RSC Advances

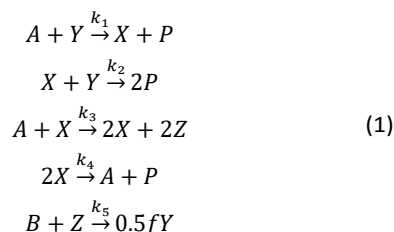## ELECTRONIC SUPPLEMENTARY INFORMATION

Oregonator Generalization as a Minimal Model of Quorum Sensing in Belousov-Zhabotinsky Reaction with Catalyst Confinement in Large Populations of Particles

E. Szabo

The purpose of this Supplementary Information is to provide more details about equations 1-5 and 11-12 in case the reader might have some doubt about how these equations were derived and how they should be interpreted. If additional clarification is not required, any part can be skipped safely.

S1. Preparatory step 1: From the Oregonator reaction mechanism to differential equations

Species involved in the famous Oregonator mechanism for a single BZ oscillator are denoted as usual: A = HBrO$_3$, B = brominated organic substrate that supplies bromide on decomposition (e.g. bromomalonic acid), X = HBrO$_2$, Y = BrO$_2$ radical, Z = oxidized state of the catalyst (Ce^{4+}, Mn^{3+}, [Fe(phen)$_3$]$^{3+}$ or [Ru(bipy)$_3$]$^{3+}$) and P = HBrO (in the Oregonator only an inert product):

$$A + Y \xrightarrow{k_1} X + P$$
$$X + Y \xrightarrow{k_2} 2P$$
$$A + X \xrightarrow{k_3} 2X + 2Z \qquad (1)$$
$$2X \xrightarrow{k_4} A + P$$
$$B + Z \xrightarrow{k_5} 0.5fY$$

The letters A, B, X, Y and Z are also used to denote the concentrations of the corresponding species. Application of the law of mass action supplies the five steps of mechanism 1 with the following rate equations:

$$v_1 = k_1 AY$$
$$v_2 = k_2 XY$$
$$v_3 = k_3 AX \qquad (S1)$$
$$v_4 = k_4 X^2$$
$$v_5 = k_5 BZ$$

The stoichiometry of the mechanism, including the very important Oregonator parameter – the tunable stoichiometric factor f, then puts these reaction rates in the following relationships to the rates of change of the individual concentrations:

$$\frac{\mathrm{d}X}{\mathrm{d}t} = v_1 - v_2 + 2v_3 - v_3 - 2v_4$$
$$\frac{\mathrm{d}Y}{\mathrm{d}t} = -v_1 - v_2 + 0.5fv_5 \qquad (S2)$$
$$\frac{\mathrm{d}Z}{\mathrm{d}t} = 2v_3 - v_5$$

Combining the stoichiometric equations S2 with the definitions of the reaction rates in S1, we obtain the fundamental description of the dynamics of a BZ oscillator, given in the paper as the set of equations 2:

$$\frac{dX}{dt} = k_1 AY - k_2 XY + k_3 AX - 2k_4 X^2$$

$$\frac{dY}{dt} = -k_1 AY - k_2 XY + 0.5 f k_5 BZ \qquad (2)$$

$$\frac{dZ}{dt} = 2k_3 AX - k_5 BZ$$

At this point it should be noted that by applying this description to our large populations of BZ oscillators, we submit to the same assumptions as implied in deriving the system 2. In particular, all oscillators are considered as homogeneous, well-stirred systems, with no further internal structure besides the variations in their overall composition as given by the differential equations above.

S2. Preparatory step 2: Population of BZ oscillators without catalyst confinement and mass transfer

Before we introduce coupling among oscillators by mass transfer, it may be beneficial to set up the formalism of the model by considering a population of BZ oscillators that are not coupled. In this case each oscillator is a closed subsystem that evolves absolutely separately, as illustrated in Figure S1. Each subsystem may start from individual, possibly unique initial conditions, and follow individual, possibly unique paths. The surrounding reaction solution, for the moment, is treated absolutely equally to the other subsystems, so it still contains all three intermediates, X, Y and Z.
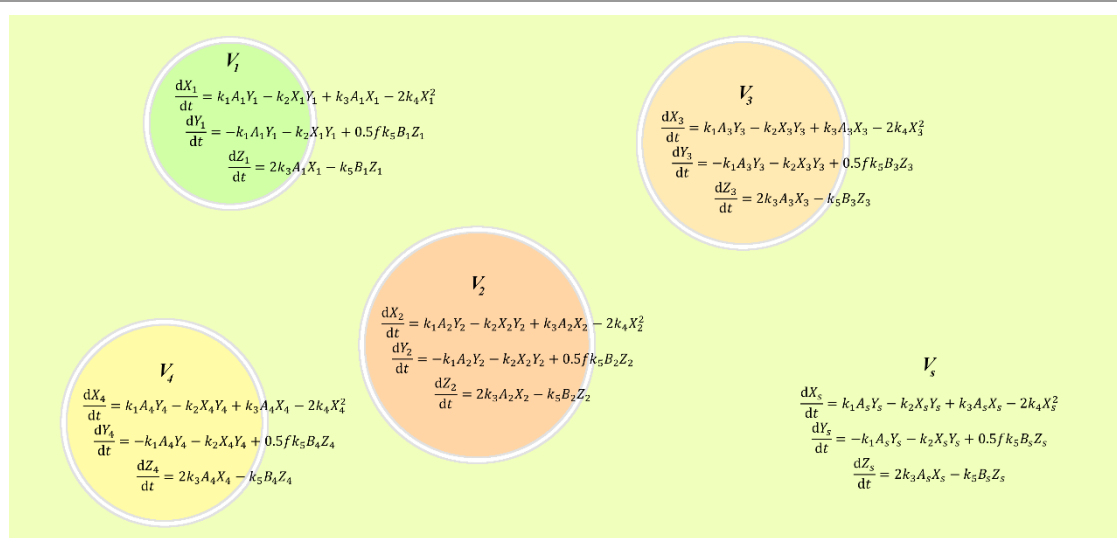

Figure S1. Collection of BZ oscillators as dynamically independent subsystems, illustrated on four oscillators representing subsystems 1-4, and the surrounding solution representing subsystem s.

At this point we note that various levels of individual variation may be assigned to the dynamics of the subsystems. As assumed in simulations by other authors, for example, each subsystem may, in principle, be assigned a slightly different value of the stoichiometric coefficient f, or even slightly different values of the rate constants k_1-k_5, for that matter. However, we preferred to limit the individuality of subsystems only to the dynamic variables, and we acknowledge the common chemical origin of all the subsystems by keeping all values of f and k_1-k_5 the same throughout.

The concentrations of Oregonator species in the i-th oscillator are denoted by A_i, B_i, X_i, Y_i and Z_i, and we already denote individually the variables for the surrounding solution as A_s, B_s, X_s, Y_s and Z_s. While there is no interaction between the subsystems, then the system of N oscillators (and the common solution) is described by simply collecting $N+1$ analogous triplets of differential equations, i.e. a total of $3N+3$ differential equations:

$$\frac{dX_i}{dt} = k_1 A_i Y_i - k_2 X_i Y_i + k_3 A_i X_i - 2k_4 X_i^2$$

$$\frac{dY_i}{dt} = -k_1 A_i Y_i - k_2 X_i Y_i + 0.5 f k_5 B_i Z_i \qquad i = s, 1, 2, \dots N \qquad (S3)$$

$$\frac{dZ_i}{dt} = 2k_3 A_i X_i - k_5 B_i Z_i$$

Before we proceed to adding coupling terms corresponding to mass transport between oscillators, we note that each subsystem has one more, very important characteristic – the volume V_i of each subsystem. These volumes do not appear in the system of equations S3, because the absolute extents of reactions do not affect the dynamical description of the system while the subsystems are isolated and all species are confined to their own subsystems with constant volumes. However, in the following steps, the absolute sizes of the subsystems will have to be taken into account every time we will need to apply mass balance. To make the balancing possible, the rates of change of concentrations, dX_i/dt, dY_i/dt and dZ_i/dt, will have to be converted into the rates of change of the number of moles $dn_{X,i}/dt$, $dn_{Y,i}/dt$ and $dn_{Z,i}/dt$.

S3. Population of BZ oscillators coupled by mass transfer through common medium

If we make the boundaries of the subsystems in Figure S1 permeable, we need to take into account the possibility that mass exchange may take place between the subsystems and their surroundings (the solution). For simplicity, we assume that all transport processes are independent from each other, whether from transport of other species, or transport of the same species in opposite direction. Right from the start we will also exploit the fact that all our subsystems are assumed to be homogeneous, and so any molar flux (per unit area) must be the same at all points of a given boundary. Therefore, instead of having to express flux J as a function of spatial coordinates (and over infinitesimal areas), it can be defined based on the total molar flow dn/dt through the whole area S of the given boundary, e.g.:

$$J_{X,i} = \frac{1}{S_i} \frac{dn_{X,i}}{dt} \qquad\qquad \text{(S4)}$$

We also adopt a simplifying approach, which was already implemented in simulations by other authors, and we limit our attention to the simplest case, where the exchanged species have equal affinities towards both sides of a boundary, i.e. in equilibrium the concentration difference is zero. Under these conditions, the mass transfer may be expressed by the traditional expression:

$$J_{X,i} = k_{ex,X}(X_s - X_i) \qquad\qquad \text{(S5)}$$

i.e. the net molar flux across an interface, in this case into the i-th oscillator, is proportional to the concentration difference between the two sides of the interface, in this case the difference between the concentration X_s in the surroundings (solution) and the concentration X_i inside. The proportionality constant $k_{ex,X}$ is the corresponding mass transfer coefficient for this species.

Before we can proceed to combining the terms for mass transfer with the rates of chemical reactions, we note that for the moment we still consider the surrounding solution to be chemically identical to the other subsystems in our problem, and we do not consider catalyst confinement, yet. However, one important difference between the oscillators and the surrounding solution must be taken into account already, as it is inherent to the spatial arrangement of the model. While we may assume that each of the N oscillators can exchange X, Y and Z only with the surrounding solution, the position of the solution is different. The solution can, obviously, exchange mass with all N subsystems simultaneously, and so the expressions for mass balance in the oscillators and in the surrounding solution will be slightly different.

We start by adding the mass transfer terms into those equations of the system S3, which describe the N oscillators. Firstly, each flux (of X, Y and Z) is converted to the total inflow of mass (in terms of number of moles per unit time) according to S4, i.e. by multiplying the expression of the flux (given by S5) with the total area S_i of the corresponding interface. In the second step, this mass transfer is expressed in terms of concentration change (per unit time) by taking into account the total volume V_i, where the mass arrives. Overall, mass balance provides the mass transfer terms in a form, which also includes S_i/V_i, the surface-to-volume ratio of the given oscillator:

$$\frac{dX_i}{dt} = k_1 A_i Y_i - k_2 X_i Y_i + k_3 A_i X_i - 2k_4 X_i^2 + k_{ex,X} \frac{S_i}{V_i}(X_s - X_i)$$

$$\frac{dY_i}{dt} = -k_1 A_i Y_i - k_2 X_i Y_i + 0.5 f k_5 B_i Z_i + k_{ex,Y} \frac{S_i}{V_i}(Y_s - Y_i) \qquad i = 1,2,\dots N \quad \text{(S6)}$$

$$\frac{dZ_i}{dt} = 2k_3 A_i X_i - k_5 B_i Z_i + k_{ex,Z} \frac{S_i}{V_i}(Z_s - Z_i)$$

Accordingly, those equations of the system S3, which describe the dynamics of X_s, Y_s and Z_s, will have to be modified with N such contributions and the overall mass transfer term will be given in the form of their sum. However, for completeness we should note that these summed terms cannot be obtained simply by taking the mass transfer terms from S6 with a negative sign. Even though it happens quite often that conservation of mass can translate into conservation of concentrations (if equal volumes occur on both sides of a process in consideration), this is clearly not the case.

The overall mass transfer into the solution will be expressed from the requirement that the total amount of each intermediate (X, Y or Z) entering or leaving the solution must be equal to the corresponding sum of amounts entering or leaving the N oscillators, in terms of number of moles. The effect of this transfer in terms of the corresponding concentrations will depend on the volumes on both sides of the transfer. In order to relate this to how we derived system S6, the conservation is applied at the point, where the fluxes are converted into total flows (of number of moles per unit time), i.e. after multiplication with the corresponding interface areas. However, to convert these summed flows into contributions in terms of rates of change of concentration, in this case we have to take into account the volume V_s of the surrounding solution:

$$\frac{\mathrm{d}X_s}{\mathrm{d}t} = k_1 A_s Y_s - k_2 X_s Y_s + k_3 A_s X_s - 2k_4 X_s^2 - \frac{k_{ex,X}}{V_s} \sum_{i=1}^{N} S_i (X_s - X_i)$$

$$\frac{\mathrm{d}Y_s}{\mathrm{d}t} = -k_1 A_s Y_s - k_2 X_s Y_s + 0.5 f k_5 B_s Z_s - \frac{k_{ex,Y}}{V_s} \sum_{i=1}^{N} S_i (Y_s - Y_i) \qquad \text{(S7)}$$

$$\frac{\mathrm{d}Z_s}{\mathrm{d}t} = 2k_3 A_s X_s - k_5 B_s Z_s - \frac{k_{ex,Z}}{V_s} \sum_{i=1}^{N} S_i (Z_s - Z_i)$$

On one hand, transferring a certain amount of X, Y or Z between one of the N oscillators and the solution may dramatically change the concentration in the small volume inside the oscillator, while the corresponding concentration change in the large volume of the surrounding solution might be hardly noticeable. On the other hand, there may be many such oscillators exchanging mass with the solution at the same time, and so their combined impact on the solution may be significant.

S4. System of equations 3: Catalyst confinement

By excluding the catalyst from the surrounding solution and confining it only inside the N oscillators, the value of Z_s becomes fixed at $Z_s = 0$, at all times. As a consequence, there will be only two variables describing the solution, and the third differential equation from S7 must be removed. The same applies to those terms in the remaining equations of S7, which have their origin in reactions involving the metal catalyst.

In the case of production of Y_s by the fifth reaction of the Oregonator mechanism, this is quite obvious, as $Z_s = 0$ sets the value of $0.5 f k_5 B_s Z_s$ to zero automatically. The situation is less obvious in the case of production of X_s according to the third reaction of the Oregonator mechanism. The term $k_3 A_s X_s$ does not contain Z_s explicitly, because the corresponding chemical equation contains Z only as a product, not as a reactant that could affect its rate. Of course, the production of Z, which is the oxidized form of the catalyst, does require the presence of the reduced form of the catalyst. In the Oregonator, this is assumed to be available in such excess quantity that its depletion by any of the reactions does not affect the rates, and so this (reduced) species is not considered explicitly. However, if we completely exclude the catalyst from the solution, it should not contain the reduced form either, and so the third reaction of the Oregonator, and the corresponding term $k_3 A_s X_s$ must also remain confined exclusively to the subsystems that contain Z.

Finally, we have to remove all mass transfer terms for Z, because there can be no exchange of this species with the solution. As a consequence, we are left with only two flux constants in our dynamics, $k_{ex,X}$ and $k_{ex,Y}$. For convenience we will also adopt the traditional assumption that the transport of X and Y proceeds very similarly, and so $k_{ex,X}$ and $k_{ex,Y}$ will be merged into a single mass transfer coefficient, k_{ex}. Furthermore, we will also adhere to the usual approach of fixing the reactants A and B at constant concentrations, and these will be assumed to be distributed homogeneously throughout.

Under these conditions, we can transform the combined system of equations S6 and S7 into the following description of our system of N catalyst-confining oscillators, coupled by mass transfer through common non-catalytic medium:

$$\frac{\mathrm{d}X_i}{\mathrm{d}t} = k_1 A Y_i - k_2 X_i Y_i + k_3 A X_i - 2k_4 X_i^2 + k_{ex} \frac{S_i}{V_i} (X_s - X_i)$$

$$\frac{\mathrm{d}Y_i}{\mathrm{d}t} = -k_1 A Y_i - k_2 X_i Y_i + 0.5 f k_5 B Z_i + k_{ex} \frac{S_i}{V_i} (Y_s - Y_i)$$

$$\frac{\mathrm{d}Z_i}{\mathrm{d}t} = 2k_3 A X_i - k_5 B Z_i \qquad \text{(3)}$$

$$\frac{\mathrm{d}X_s}{\mathrm{d}t} = k_1 A Y_s - k_2 X_s Y_s - 2k_4 X_s^2 - \frac{k_{ex}}{V_s} \sum_i S_i (X_s - X_i)$$

$$\frac{\mathrm{d}Y_s}{\mathrm{d}t} = -k_1 A Y_s - k_2 X_s Y_s - \frac{k_{ex}}{V_s} \sum_i S_i (Y_s - Y_i)$$

S5. System of equations 4: From individual oscillators to bulk description as a single catalytic phase

The main motivation of the paper is the idea that investigating the dynamics of a coupled population of oscillators, as described by the system of equations 3, could begin by differentiating the consequences of catalyst confinement into two distinct levels. On one hand, we should distinguish those features of the collective behavior, which can only be understood through fine-grained approaches and with full resolution in phase information, e.g. clustering, chimera symmetry breaking, etc. On the other hand, we should strive to separate those features, which might be seen as bulk effects, due to modified overall stoichiometry of the system, and may be interpreted without regard to the phases of individual oscillators.

To achieve this, we need to concentrate on what happens when all oscillators in the population are perfectly synchronized all the way through. By eliminating the possibility of various phases, we should be able to isolate those features of the system, which persist despite the uniformity, and separate them from those that are found in other situations, due to finer effects.

Therefore, we are interested in those solutions of 3, where every oscillator, at any time, has the same chemical composition as all other oscillators. In this case, describing the population of N oscillators will not require N triplets of variables X_i, Y_i and Z_i, but only a single triplet of the "unison" values, which will be denoted as X_b, Y_b and Z_b (opposed to X_s and Y_s, remaining for the description of the surrounding solution) common for the entire phase of the catalytic beads:

$$X_1(t) = X_2(t) = \cdots = X_N(t) = X_b(t) \qquad \text{(S8)}$$

This has two conditions. Oscillators must already start from identical initial conditions, and the equations governing their subsequent evolution must have the same form for each oscillator. In the case of system 3, this means that all oscillators must have the same surface-to-volume ratio. If we assume perfectly spherical particles, the population must be monodisperse, and the value of S_i/V_i will be that of a sphere with the chosen radius r, for all particles:

$$\frac{S_1}{V_1} = \frac{S_2}{V_2} = \cdots = \frac{S_N}{V_N} = \frac{4\pi r^2}{4\pi r^3/3} = \frac{3}{r} \qquad \text{(S9)}$$

Besides that, equations for the dynamics of X_b and Y_b will "inherit" the same mass transfer terms as were given for X_i and Y_i in system 3. To derive the new counterpart transfer terms for the surrounding solution, we just need to note that even for a collection of many perfect spheres, the total surface area $S_{b,tot}$ (as found by adding up N surfaces S_b of individual particles) must obey the same ratio to their total volume $V_{b,tot}$ as seen for the geometry of a single sphere:

$$\frac{k_{ex}}{V_s}\sum_{i=1}^{N} S_b(X_s - X_b) = \frac{k_{ex}}{V_s}NS_b(X_s - X_b) = k_{ex}\frac{S_{b,tot}}{V_s}(X_s - X_b) = k_{ex}\frac{3V_{b,tot}}{rV_s}(X_s - X_b) \qquad \text{(S10)}$$

Altogether, the bulk description of the extremely unison limit in the behavior of a population of catalyst-confining BZ oscillators coupled by mass transfer with common non-catalytic solution is found as the following system of equations:

$$\frac{dX_b}{dt} = k_1AY_b - k_2X_bY_b + k_3AX_b - 2k_4X_b^2 + \frac{3k_{ex}}{r}(X_s - X_b)$$

$$\frac{dY_b}{dt} = -k_1AY_b - k_2X_bY_b + 0.5fk_5BZ_b + \frac{3k_{ex}}{r}(Y_s - Y_b)$$

$$\frac{dZ_b}{dt} = 2k_3AX_b - k_5BZ_b \qquad \text{(4)}$$

$$\frac{dX_s}{dt} = k_1AY_s - k_2X_sY_s - 2k_4X_s^2 - \frac{3k_{ex}V_{b,tot}}{rV_s}(X_s - X_b)$$

$$\frac{dY_s}{dt} = -k_1AY_s - k_2X_sY_s - \frac{3k_{ex}V_{b,tot}}{rV_s}(Y_s - Y_b)$$

where, for recapitulation, X_b, Y_b and Z_b are the "unison" concentrations of the intermediates in the catalytic beads (as would be observed for these particles in bulk, or each one of them individually), X_s and Y_s are the concentrations in the surrounding solution, A and B are concentrations of the reactants, considered to be constant and the same everywhere in the system, f is the Oregonator's variable stoichiometric factor, k_1-k_5 are the rate constants describing the rate laws of individual reactions, k_{ex} is the mass transfer coefficient characterising the mass exchange for both, X and Y, and finally, V_s is the volume of the solution, $V_{b,tot}$ is the total volume of the entire population of the catalytic particles and r is their (uniform) radius.

Looking for further simplification of the system 4, one alternative is presented by the approach of Dockery and Keener (Ref. 81). Although their model was developed to represent bacterial quorum sensing derived from biochemical processes with completely

different kinetics, their equations are similar to 4 in that they are also expressed in terms of "bulk" concentrations, uniform throughout the given phase, whether the solution or the interior of the cells.

In the case of Dockery and Keener, further simplification of the model was achieved by keeping the full dynamics only for the species inside the cells, and the same species in the extracellular medium were eliminated from the equations based on the steady-state approximation. However, this approach was not suitable for our model. First of all, equations for the concentrations of species in the solution and in the catalytic beads have terms with a very similar structure, and so it does not seem to be correct to assume that either of the phases of the system is more likely to be in the steady state than the other phase. But most importantly, in our case the following simplification is not motivated only by the need to reduce the number of variables. To the contrary, the simplification only reflects the underlying idea of searching for those features of the system, which can be seen as bulk effects, arising globally rather than locally.

S6. System of equations 5: The limit of unconstrained mass transfer

The system of equations 4 implements the assumption of all catalytic particles evolving in perfect synchrony, but in principle, this still includes the possibility of having two very different extreme scenarios. Depending on the value of k_{ex}/r, the population of oscillators may be completely decoupled from, but also completely coupled to the surrounding solution.

We continue looking for the most universal features of the catalyst confinement – those that can persist (in the form of modified overall stoichiometry) even in the least structured models. Therefore, we need to consider an extreme case, where Z is confined, but the dynamics of X and Y is not, i.e. the extra production or consumption of X and Y coming from the catalytic phase is manifested everywhere in the same way.

In other words, when we assume confinement of Z, it must be the only structure we admit in our model. For species X and Y we require exactly the opposite – keeping perfect mobility all over the entire system, so that any inhomogeneities, which could arise due to different rates of production and consumption of X and Y in the catalytic phase, will be immediately evened out, and these species will remain distributed homogeneously throughout, at all times.

Regarding the validity of such approach, we have to note that these assumptions are, in fact, not too distant from what has already been implemented in previous models by other authors. Even though the oscillators were treated individually, for simplicity they were always considered to be perfectly homogenous, with no internal structure in their composition. Of course, it is absolutely reasonable to assume that if the catalytic particles are small enough, the difference between the composition of their cores and their outer shells should be small, too. In fact, experiments in the early stages of investigation of catalyst confinement in cation-exchange resin particles really demonstrated that there is a critical radius, below which the oscillations of the particle stop being exhibited as spatial patterns, and the particle oscillates as a whole.

If we can accept this, it should not seem any less reasonable to make similar assumptions for the concentrations inside the particles and in the solution. It also should be only a matter of having small enough particles (with high enough contact surface), and even those inhomogeneities between the particles and the surrounding solution should, eventually, become evened out very efficiently. At some point, we should be able to neglect concentration differences between the particles and the solution, just like we neglect the differences within the particles. For completeness we note that this does not imply unrealistic values of mass transfer coefficients k_{ex}, it is only a matter of appropriate value of r in the ratio k_{ex}/r.
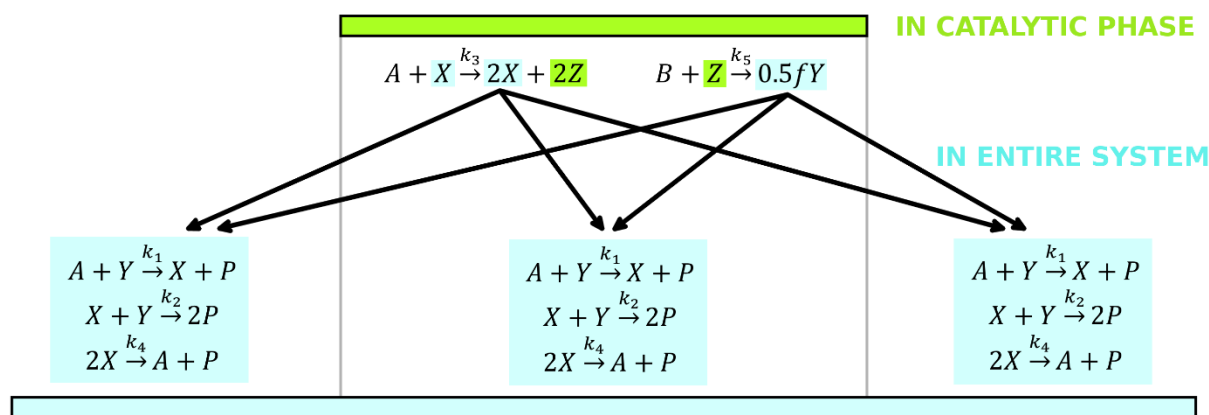

Figure S2. Illustration of distribution of production and consumption of species in the system. The bottom level represents the reactions running globally, in every part of the system, and the top level represents the production and consumption contributed exclusively by the fraction of the system, where the catalyst and its reactions are confined.

Finally, we are ready to express the proposed model in differential equations. Firstly, as there will be no distinction between X_b and X_s, nor between Y_b and Y_s, this leaves only two dynamic variables for these species, which will be denoted simply as X and Y. From the point of view of their overall mass balance, it makes sense now to differentiate the terms in their dynamics based on the volumes that contributed those terms, as illustrated in Figure S2.

The reactions, which are not confined, contribute to the overall mass balance with productions and consumptions by the entire volume of the system (in Figure S2 illustrated at the bottom, the larger part). On the other hand, we have some extra production and consumption of species by the reactions specific to the catalyst (in Figure S2 at the top, representing a somehow smaller part of the system). These contributions will also have to distribute over the entire volume of the system, but unlike the global contributions coming from the entire volume, these extra reactions come only from a limited fraction of the system. The corresponding volumes have to be acknowledged in the overall mass balance accordingly:

$$\frac{dn_X}{dt} = V_{tot}(k_1AY - k_2XY - 2k_4X^2) + V_{b,tot}\, k_3AX$$

$$\frac{dn_Y}{dt} = V_{tot}(-k_1AY - k_2XY) + V_{b,tot}\, 0.5fk_5BZ$$

(S11)

The mass balance for Z is somehow simpler. Its production and consumption occurs only in the catalytic part of the system, but unlike X and Y, species Z cannot distribute over entire system, so the same volume is where these reactions cause effects. Just as the volume $V_{b,tot}$ of the catalytic phase appears in the balance of the number of moles of Z, in the same way it disappears when this is expressed in terms of the corresponding concentrations in this volume. Therefore, the equation for the dynamics of Z will be, in the end, the same as it appeared in the system 4.

On the other hand, the balance equations S11 apply to the entire volume V_{tot} and so the volume factors do not cancel out for the last terms in each equation, where we obtain the ratio $V_{b,tot}/V_{tot}$, i.e. the volume fraction φ that the catalytic phase occupies in the system. Using this also as a subscript in Z_φ to denote that this species is confined, unlike other species, exclusively to this fraction of the system, we obtain the final description of the dynamics of the system, given in the paper as the set of equations 5:

$$\frac{dX}{dt} = k_1AY - k_2XY - 2k_4X^2 + \varphi k_3AX$$

$$\frac{dY}{dt} = -k_1AY - k_2XY + 0.5f\varphi k_5BZ_\varphi$$

(5)

$$\frac{dZ_\varphi}{dt} = 2k_3AX - k_5BZ_\varphi$$

Finally, as noted in the paper, while φ was obtained primarily as the volume fraction of the system that is occupied by the catalytic phase, exactly the same dynamical equations for the system could be derived from a modified Oregonator mechanism, where the value of φ could be identified as an additional stoichiometric factor, directly tuning the extent of production and consumption of X and Y in reactions involving the catalyst. This leads us to the final conclusion that (at least some part of) the impact of confining the metal catalyst of the BZ reaction into a population of particles of cation-exchange resin should be explainable from the point of view that this catalyst confinement is, in fact, manifested in modified overall stoichiometry of the mechanism.

S7. System of equations 12: Synchronization of two populations

From the set of equations 10 we derived an Oregonator-based description of two initially distinct populations of catalytic particles in BZ reaction, strongly coupled BZ through fast mass transfer, as follows:

$$\varepsilon\frac{dx}{d\tau} = x(\varphi_1 + \varphi_2 - x) + f(\varphi_1z_1 + \varphi_2z_2)\frac{q-x}{q+x}$$

$$\frac{dz_1}{d\tau} = x - z_1$$

(11)

$$\frac{dz_2}{d\tau} = x - z_2$$

In order to transform this set of equations into the set 12, we applied the following change of variables (we note that in order to arrive to the most concise description of the system, the best choice is to keep the volume fraction for one population, and define the z-variable not for the same population, but for the other one):

$$\varphi = \varphi_1$$

$$\varphi_{tot} = \varphi_1 + \varphi_2 = \varphi + \varphi_2$$

(S12)

$$z = z_2$$

$$\zeta = z_1 - z_2 = z_1 - z$$

Based on these transformations we find the following expressions for the individual terms in 11:

$$\varphi_1 + \varphi_2 - x = \varphi_{tot} - x$$
$$\varphi_1 z_1 + \varphi_2 z_2 = \varphi(z + \zeta) + (\varphi_{tot} - \varphi)z = \varphi_{tot}z + \varphi\zeta$$
$$\frac{dz_1}{d\tau} = \frac{d\zeta}{d\tau} + \frac{dz}{d\tau}$$

(S13)

$$x - z_1 = x - z - \zeta$$
$$\frac{dz_2}{d\tau} = \frac{dz}{d\tau}$$
$$x - z_2 = x - z$$

Substitution of the expressions from S13 into the set of equations 11 we obtain:

$$\varepsilon \frac{dx}{d\tau} = x(\varphi_{tot} - x) + f(\varphi_{tot}z + \varphi\zeta)\frac{q - x}{q + x}$$

$$\frac{d\zeta}{d\tau} + \frac{dz}{d\tau} = x - z - \zeta$$

(S14)

$$\frac{dz}{d\tau} = x - z$$

Finally, some manipulation of the last two equations is required in order to separate the variables, but very easily we arrive to the set of equations 12, as given in the paper:

$$\varepsilon \frac{dx}{d\tau} = x(\varphi_{tot} - x) + f\varphi_{tot}z\frac{q - x}{q + x} + f\varphi\zeta\frac{q - x}{q + x}$$

$$\frac{dz}{d\tau} = x - z$$

(12)

$$\frac{d\zeta}{d\tau} = -\zeta$$