Oscillations in catalytic reactions on the nm scale

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We present Monte Carlo simulations of the oscillatory kinetics of CO oxidation on catalytic metals in the case when the reaction is accompanied by the formation of surface oxide. The lattice size is varied from 50×50 to 3×3 in order to mimic nm catalyst particles. More or less regular oscillations are found for the sizes down to 15×15.

Keywords: regular and irregular kinetic oscillations, nm catalyst particles, CO oxidation, oxide formation, Monte Carlo simulations

The first report on oscillations in heterogeneous catalytic reactions was published in the early 1970s by Hogo [1], who studied CO oxidation on Pt in a flow reactor. Since then, regular and chaotic oscillations were found in about thirty reactions on practically all types of catalysts including single crystals, polycrystalline samples (foils, ribbons and wires) and supported catalysts at a pressure range from 10^{-12} bar to atmospheric pressure [2–5]. The experience accumulated indicates that often oscillations are observed in the systems where a rapid bistable catalytic cycle is combined with a relatively slow "side" process, e.g., with oxide formation [6], carbon deposition [7] or adsorbate-induced surface restructuring [4,5]. Despite the fact that in many cases a mechanism of oscillations is considered to be established, the understanding of this intriguing phenomenon is still limited, especially in the situations when the experiments are executed on supported catalysts. For example, we refer to two interesting studies of oscillations observed in CO oxidation over zeolite-supported Pd [8] and silica-supported Pt [9] under nearly isothermal conditions. In both cases, the metal crystallites with the size about 10 nm were located primarily inside pores (even though the size of Pd particles exceeded the largest cages of the host lattice). In the former case, the total pressure and temperature were 1 atm (20 vol% O_2 and $\leqslant$0.15 vol% CO) and 450 K, respectively. In the latter case, oscillations were found at $P = 10$–100 mTorr ($0.04 \leqslant \mathrm{CO/O_2} \leqslant 1.7$) and $T = 400 - 600$ K. The two questions naturally arising in connection with such observations are: how do the oscillations depend on the size of metal particles? and how are the oscillations synchronized? or, more specifically, how are the mass-transport limitations affecting oscillations? Addressing the first question, we present Monte Carlo (MC) simulations of the oscillatory kinetics of CO oxidation on Pt or Pd on a lattice with the sizes corresponding to nm particles.

Taking into account that the mechanism of oscillations in CO oxidation on nm Pt and Pd particles is usually believed (see, e.g., [8]) to include slow oxidation and reduction of the catalyst, we employ the corresponding model proposed by Sales, Turner and Maple (STM) [6]. The elementary steps involved into this process are as follows:

$$\mathrm{A_{gas}} \rightleftharpoons \mathrm{A_{ads}} \tag{1}$$

$$\mathrm{(B_2)_{gas}} \rightarrow 2\mathrm{B_{ads}} \tag{2}$$

$$\mathrm{A_{ads}} + \mathrm{B_{ads}} \rightarrow \mathrm{(AB)_{gas}} \tag{3}$$

$$\mathrm{B_{ads}} \rightarrow \mathrm{B^{*}_{ads}} \tag{4}$$

$$\mathrm{A_{ads}} + \mathrm{B^{*}_{ads}} \rightarrow \mathrm{(AB)_{gas}} \tag{5}$$

where A stands for CO, B_2 for O_2, B for chemisorbed oxygen and B^* for the oxide form of oxygen.

The kinetics predicted by the scheme above depend on the ratio between the rates of elementary reaction steps and reactant diffusion. In CO oxidation, diffusion of adsorbed CO molecules is much faster than the Langmuir–Hinshelwood (LH) step (3), which is rapid compared to reactant adsorption [10]. The slowest processes are the substrate oxidation and reduction. The MC analysis of the STM model with this ratio of elementary steps was recently performed in [11]. The attention was focused on cooperative effects resulting from lateral interactions between adparticles. The infinitely extended surface was replaced by a (200×200) square lattice with periodic boundary conditions (for a lattice of this or larger size, the effect of the boundary conditions on oscillations is almost negligible). In the present simulations, we neglect cooperative effects and focus on the dependence of oscillations on the lattice size, L. Specifically, we show the kinetics for $3 \leqslant L \leqslant 50$. The approach we use is basically the same as earlier [11]. The only difference is that we replace the periodic boundary conditions by open boundary conditions, because the latter conditions are more appropriate in order to mimic nm particles.

Illustrating the dependence of the reaction kinetics on the lattice size, we neglect changes in the reactant pressures. In the full-scale simulations of reactions on nm supported particles, the reactant pressures should be calculated self-consistently with the reaction kinetics. At present, due to computational limitations, the self-consistent treatment can however be done only by using the mean-field (MF) equations (see, e.g., recent simulations [12] of oscillations in a continuous stirred tank reactor). The MF approach does not however make it possible to scrutinize the reaction kinetics on the nm scale. Under such circumstances, the MC and MF treatments are complementary. In particular, our results show the limits of applicability of the MF approximation.

In our simulations, A and B_2 adsorption is assumed to occur on vacant sites and pairs of nearest-neighbour (nn) vacant sites, respectively. Desorption of A particles and oxide formation are treated as first-order processes. Reactions (3) and (5) occur between nn particles. Diffusion of A particles is realized via jumps to nn vacant sites. B diffusion is neglected (because this process is assumed to be slow compared to the LH step).

To simulate the reaction kinetics, we introduce the dimensionless parameters, $p_{\rm rea}$, characterizing the relative rates of reaction (steps (1)–(5)) and A diffusion. The rates of these processes are considered to be proportional to $p_{\rm rea}$ and $1 - p_{\rm rea}$, respectively. More specifically, we use the number $N_{\rm dif} \equiv (1 - p_{\rm rea})/p_{\rm rea}$ characterizing the ratio of the rates of A diffusion and reaction. As noted earlier [11], the results of simulations are nearly independent of $N_{\rm dif}$ at $N_{\rm dif} \geqslant 10$. In our present study, we employ $N_{\rm dif} = 100$.

The rates of A and B_2 adsorption and A desorption are considered to be proportional to $p_{\rm A}$, $p_{{\rm B}_2}$ and $p_{\rm des}$. The rate of the LH step (3) is proportional to $1 - p_{\rm des}$. In addition, we introduce the parameters, $p_{\rm ox}$ and $p_{\rm red}$, characterizing the rates of substrate oxidation (4) and reduction (5). All these parameters should be much lower than unity, because the LH step is rapid compared to the other steps (except A diffusion).

The MC algorithm for simulating the reaction kinetics consists of attempts to realize reaction or A diffusion steps:

(1) A random number ρ ($0 \leqslant \rho \leqslant 1$) is generated. If $\rho > p_{\rm rea}$, an A-diffusion trial is performed (item (2)). If $0 < \rho < p_{\rm rea}$, a reaction trial is executed (item (3)).

(2) For A diffusion, an adsorption site is chosen at random. If the site is vacant, the trial ends. Otherwise, an A particle located in this site tries to diffuse. In particular, an adjacent site is randomly selected, and if the latter site is vacant, the A particle is replaced into it. For boundary sites, an adjacent site is chosen among all the nn sites including the sites outside the $L \times L$ lattice. If the site selected does not belong to the $L \times L$ lattice, the trial ends.

(3) A reaction trial contains several steps: (i) An adsorption site is chosen at random. (ii) A new random number ρ' is generated. (iii) If the site selected is vacant, A or B_2 adsorption acts are realized provided that $\rho' < p_{\rm A}$ and $p_{\rm A} < \rho' < p_{\rm A} + p_{{\rm B}_2}$, respectively. For B_2 adsorption, one of the nn sites is chosen at random, and the trial is accepted provided that the latter site is vacant and belongs to the $L \times L$ lattice. (iv) If the site selected is occupied by A, A desorption or reaction act is executed for $\rho' < p_{\rm des}$ and $\rho' > p_{\rm des}$, respectively. For A reaction, one of the nn sites is chosen at random, and the trial is considered to be successful if the latter site is occupied by B. If the site is occupied by B^*, the reaction occurs with the probability $p_{\rm red}$. (v) If the site selected is occupied by B, step (4) is performed provided that $\rho' < p_{\rm ox}$.

All the MC runs were started from the clean surface. To measure time, we use MC steps (MCS). One MCS is defined as $L \times L$ attempts of the adsorption–reaction events. This means that the MC and real times are interconnected as $t_{\rm MC} = (k_{\rm des} + k_{\rm LH})t$, where $k_{\rm des}$ and $k_{\rm LH}$ are the rate constants for A desorption and LH reaction. (In principle, one might define one MCS as $L \times L$ trials of adsorption, reaction and A diffusion. In the latter case, the time scale would primarily be connected with A diffusion, because in our simulations this process is rapid compared to other steps. Our experience indicates however that the effect of diffusion on the period of oscillations is fairly weak, provided that diffusion is fast and the time scale is not directly related to the diffusion rate. Under such circumstances, it does not seem to be reasonable to choose the diffusion-based time scale.)

The simulations were executed for $p_{{\rm B}_2} = 0.01$, $p_{\rm des} = 0.002$, $p_{\rm ox} = 0.003$, $p_{\rm red} = 0.001$, and $N_{\rm dif} = 100$. With this choice, there is only one governing parameter, $p_{\rm A}$. Well developed oscillations are found to occur near $p_{\rm A} = 0.01$.

The results of simulations with $p_{\rm A} = 0.01$ are shown in figures 1 and 2. For $L = 50$ (figure 1(a)), the oscillations are close to those observed earlier [11] on large lattices. The only difference is that the period of oscillations slightly fluctuates. With decreasing L down to 30 (figures 1(b) and 2) and then to 20 (figure 1(c)), the period and amplitude of oscillations slightly increase. The fluctuations increase as well. For $L = 10$ and 5 (figure 1 (d) and (e)), the oscillations are irregular. For $L = 3$ (figure 1(f)), the system first oscillates and then is trapped to the non-reactive state when the surface is completely covered by oxide. (The non-reactive state may be avoided if the repulsive interaction between nn B particles is so strong that B_2 adsorption occurs on next-nearest-neighbour sites [10]. If necessary, this effect can be easily introduced into the model.)

Typical configurations of adsorbed particles during oscillations are exhibited in figure 2 for $L = 30$. Scrutinizing the snapshots presented, one can easily find deviations from the random distribution. In particular, the B^* particles are seen (panels (c) and (d)) to be located primarily inside islands. The size of islands is however rather small (∼5).

In summary, our analysis of the STM model indicates that more or less regular oscillations related to oxide formation can be observed down to $L = 15$. Thus, in principle, one can employ the MF model even for very small (∼5 nm)

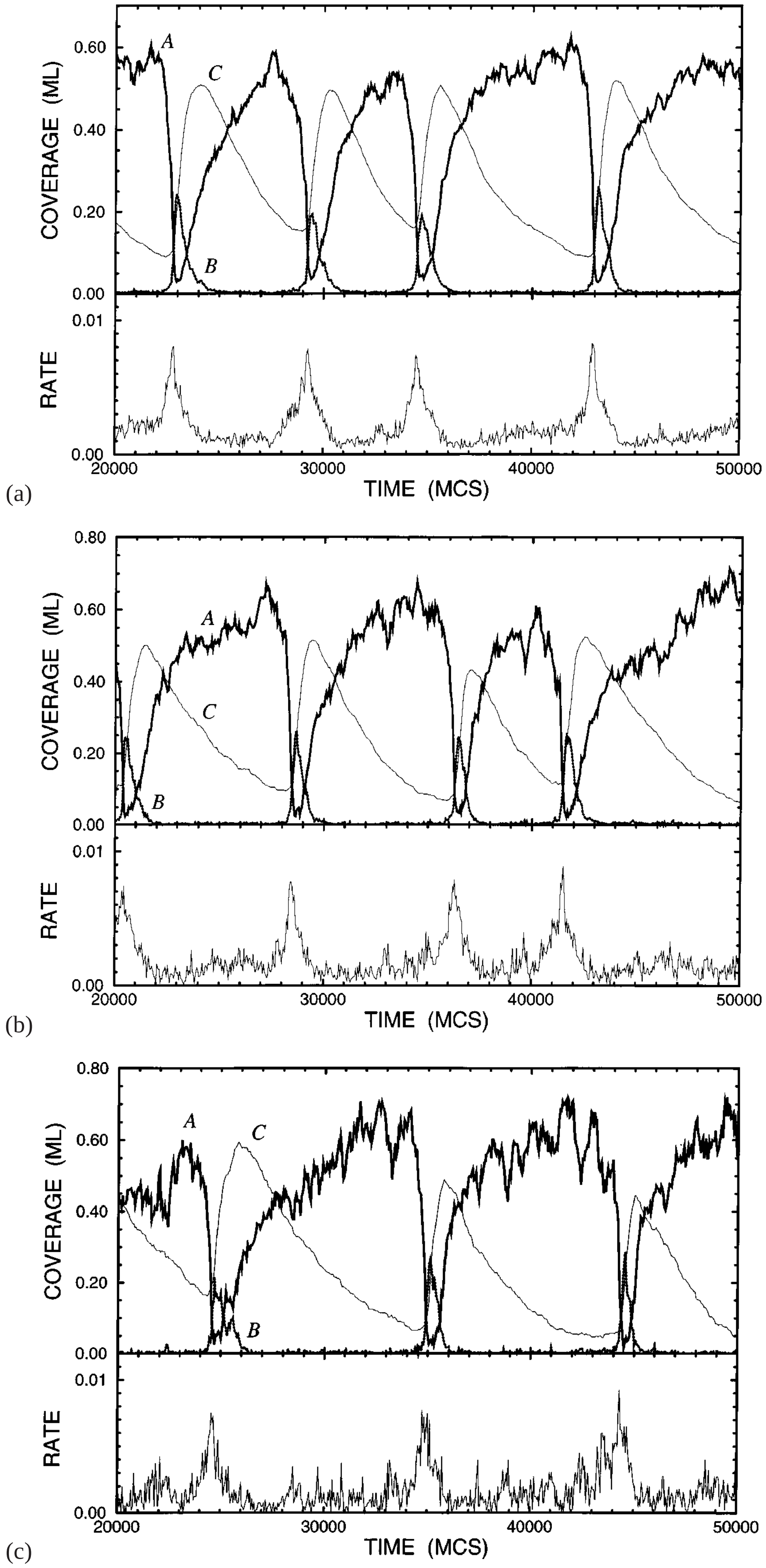

Figure 1. A, B and B* coverages (C is for B*) and reaction rate (AB molec. per site per MCS) as a function of time for $p_{\mathrm{A}} = 0.01$, $p_{\mathrm{B}_2} = 0.01$, $p_{\mathrm{des}} = 0.002$, $p_{\mathrm{ox}} = 0.003$, $p_{\mathrm{red}} = 0.001$, $N_{\mathrm{dif}} = 100$ and $L = 50$ (a), 30 (b), 20 (c), 10 (d), 5 (e) and 3 (f). The interval between the data points is 50 MCS. The reaction rate was calculated as an average over 10 MCS.

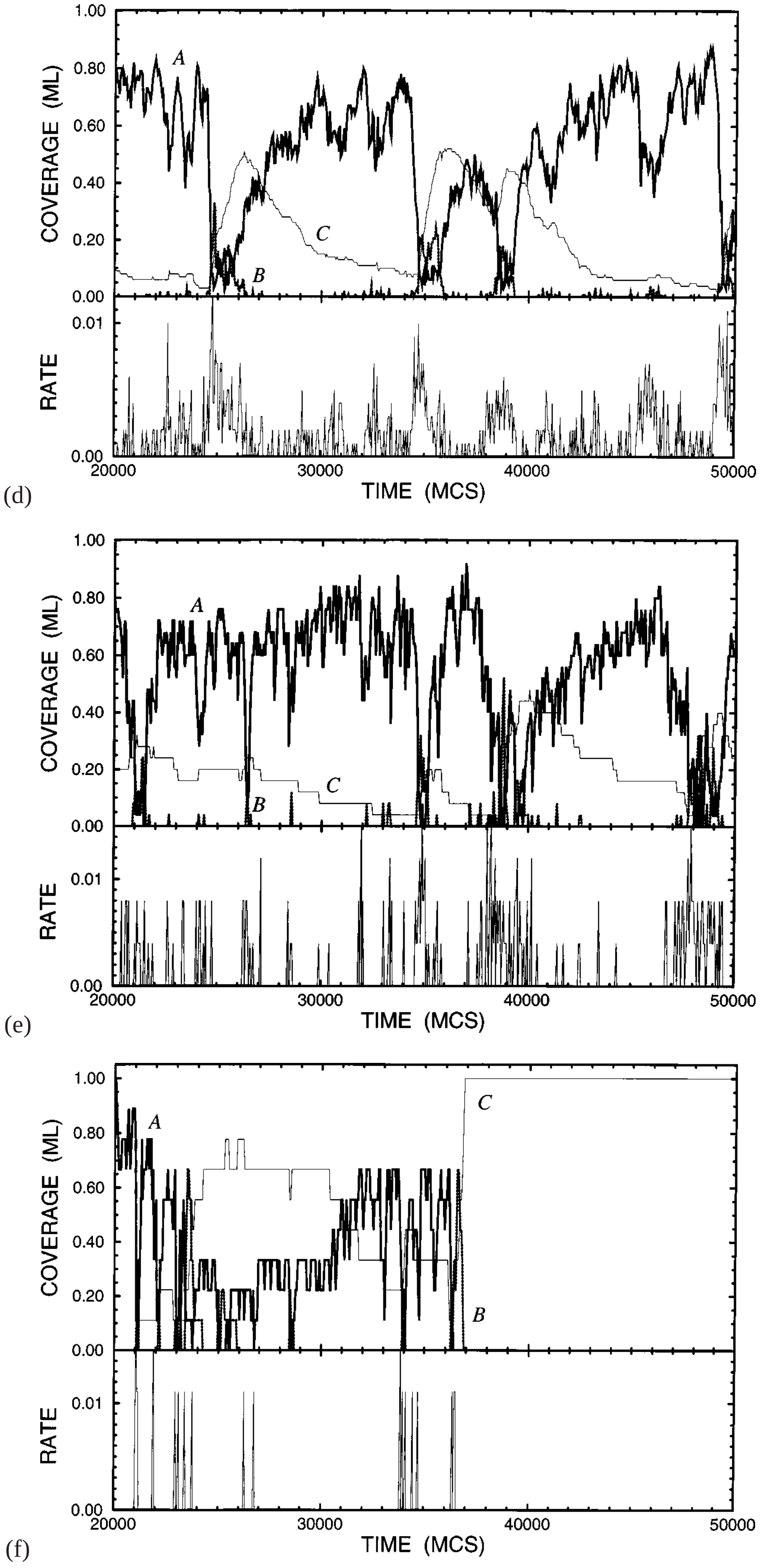

Figure 1. (Continued.)

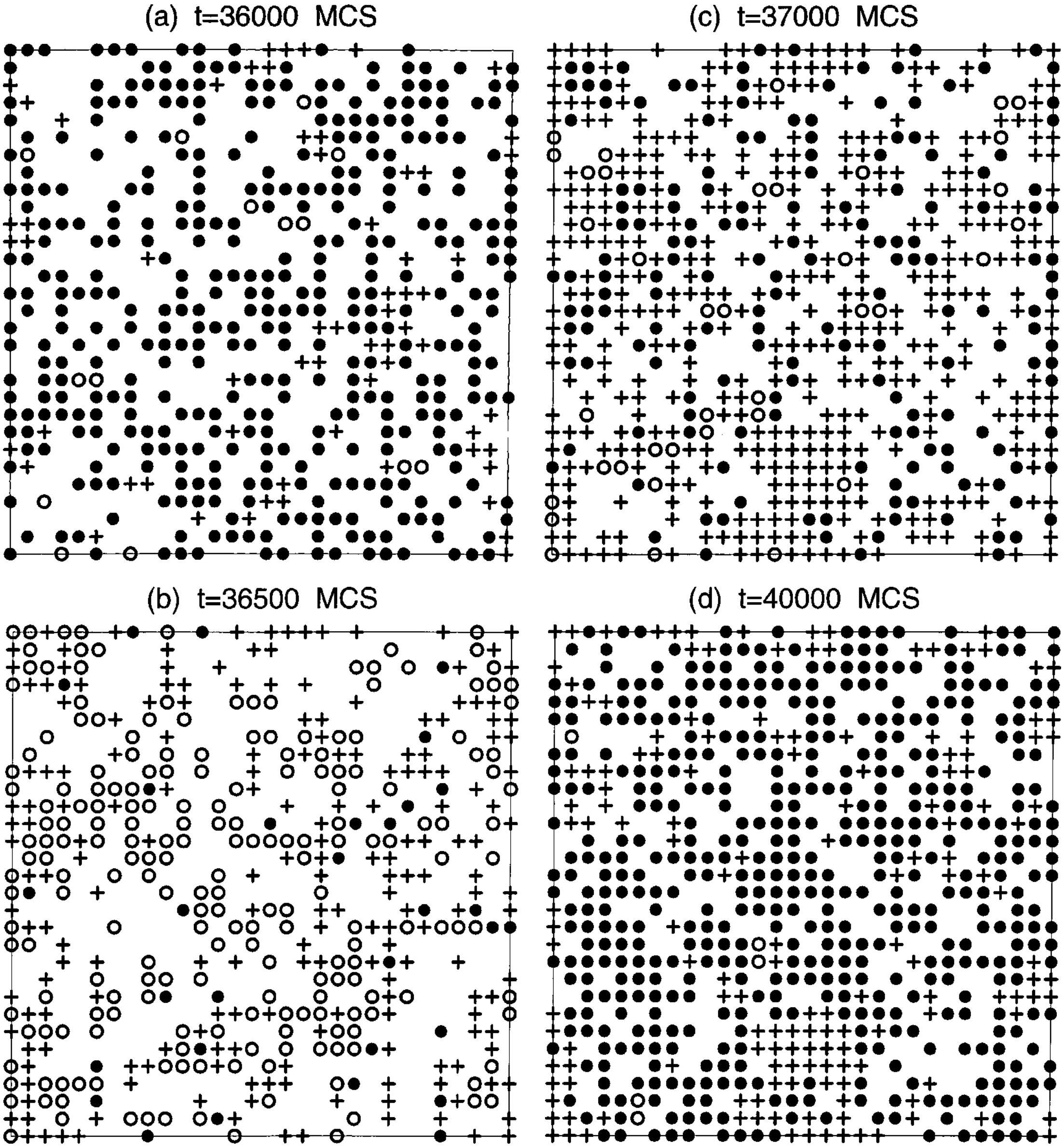

Figure 2. Snapshots of a 30 × 30 lattice for the MC run shown in figure 1(b); (•) A, (○) B and (+) B* particles, respectively. Vacant sites are not indicated. Oxide coverage is (a) minimum, (b) between minimum and maximum, (c) maximum and (d) between maximum and minimum.

catalyst particles. There is however no guarantee that the MF treatment can really be applied for such particles, because on this scale the reaction kinetics can be complicated by many other factors, e.g., by reactant supply via the support, the interplay of processes occurring on different facets of a catalyst particle, etc. [13].

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