, then the stochastic effects can be neglected. This does not depend on the specific details of the chemical reactions at each site, which, however, affect the amplitude of reaction times. Considering only the mean reactions times, a system with N sites with the rates $(u_j; w_j)$ $[j = 1, 2, ..., M]$ behaves exactly like a system with an "effective" single catalytic site with the rescaled rates $(Nu_j; Nw_j)$. To further clarify the fact that the mean reaction times are independent of the nature of catalyzed chemical reactions at each site, these observations are illustrated in Figure 3.

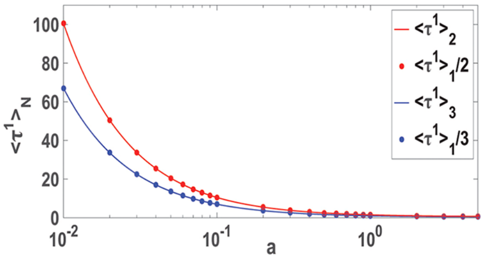

Figure 3. Mean reaction times for the system with N catalytic sites as a function of the effective rate a with $u_M = w_M = 1$.

The effective rate a plays an important role in our analysis. Here we show how it can be explicitly expressed in terms of the intrinsic transition rates (u_j, w_j). We notice that this parameter depends only on the number of intermediate states M, but it is independent of the number of catalytic sites N. For $N = 1$, the flux is given by[18]

$$J_1 = \frac{au_M}{a + u_M + w_M} = \frac{1}{R_M} \tag{5}$$

The parameter R_M has been evaluated before[18]

$$R_M = \sum_{j=0}^{M} r_j \tag{6}$$

where

$$r_j = \frac{1}{u_j}\left[1 + \sum_{k=1}^{M} \Pi_{l=j+1}^{j+k} \frac{w_l}{u_l}\right] \tag{7}$$

Then, from eq 5, we obtain

$$a = \frac{u_M + w_M}{u_M R_M - 1} \tag{8}$$

One can easily see that for $M = 1$, we have $a = u_0$.

Because the mean reaction times do not reflect the stochasticity of the system and do not allow us to obtain the molecular information on the mechanisms of chemical reactions at each site, we have to investigate the higher moments of the reaction times. For this purpose, we introduce a method based on the first-passage probability calculations of the catalytic times distributions. The discrete-state stochastic scheme for this approach is presented in Figure 4. We define $F_n(t)$ as a probability density function to complete the catalytic cycle and to make the product P for the first time at time t if at $t = 0$ the system started in the state n (n catalytic sites are in the conformation CS_M). The temporal evolution of these first-passage probabilities is governed by a set of backward master equations[19]

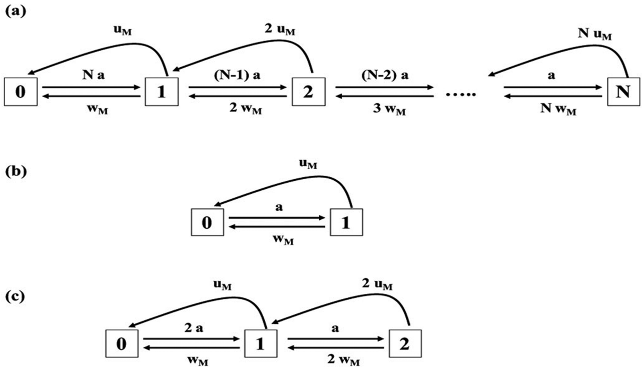

Figure 4. (a) Theoretical framework for first-passage analysis for a system with N catalytic sites involving chemical reactions with M intermediate states. Representation of the system for (b) one catalytic site ($N = 1$) and (c) two catalytic sites ($N = 2$) and arbitrary values of M.

$$\begin{aligned}
\frac{dF_0(t)}{dt} &= NaF_1(t) - NaF_0(t) \\
\frac{dF_1(t)}{dt} &= (N-1)aF_2 + w_M F_0(t) + u_M F_P(t) \\
&\quad - [(N-1)a + u_M + w_M]F_1(t) \\
\frac{dF_n(t)}{dt} &= (N-n)aF_{n+1} + nw_M F_{n-1}(t) + nu_M F_P(t) \\
&\quad - [(N-n)a + n(u_M + w_M)]F_n(t) \\
\frac{dF_N(t)}{dt} &= Nw_M F_{N-1}(t) + Nu_M F_P(t) - N(u_M + w_M)F_N(t)
\end{aligned} \tag{9}$$

where $F_P(t)$ is for the product state with $F_P(t) = \delta(t)$. The physical meaning of this relation is that if the system is already in the product state, then the reaction is immediately finished. These equations can be solved for any number of active sites (e.g., using Laplace transformations), which will yield the distributions of reaction times. All dynamic properties in the system can be evaluated from these distributions. For example, the first and second moments of the reaction times starting from the state n are given by (in terms of the derivatives of Laplace transformations for the first-passage probability functions $\widetilde{F}_n(s)$[19])

$$\langle T_n \rangle = -\left(\frac{\partial \widetilde{F}_n(s)}{\partial s}\right)_{s=0}, \quad \langle T_n^2 \rangle = \left(\frac{\partial^2 \widetilde{F}_n(s)}{\partial s^2}\right)_{s=0} \tag{10}$$

To illustrate this approach, let us consider several specific cases. For $N = 1$, the Laplace transforms of the reaction times distributions can be easily evaluated, yielding

$$\begin{aligned}
\widetilde{F}_0(s) &= \frac{au_M}{s^2 + s(u_M + w_M + a) + au_M}, \\
\widetilde{F}_1(s) &= \frac{u_M(s + a)}{s^2 + s(u_M + w_M + a) + au_M}
\end{aligned} \tag{11}$$

from which we obtain the first and the second moments of the reactions times

$$\langle\tau\rangle_1 = \langle T_0\rangle = \frac{u_M + w_M + a}{a u_M},$$
$$\langle\tau^2\rangle_1 = 2\left[\left(\frac{u_M + w_M + a}{a u_M}\right)^2 - \frac{1}{a u_M}\right] \tag{12}$$

which can be rewritten as

$$\langle\tau^2\rangle_1 = \langle T_0^2\rangle = 2(\langle\tau\rangle_1)^2 - \frac{2}{a u_M} \tag{13}$$

The analysis can be extended to the systems with $N = 2$ and $N = 3$ catalytic sites, as explained in detail in the Supporting Information. It gives

$$\langle\tau^2\rangle_2 = \frac{1}{4}\left[\langle\tau^2\rangle_1 + \frac{2}{(a u_M)^2(\langle\tau\rangle_1)^2}\right] \tag{14}$$

and

$$\langle\tau^2\rangle_3 = \frac{1}{9}\left[\langle\tau^2\rangle_1 - \frac{4}{(a u_M)^2(\langle\tau\rangle_1)^2} + \frac{16}{2(a u_M)^2(\langle\tau\rangle_1)^2 + a u_M}\right] \tag{15}$$

If multiple active sites can be viewed as a single new effective catalytic site with the properly rescaled transition rates, then one would expect the following scaling relation, $\langle\tau^2\rangle_N = \langle\tau^2\rangle_1/N^2$. However, eqs 14 and 15 clearly show deviations from this behavior. Thus the effect of the stochasticity of individual chemical reactions exhibits itself in the second and higher moments of reaction times. In addition, the molecular details of these chemical reactions specify the degree of deviations from the previously mentioned scaling relation. Figure 5 illustrates these observations for several numerical examples.

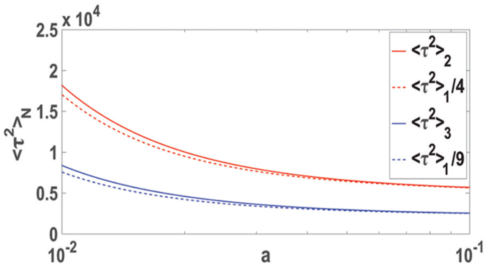

Figure 5. Mean-squared reaction times $\langle\tau^2\rangle_N$ (in s^2) for the system with N catalytic sites as a function of the effective rate a (in s^{-1}) for $u_M = 0.01$ s^{-1} and $w_M = 0.001$ s^{-1}.

The degree of stochastic fluctuations is frequently measured by a dimensionless parameter known as the randomness[19,20]

$$R = \frac{\langle\tau^2\rangle - \langle\tau\rangle^2}{\langle\tau\rangle^2} \tag{16}$$

But note that slightly different definitions of the randomness are also possible.[20] The value of the randomness quantifies the degree of stochastic noise in dynamic processes. Low fluctuations are observed for $R \approx 1$, whereas any deviation from unity is the sign of strong fluctuations. Our theoretical method allows us to explicitly evaluate the randomness $R_{N,M}$ for the system with N active sites and M intermediate states. For example, for a system with one catalytic site ($N = 1$), we obtain

$$R_{1,M} = 1 - \frac{2}{(\langle\tau\rangle_1)^2 a u_M} \tag{17}$$

for $N = 2$ catalytic sites, we have

$$R_{2,M} = 1 - \frac{2}{(\langle\tau\rangle_1)^2 a u_M}\left(1 - \frac{1}{(\langle\tau\rangle_1)^2 a u_M}\right) \tag{18}$$

and for $N = 3$, we derive

$$R_{3,M} = 1 - \frac{2}{(\langle\tau\rangle_1)^2 a u_M}\left(1 + \frac{2}{(\langle\tau\rangle_1)^2 a u_M} - \frac{8}{1 + 2(\langle\tau\rangle_1)^2 a u_M}\right) \tag{19}$$

Figure 6a presents the dependence of the randomness on the effective transition rate a for $N = 1$, 2, and 3 for an arbitrary number of intermediate states M. It shows a nonmonotonic behavior of the randomness. The largest noise is expected for intermediate values of a, whereas the noise is diminished for very small and very large transition rates a. This observation can be explained with the help of the discrete-state scheme in Figure 2. For $a \to 0$, the system is mainly found in the state $(N - 1)$, and there are not many stochastic fluctuations. Similarly, for $a \gg 1$ the system prefers to be in the state N, and this again leads to very small stochastic fluctuations. Only for intermediate values of a are all discrete states in the system fully explored, leading to large noise. Our theory, however, also predicts that increasing the number of catalytic sites should lower the degree of stochastic fluctuations (see Figure 6a), in agreement with experimental observations.[15] The degree of stochastic noise also depends on the complexity of the chemical reactions at each catalytic site. This is illustrated in Figure 6b, where the randomness is presented as a function of the transition rate u_0. One can see that increasing the number of intermediate states M influences the degree of stochastic noise in the system. These observations suggest that the analysis of experimentally obtained randomness parameters can assist in determining the molecular details of the chemical

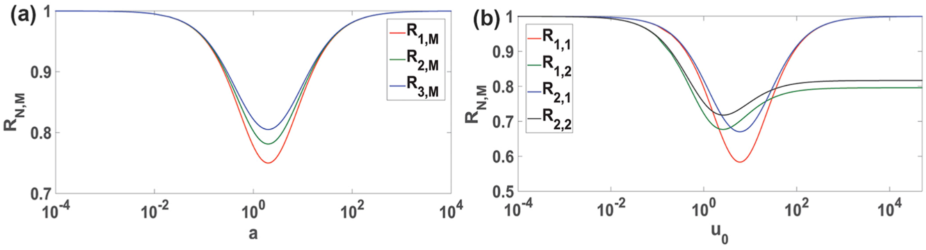

Figure 6. Randomness parameter $R_{N,M}$ (a) as a function of the effective rate a (in s^{-1}) for a system with $N = 1$ (red line), $N = 2$ (green line), and $N = 3$ (blue line) catalytic sites for an arbitrary number of intermediate states M and (b) as a function of the transition rate u_0 (in s_1) for a system with one and two catalytic sites and having one ($M = 1$) and two ($M = 2$) intermediates.

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reactions at each catalytic site.[21,22] Our theoretical method can help to explicitly quantify these relations.

One of the advantages of our theoretical approach is that it can be extended in several directions to present a more realistic description of the complex processes on the nanocatalysts. For example, we can analyze a system with two types of catalytic sites, as shown in Figure 1b. There are N_1 active sites where there are chemical reactions with transition rates (u_j, w_j) and N_2 active sites where there are chemical reactions with transition rates (p_j, q_j) with $N = N_1 + N_2$. As shown in the Supporting Information, the reaction dynamics in the system with two types of particles can be explicitly analyzed. Assuming that all reactions have M intermediate states, we obtain for the mean reaction time

$$\langle \tau^1 \rangle_N = \frac{(a + u_M + w_M)}{N_1 a u_M} + \frac{(b + p_M + q_M)}{N_2 b p_M} \tag{20}$$

where a and b are effective transition rates before the production steps. (See the Supporting Information.) This result again shows that the stochasticity effects can be neglected when considering the mean turnover times, whereas the molecular details of underlying chemical reactions will influence the higher moments of catalytic times.

In this Letter, we developed a theoretical method to analyze the dynamics of chemical processes of catalytic particles with multiple active sites. Using the discrete-state stochastic description, dynamic properties of the chemical reactions on nanocatalysts are explicitly evaluated via stationary-state and first-passage probability calculations. Our analysis shows that the mean reaction times in the system are inversely proportional to the number of active sites, independently of the details of underlying chemical reactions. This result suggests that the stochastic effects are averaged out due to the cancellation of noise by chemical processes taking place independently at different catalytic sites for the mean chemical reaction rates, and the nanocatalyst with multiple active sites can be viewed as one new effective catalyst with a single site if only these average quantities are considered. Careful consideration of higher moments of reaction times leads, however, to a different conclusion. For this situation, the stochastic effects are important. In addition, it is found that the higher moments are affected by the details of the chemical reactions at each active site. Physical−chemical arguments to explain these observations are presented. We also argue that because of exact analytical results from our calculations, the proposed theoretical method can be utilized for uncovering the quantitative features of the complex processes on nanocatalysts. It will be critically important to test our theoretical predictions in experimental studies as well as in the more advanced computational methods.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.0c00316.

> Calculation of moments of catalytic time distribution using the master equation approach. Calculation of flux for systems with different types of catalytic sites using steady-state analysis (PDF)

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Notes

The authors declare no competing financial interest.

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