

KINETIC INSTABILITIES IN HETEROGENEOUSLY CATALYZED REACTIONS—II

OSCILLATORY INSTABILITIES WITH LANGMUIR-TYPE KINETICS

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Abstract—An analysis of the kinetic model studied in Part I of this contribution gave no indication for the occurrence of periodic solutions. However if an additional slow chemisorption ("buffer") step is added to the model, relaxation oscillations can develop in regions where the original model exhibited multiple solutions. The behaviour of the extended model is analysed via the singular perturbation approach and by simulation. It is shown that a broad variety of slow chemisorption steps can serve as buffer with the restriction that the buffer step should not, or at least only slightly, contribute to the surface reaction.

In addition to rate multiplicity, discussed in Part I of this contribution [1], dynamic instabilities, resulting in sustained oscillations of the conversion have been reported from experiments. In a number of cases the oscillations occurred in stirred tank or loop reactors [2-4]; here a mathematical model would consist of the model of the surface kinetics and of the balance equations for the reactants. Other experiments with single pellets [5] or platinum and nickel wires and foils [6, 7] clearly demonstrated that sustained oscillations are also possible due to the intrinsic kinetics of the surface reaction. In the following discussion only the latter cases are considered and the question is posed whether these oscillations can be described by the general kinetic model, eqns (10)–(13) of Part I.

Again the analysis will be confined to special cases. The steady state analysis revealed that the ignition-extinction instabilities are brought about by the competing chemisorption of two components of the reaction mixture. The third component played only a secondary role. This leads to the assumption that the dynamics of only two surface species may be responsible for the occurrence of oscillations while the third surface component is in equilibrium or in quasi steady state. This assumption reduces the kinetic model (eqns. 10–13, Part I) to a second order system and allows the application of the criterion of Bendixon–Dulac [8] to study whether oscillations can occur or not.

Since A and B are equivalent in the kinetic model, only two cases have to be analysed. In the first case the product concentration $[CX_i]$ is in quasi steady state, in the second case either $[AX_n]$ or $[BX_m]$ are considered quasisteady. Taking $l = 1$ the first case leads to the second order system

$$\frac{d[AX_n]}{dt} = F1([AX_n], [BX_m]);$$

$$\frac{d[BX_m]}{dt} = F2([AX_n], [BX_m])$$

where $F1$ and $F2$ are nonlinear, explicit functions of $[AX_n]$ and $[BX_m]$. The criterion of Bendixon states that periodic solutions in the above system can not occur provided that $\{\partial F1/\partial [AX_n] + \partial F2/\partial [BX_m]\}$ does not change sign for all possible $[AX_n]$, $[BX_m]$.

Since the calculation shows that $\partial F1/\partial [AX_n]$ and $\partial F2/\partial [BX_m]$ are both negative for all $[AX_n]$, $[BX_m]$, periodic oscillations between $[AX_n]$ and $[BX_m]$ can be excluded.

The second case was studied for $m = 1$ and equilibrium of the B -chemisorption. Here the calculation is more involved. Details are given in [9]. The result is that global oscillatory stability can be guaranteed as long as $p \leq (l/n)$ or $\{p \leq 2, q \leq 2\}$. Thus in the cases of practical importance with values for m, n, p, q of 1 or 2, sustained oscillations will neither be possible in the first nor in the second case.

RELAXATION OSCILLATIONS

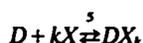
The above stability analysis gives strong evidence that sustained oscillations can only be modeled by the Langmuir type kinetics considered if additional reaction steps are included in the mechanism. Looking for such additional steps it seems appropriate to turn back to the experimental results. The oscillations on single pellets, observed by Fieguth and Wicke [5, 10] occurred under conditions under which rate multiplicity had also been observed. In addition the oscillations frequently had the character of relaxation oscillations and thus Wicke *et al.* interpreted them as periodic successions of ignited and extinguished states.

In Part I of this contribution an extinction of the reaction was explained by the depletion of empty active sites due to blocking chemisorption of A or B . During the ignition active sites were set free and enhanced the increasing reaction. A periodic succession of ignited and extinguished states should therefore be possible if a buffer or storage is available which provides empty sites after the reaction is extinguished and which consumes empty sites after an ignition has taken place.

Probably the most simple additional reaction step which fulfills these buffer requirements is the reversible

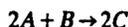
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reaction

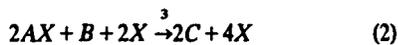


where D can be any component of the reaction mixture and DX_k does not further take part in the reaction. The dynamics of the chemisorption/desorption of D however have to be slow compared to the ignition/extinction dynamics, to ensure that the buffer step comes into effect *after* ignition or extinction has taken place.

The influence of the additional buffer step in the reaction mechanism will be discussed using the introductory example of Part I. The reaction



is assumed to proceed along the following steps



where the first two steps are identical with the example in Part I, assuming that B reacts via a chemisorbed BX_2 which is available only in a very low concentration. The third step is the additional buffer step where B is supposed to chemisorb linearly and BX does not further take part in the reaction.

With the empty site concentration

$$[X] = \alpha - [AX], \quad \alpha = 1 - [BX]$$

the mathematical model for the above mechanism consists of the two balance equations

$$\frac{d[AX]}{dt} = k_1[A](\alpha - [AX]) - k_{-1}[AX] - 2k_3[B][AX]^2(\alpha - [AX])^2 \quad (4)$$

$$\frac{d\alpha}{dt} = k_5[B][AX] + k_{-5} - \alpha(k_5[B] + k_{-5}) \quad (5)$$

where α is used as state variable instead of $[BX]$.

In the steady state the relation

$$\underbrace{ak_1[A] - [AX](ak_1[A] + k_{-1})}_{r_C} = \underbrace{2a^2k_3[B][AX]^2(1 - [AX])^2}_{r_R} \quad (6)$$

with

$$a = \frac{1}{1 + K_5[B]}; \quad K_5 = k_5/k_{-5} \text{ results.}$$

Equation (6) is equivalent to eqn (3) in Part I of this contribution. It leads to similar steady state rate dependencies including rate multiplicity due to A -blocking if k_{-1} is sufficiently small.

The analysis of the dynamic behaviour of the model eqns (4) and (5) is greatly simplified in view of the aforementioned consideration that the dynamics of the buffer step should be slow compared to the dynamics of ignition and extinction. In the limit eqn (4) can be considered quasisteady and the dynamics are almost completely determined by eqn (5). This "singular perturbation" approach is common in the analysis of relaxation oscillations[11-13]. It will be used in the following discussion.

In the steady state eqn (4) is a quadratic equation in $(\alpha - [AX])$ with the two solutions

$$\alpha = [AX] + \frac{k_1[A]}{4k_3[B][AX]^2} \left\{ 1 \pm \sqrt{\left(1 - \frac{8k_3[B]k_{-1}[AX]^3}{k_1^2[A]^2} \right)} \right\} \quad (7)$$

which merge and vanish at

$$[AX] = [AX]_z = \sqrt[3]{\left(\frac{k_1^2[A]^2}{8k_3[B]k_{-1}} \right)} \quad (8)$$

Figure 1 shows two typical cases ("d[AX]/dt = 0").

The steady state of the α -balance (eqn 5) is the linear relation

$$\alpha = \frac{1}{1 + K_5[B]} + \frac{K_5[B]}{1 + K_5[B]} [AX] \quad (9)$$

("da/dt = 0" in Fig. 1) thus either one (Fig. 1a) or three steady states (Fig. 1b) are possible.

Using the singular perturbation approach, the phase-portrait of the system eqns (4) and (5) can now be obtained directly: All phase trajectories not identical with d[AX]/dt = 0 are horizontal lines since [AX] tends to establish its steady state rapidly ("fast transient").

The sign of d[AX]/dt determines the direction of the trajectory and it can be seen that only the two outer branches of d[AX]/dt = 0 are approached, the middle one (broken line) being unstable. As soon as a trajectory has reached a stable branch of d[AX]/dt = 0, the [AX]-balance is in quasi steady state and the dynamics of the system (the direction of the trajectory on d[AX]/dt = 0) are determined only by the α -balance, eqn 5 ("slow transient").

It is obvious that in Fig. 1b the two outer steady states are stable nodes and the middle one is an (unstable) saddle point. The behaviour is similar to that of the introductory example with the left stable state being the ignited and the right one the extinguished steady state.

With somewhat changed parameters however a phase portrait as in Fig. 2(a) will develop. Now the only steady state is unstable since it lies on the unstable branch of d[AX]/dt = 0. All trajectories approach the depicted limit cycle. Surface concentrations and reaction rate perform relaxation oscillations (Fig. 2b), where the AX-concentration jumps from ① to ③ and from ④ to ⑤. Since the reaction rate is proportional to ([AX]($\alpha - [AX]$))² the respective rate can be calculated from the area [AX]($\alpha - [AX]$) in Fig. 2(a).

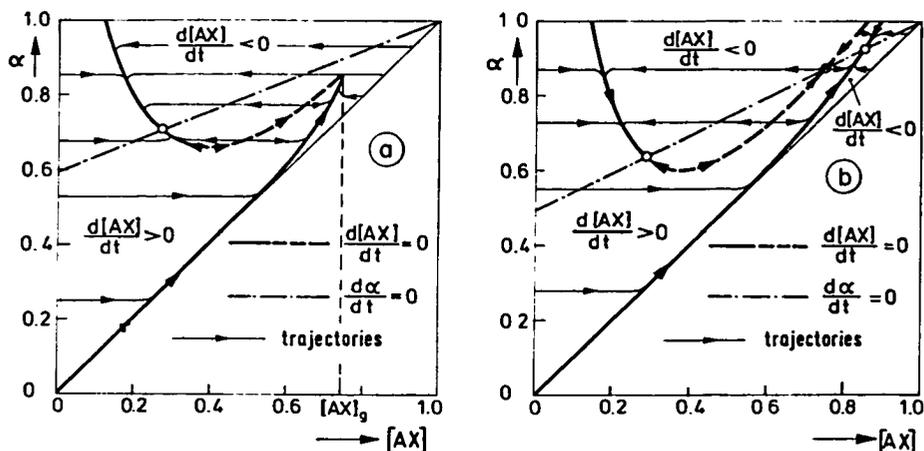


Fig. 1. Phase plot (a) with one, (b) with three steady states (singular perturbation approach).

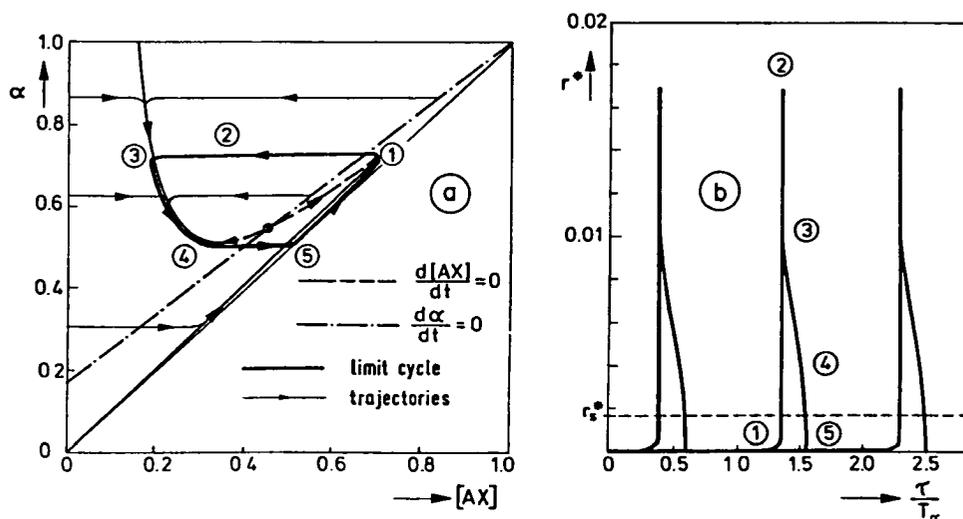


Fig. 2. Relaxation oscillation: (a) phase plot of the limit cycle; (b) corresponding rate oscillation. ($k_{13}^* = 0.02$, $[AX]_g = 0.7$, $k_3^* = 5$, $T_\alpha = 20,000$). Corresponding points in Figs. 2(a) and (b) are marked by Nos. ①-⑤.

A fourth modification of the phase plot under singular perturbation conditions is given in Fig. 3. Here the only stable steady state is the extinguished (right) state.

NUMERICAL RESULTS

The results which have been discussed were obtained under the assumption of quasi steady state for the $[AX]$ balance. If this assumption is dropped the dynamics of the model eqn's (4) and (5) are determined by the 4 parameters:

$$k_{13}^* = \frac{k_1[A]}{2k_3[B]}, \quad k_5^* = \frac{k_5[B]}{k_{-5}}, \quad T_\alpha = 2k_3[B]/k_{-5} \quad (10)$$

and $[AX]_g$ (see eqn 8). In the following results the reduced rate $r^* = [AX]^2(\alpha - [AX])^2$ will be plotted over the reduced time $\tau/T_\alpha = k_{-5}t$.

Figure 4 shows the influence of T_α upon rate oscillation and limit cycle. With decreasing T_α the shape changes from relaxation oscillations to almost harmonic oscillations with small amplitudes at $T_\alpha = 1250$ (no picture). At $T_\alpha = 1200$ the steady state is stable. The

development of oscillations is not always as smooth as in the above case.

Figure 5 gives an example where the depicted limit cycle vanishes if T_α is reduced below $T_\alpha = 4000$.

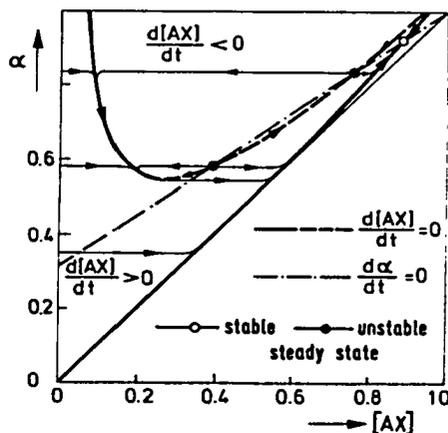


Fig. 3. Phase plot with two unstable steady states (singular perturbation approach).

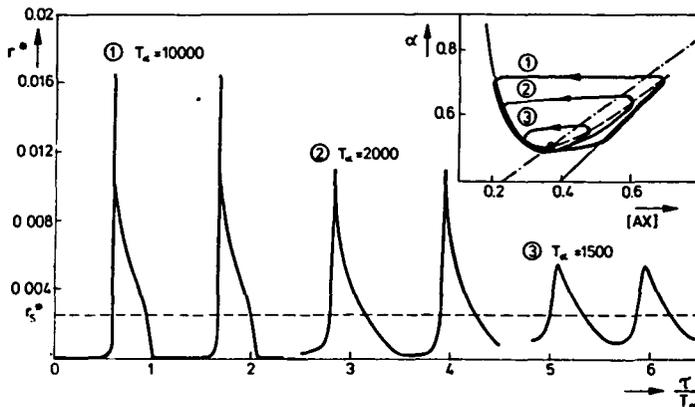


Fig. 4. The influence of T_∞ upon oscillation and limit cycle ($k\tau_3 = 0.02$, $[AX]_e = 0.7$, $k\tau = 3.5$).

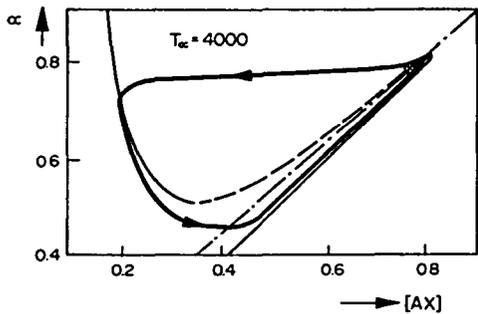


Fig. 5. Smallest stable limit cycle (stable steady state below $T_\infty = 4000$) $k_{13} = 0.02$, $[AX]_e = 0.8$, $k\tau = 10$.

Sudden changes between oscillatory stable and unstable states as well as apparently spontaneous ignitions and extinctions have frequently been reported from the experiments [5, 7, 10, 14]. They were attributed to the high parametric sensitivity of the reaction. Figures 6 and 7 show how these effects may be explained by the model considered. In Fig. 6 both stable states are close to the stability limit. A $\pm 3\%$ change in k_{13}^* (i.e. in the gas concentrations A or B) lasting for $\tau = 0.1T_\infty$ causes ignition or extinction of the reaction.

In Fig. 7 a single steady state is close to the stability limit. The response upon minor variations in k_{13}^* (i.e. in the gas concentrations) leads from single extinctions/ignitions over sustained relaxation oscillations of large amplitude to slowly decaying quasiharmonic oscillations of small amplitude.

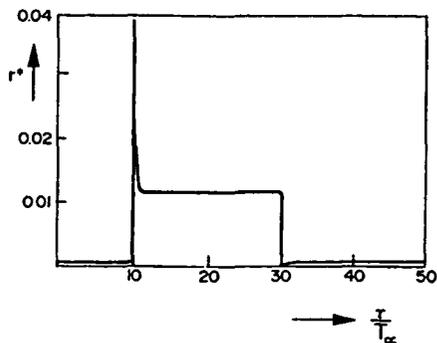
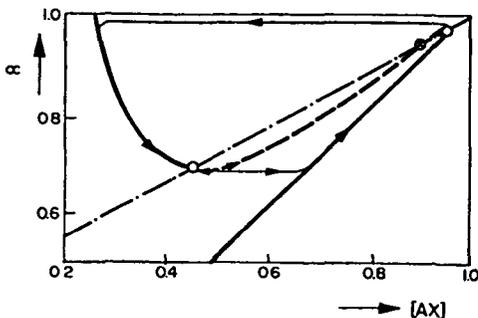


Fig. 6. Ignition and extinction due to $\pm 3\%$ disturbance in the A- or B-gas concentration lasting for $\tau = 0.1T_\infty$ at $\tau = 10T_\infty$ and at $\tau = 30T_\infty$. ($k_{13}^* = 0.05$, $[AX]_e = 0.95$, $k\tau = 1.3$).

In the above examples, only a few cases interesting from the point of observed experimental results, are considered. A thorough discussion of the stability of the model eqn's (4) and (5) has meanwhile been performed by Sagirow and Retzbach [15]. They show that limit cycles are also possible in case of three steady states, where the cycle surrounds either the ignited steady state or all three steady states.

POSSIBLE BUFFER STEPS

Of decisive importance for the occurrence of relaxation oscillations with the kinetic model considered was the introduction of an additional slow chemisorption step. This "buffer" step causes the sequence of ignitions and extinctions of the reaction by the alternating provision and consumption of empty active sites.

The general form of this buffer step is



where D can be a reactive or inert component of the reaction mixture or—as shown subsequently—a chemisorbed species thereof. The only restriction is that DX_k is not, or only slightly, involved in the surface reaction.

An example with $D = B$, $k = 1$ was considered above.

In case of $k > 1$ the results will be similar with the exception that the steady state α -balance (" $da/dt = 0$ ") will have a shape as depicted in Fig. 8.

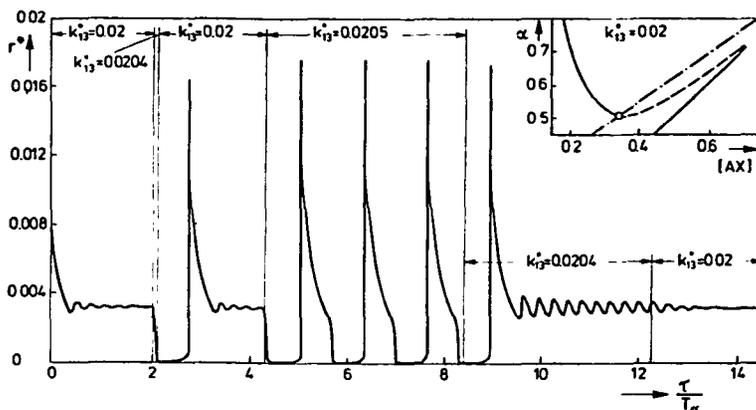


Fig. 7. Parametric sensitivity of the reaction to small changes of k'_{13} . ($[AX]_0 = 0.7$, $k'_2 = 3$, $T_a = 10,000$).

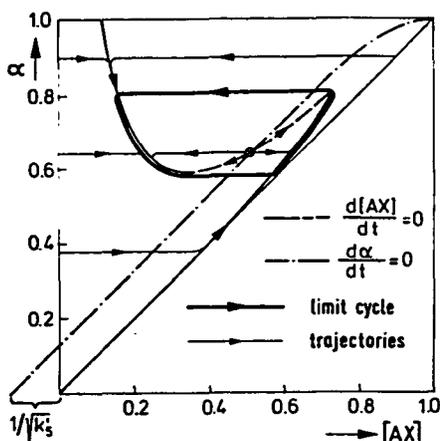
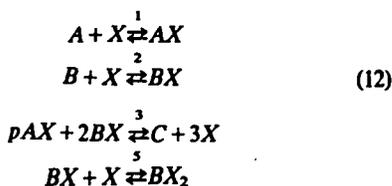


Fig. 8. Phase plot of relaxation oscillations, model eqns (13) and (14).

An example where D is a chemisorbed species is considered assuming the mechanism



where the last step is the buffer step. If step 2 is in equilibrium, the reaction will be described by the differential equations

$$\frac{d[AX]}{d\tau} = k'_{13}(\alpha - [AX]) - k'_{-13}[AX] - [AX]^p(\alpha - [AX])^2 \quad (13)$$

$$T'_a \frac{d\alpha}{d\tau} = 1 - \alpha - k'_5(\alpha - [AX])^2 \quad (14)$$

where $\alpha = 1 - 2[BX_2]$ and the k'_i are combinations of rate constants and gas concentrations.

For $p \geq 1$ the steady state solution of eqn (13)

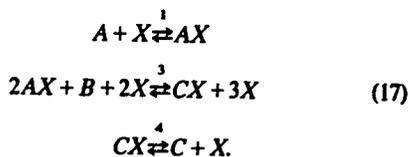
$$\alpha_{1/2} = [AX] + \frac{k'_{13}}{2[AX]^p} \left\{ 1 \pm \sqrt{\left(1 - \frac{4k'_{-13}}{k'_{13}} [AX]^{p+1} \right)} \right\} \quad (15)$$

is similar to eqn (7). The steady state α -balance

$$[AX] = \alpha - \sqrt{\left(\frac{1}{k'_5} (1 - \alpha) \right)} \quad (16)$$

is no longer linear but has a shape as depicted in Fig. 8. Again relaxation oscillations can be expected (Fig. 8) and the dynamic behaviour will be similar to the one discussed before.

The question may arise, whether the product desorption step of the general mechanism, eqn (9), Part I, or the last step in the following mechanism can be used as buffer step:



Indeed the analysis of the $[AX]$ - and α -balance (here: $\alpha = 1 - [CX]$) leads to steady state dependencies (" $d[AX]/dt = 0$ ", " $d\alpha/dt = 0$ ") as depicted in Fig. 8. However, since $[AX]$ and $\alpha = 1 - [CX]$ are coupled through the mechanism, $[AX]$ can never be in quasi steady state as compared to α . The above system is oscillatory stable, confirming the initial stability analysis and the restriction that the buffer (here CX) should not be involved in (here: be a product of) the reaction.

CONCLUSIONS AND DISCUSSION

Necessary for the occurrence of relaxation oscillations is a switching element and a storage. In surface reactions the switching characteristic can be brought about by non-unique reaction rates as studied in Part I of this contribution. A slow, reversible chemisorption step can serve as a simple storage or buffer. A great variety of possible buffer steps can be considered. In the numerical example, eqns (1)–(3), B was assumed to chemisorb in linear (buffer BX) and bridged form (reactant BX_2), where the reactivity of BX was considered negligible compared to that of BX_2 . Such a model with A corresponding to CO and B to O_2 has been used successfully [9, 16] to describe oscillations in a loop

reactor during the CO oxidation on platinum, measured by Hugo and Jakubith[2]. Alternatively, a kinetic model for the CO oxidation on Pt may be considered where CO instead of O₂ chemisorbs in two modifications with different reactivity. It is generally accepted that at least two different adsystems are found for the chemisorption of CO on Pt and that the reactivity of the adsystems differs considerably[17-19].

The experimental results for the CO oxidation on Pt have been characterized by high parametric sensitivity where oscillations or single ignitions/extinctions could occur without obvious changes of operating conditions. Simulations have shown that such high parametric sensitivity is inherent in the range in which relaxation oscillations occur.

It has been argued frequently that the knowledge of kinetic models for the experimentally observed instabilities would allow a deeper insight into the microkinetic mechanisms of heterogeneous catalysis. The kinetic models originated by Belyaev *et al.*[7] and studied in detail by Sheintuch and Schmitz[20] as well as the group of models proposed in this contribution should provide a broad variety of possible candidates.

Although, considering the microkinetic complexity of heterogeneous reactions it seems questionable whether these models can yield much more than a formal description of complex microkinetics. The main advantage however seems to be that the influence of the considered kinetic instabilities in chemical reaction engineering applications will now become calculable.

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