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# Kinetic aspects of operando studies: state-of-the-art and unexplored possibilities

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## *S1. The methods suitable for in situ measurements of catalysts properties*

Currently, *in situ* catalyst state investigation under real reaction conditions can be achieved using methods based on the following techniques:

*The methods based on X-ray absorption*. There are several modifications of the XAS (X-ray absorption spectroscopy) that used for the study of catalytic processes. EXAFS (extended X-ray absorption fine structure) is used to determine the structure of the solid material (i.e. size, shape, coordination numbers and interatomic distances)[1,2]. Another method allowing determining the electronic properties of the sample is XANES (X-ray absorption near-edge structure). These methods are very attractive for the investigations of different catalysts due to the possibility of the analysis of the multicomponent samples with low concentrations of the elements under consideration with high sensitivity that cannot be realized by traditional XPS (X-ray photoelectron spectroscopy) that is one of the most intensively used in surface chemistry method.

*Raman spectroscopy*. It is the experimental technique allowing the obtaining an information about molecular structure of solid support. To the moment Raman spectroscopy has been used to study

the properties of different catalytic material, such as bulk and supported metals, metal oxides, sulfides etc[3].

*IR spectroscopy*. There are a lot of modifications of physical investigation methods using IR-spectroscopy to establish possible presence of any functional groups in the sample studied. Nowadays IR spectroscopy is widely applied to analyze solid catalysts by absorption spectra (TIRS - transmission Fourier transform infrared spectroscopy) as well as reflection spectra (DRIFTS - diffuse reflectance infrared Fourier transform spectroscopy, ATR-IRS - attenuated total reflection infrared spectroscopy, PM-IRRAS - polarization modulation infrared reflection absorption spectroscopy)[4]. The latter is especially important because of many materials very strong absorbs IR, so absorption spectra cannot be obtained. The listed methods can give information about such properties of surface as its structure, species adsorbed etc.

*UV-vis-spectroscopy*. In situ application of UV-vis-spectroscopy is used for monitoring of dissolved molecular species as well as nanosized particles quite for a long time. Its application allows revealing the composition of complexes in solution as well as size of metal nanoparticles formed[5,6].

*Electron microscopy*. Such 'classical' ex situ methods as scanning or transmission electron microscopy being the very important for the investigations of the properties of heterogeneous catalysts is nowadays adapted for in situ measurement[7,8]. This possibility appeared due to the development of the new specific equipment for the analysis, allowing accurate selective environment of reaction mixture around a catalyst by using special pumps/needles[8]. Therefore, ETEM (environmental transmission electron microscopy) and ESTEM (environmental transition scanning electron microscopy) including high-resolution modifications are available to be used in situ. It should be noted separately the method of electron energy loss spectrometry (EELS), applied in combination with STEM and allowing obtaining the precise chemical identification of type and the oxidation state of the nuclei presented in the samples[9].

***S2. Molecular and stoichiometric matrices of the chemical systems***

The molecular matrix of the system is the following rectangular matrix:

$$B = \begin{bmatrix} \alpha_{11} & \alpha_{12} & & \alpha_{1k} \\ \alpha_{21} & \alpha_{22} & \ldots & \alpha_{2k} \\ \ldots & \ldots & \ldots & \ldots \\ \alpha_{n1} & \alpha_{n2} & \ldots & \alpha_{nk} \end{bmatrix}$$

where $k$ is the number of chemical elements being a part of the components (i.e. chemical compounds) of the system; $n$ is the number of the components (i.e. chemical compounds) of the system; $\alpha_{nk}$ – the number of gram-atoms of the element $k$ in the component $n$.

The stoichiometric matrix of the system is the following rectangular matrix:

$$A = \begin{bmatrix} \alpha_{11} & \alpha_{12} & & \alpha_{1n} \\ \alpha_{21} & \alpha_{22} & \ldots & \alpha_{2n} \\ \ldots & \ldots & \ldots & \ldots \\ \alpha_{m1} & \alpha_{m2} & \ldots & \alpha_{mn} \end{bmatrix}$$

In this case, $n$, as above, is the number of the components (i.e. chemical compounds) of the system; $m$ is the number of the stoichiometric equations describing the conversions proceeding in the systems; $\alpha_{mn}$ is the stoichiometric coefficient of the component $n$ in the stoichiometric equation m.

Based on the law of conservation of mass, the relation between the $A$ and $B$ matrices presents the follows:

$A \times B = 0$.

If the elements of the $B$ matrix (i.e. the composition of the system components) are known, it becomes possible to find one of an infinite number of the linearly dependent variants of the $A$ matrix, i.e. one of possible linearly dependent sets of stoichiometric coefficients of the stoichiometric equations describing all the chemical transformations proceeding in the systems[10].

***S3. On the insufficiency of the knowledge about the composition/structure of the components of the chemical systems for the establishing of the mechanism of their interconversions***

The viewpoint that the establishing the structure and the composition of the products and intermediates of the reaction is enough for the establishing the reaction mechanism including the mechanistic reaction scheme, is still prevailed. Let's demonstrate the invalidity of this statement, assuming the hypothetic situations when the absolutely all components of a chemical reaction are succeeded to indentify (i.e. all the components were observable by any set of analytical method used) under the reaction investigation.

*Example 1.* Let's consider the example of the very simple (primitive) reaction with moderate number of the intermediates and elementary steps, where the one product is formed as a result of the substrate conversion. For instance, if in dehydrogenation reaction the following components [Cat•Alkane], [Alkene] and [$H_2$] were detected along with the [Cat] and [Alkane] being the initial reagents, it may seem that the composition of the intermediates and products unambiguously points to the consequence of their appearance in the reaction, and, accordingly, that the sole mechanistic reaction scheme may presents the following set of the stoichiometric equations of the steps:

$$[\mathrm{Cat}] + [\mathrm{Alkane}] = [\mathrm{Cat} \bullet \mathrm{Alkane}]$$
$$[\mathrm{Cat} \bullet \mathrm{Alkane}] = [\mathrm{Cat}] + [\mathrm{Alkene}] + [\mathrm{H_2}].$$

However, infinite number of linearly dependent stoichiometric equations (i.e. infinite number of *A* stoichiometric matrices) consistent also with the composition of the observed reaction components (i.e. with *B* molecular matrix) exists. For instance, another set of the equations distinct from the previous one by the appearance of the additional equation being the linear combination of two equations of the previous system (e.g. their sum):

$$[\mathrm{Cat}] + [\mathrm{Alkane}] = [\mathrm{Cat} \bullet \mathrm{Alkane}]$$
$$[\mathrm{Cat} \bullet \mathrm{Alkane}] = [\mathrm{Cat}] + [\mathrm{Alkene}] + [\mathrm{H_2}]$$
$$[\mathrm{Alkane}] = [\mathrm{Alkene}] + [\mathrm{H_2}]$$

This is also consistent with the composition of the products observed. From the chemical viewpoint, the appearance of the third equation means the possibility of the parallel reactions of

alkane proceeding (the 1st and the 3rd equations). Analyzing the system the question appears, what consequence of the steps indeed makes the major contribution to the conversion of alkane to alkene, and what is such contribution? In other words, do the products [Alkene] and [$H_2$] form with the catalyst participation (i.e. through the intermediates [Cat] and [Cat●Alkane]) according to the equations 1 and 2 of the system, or else from [Alkane] directly according to the equation 3 of the system? It is obvious, that an answer to this question is impossible to be found without the study of the reaction kinetics, i.e. (as minimum) the obtaining the temporal profiles of the amounts of all the reaction system compounds. By virtue of the system simplicity, is it easy to plan the discriminating experiment where [Cat] is excluded from the reaction components. However, in such case also the estimation of the reaction rates under presence as well as under absence of [Cat] is all the same needed for the establishing the contributions of two variants of the reaction mechanisms, that actually are the kinetic studies.

Therefore, the establishing of the composition of the reaction components is insufficient for the clarification of the reaction mechanistic scheme. Additional kinetic data are necessarily.

*Example 2*. Let's consider that in the ethylene hydrogenation on a Ni catalyst it is succeeded to detect and identify the composition of all the components: [Ni], [$H_2$], [$C_2H_4$], [$C_2H_6$], [Ni●$H_2$], [$C_2H_4$●Ni], [$C_2H_4$●Ni●$H_2$]. An application of a standard method of solving of the system of linear algebraic equations (for instance, the Gauss-Jordan method) for the *B* molecular matrix of these components gives one of variants of stoichiometric matrix *A* (hereinafter the 1st variant of *A* matrix), i.e. the system of linearly independent stoichiometric equations:

$$\left.\begin{array}{l} [H_2]+[C_2H_4]=[C_2H_6] \\ [Ni]+[H_2]+[C_2H_4]=[C_2H_4\bullet Ni\bullet H_2] \\ [Ni]+[C_2H_4]=[C_2H_4\bullet Ni] \\ [Ni]+[H_2]=[Ni\bullet H_2] \end{array}\right\} \text{ the 1st variant of } A \text{ matrix}$$

The cursory analysis of these equations points to the negligible probability of their correspondence to the equations of real elementary steps of the reaction mechanism. For instance, the second

equation corresponds to the reaction with the third kinetic order, and the product of the reaction (i.e. $[C_2H_6]$) is formed in the first equation without any participation of the Ni catalyst. This is not surprising because of the present system (the 1st variant of *A* matrix) is one from infinite number of linearly dependent set of the equations, and the set corresponding to the equations of the elementary steps of the real reaction mechanism is hidden among them.

Let's assume that the data about the reactivities of the reaction components are at researcher's disposal among the data about their composition. For instance, based on the data of model experiments carried out under stoichiometric conditions (that is the frequently used trick in catalysis) the data about the possibility of the following five reactions are had:

$$\left.\begin{array}{l} [Ni]+[H_2]=[Ni\bullet H_2] \\ [Ni]+[C_2H_4]=[C_2H_4\bullet Ni] \\ [Ni\bullet H_2]+[C_2H_4]=[C_2H_4\bullet Ni\bullet H_2] \\ [C_2H_4\bullet Ni]+[H_2]=[C_2H_4\bullet Ni\bullet H_2] \\ [C_2H_4\bullet Ni\bullet H_2]=[Ni]+[C_2H_6] \end{array}\right\} \text{ the } 2^{nd} \text{ variant of } A \text{ matrix.}$$

These equations do not contradict the common theoretic notions about catalytic reactions and, as for the 1st variant, correspond to the observed composition of the components. Let's assume that they may be considered as more reliable hypothesis of the reaction mechanism. In so doing, it is easy to demonstrate that the 2nd set of the equations is the result of linear transform of the 1st set of the reaction stoichiometric equations that was obtained by the formal solution of the system of algebraic equations derived from the *B* molecular matrix.

Indeed, if the second equation from the 1st variant of *A* is multiplied by (-1) and summed up the first one, the fifth equation of the 2nd variant of *A* is obtained:

$$[C_2H_4\bullet Ni\bullet H_2]=[Ni]+[C_2H_6]$$

If the third equation from the 1st variant of *A* is multiplied by (-1) and summed up the second one, the fourth equation of the 2nd variant of *A* is obtained:

$$[C_2H_4\bullet Ni]+[H_2]=[C_2H_4\bullet Ni\bullet H_2]$$

If the fourth equation from the 1st variant of *A* is multiplied by (-1) and summed up the second one, the third equation of the 2nd variant of *A* is obtained:

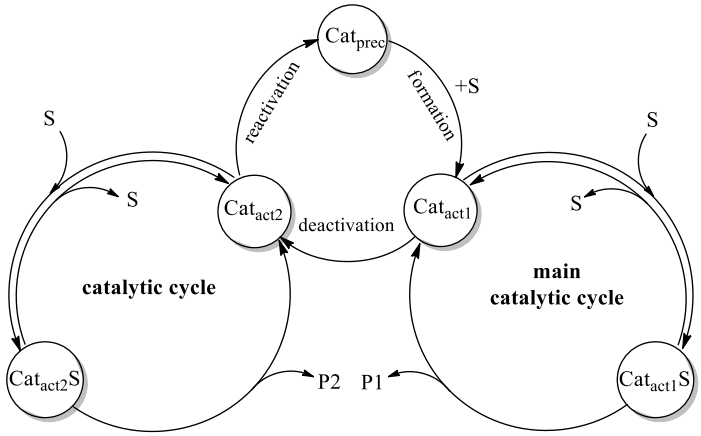
$$[Ni \bullet H_2] + [C_2H_4] = [C_2H_4 \bullet Ni \bullet H_2]$$

At the same time, the third and the fourth equations of the system from the 1st variant of *A* correspond to the second and the first equations of the system from the 2nd variant of *A*. Therefore, it is succeeded to obtain all the five equations from the 2nd variant of *A* by linear transform of the equations of the system from the 1st variant of *A*.

However, the analysis of the equations from the 2nd variant of *A* does not allow making any conclusions about what of two parallel routes of the product $C_2H_6$ formation gives the dominating contribution for the $C_2H_4$ conversion – through the $[Ni \bullet H_2]$ or the $[C_2H_4 \bullet Ni]$ intermediate. At the same time, it is possible that one of these intermediates exists outside the catalytic cycle and presents the product of a catalyst deactivation by a substrate. Note, that the quantitative ratio of these intermediates during the reaction proceeding cannot be the reason for the establishing of their contribution to the product formation and of their roles in catalysis. The sole possibility for the elucidation of the questions can be information about the dependences of the rates of the intermediates accumulation/consumption on their quantities with required synchronization of these data with the data about the rate of formation of the catalytic reaction product.

***S4. The simulation of the [species amount] - [catalytic reaction rate] dependences***

For the simulation the [species amount]- [catalytic reaction rate] dependences the complex mechanism of the catalytic reaction was used where in two catalytic cycles of the Michaelis-Menten type two products P1 and P2 are formed through the active species $Cat_{act1}$, $Cat_{act1}S$ and $Cat_{act2}$, $Cat_{act2}S$, respectively, formed from inactive catalyst precursor $Cat_{prec}$:




Note, that $Cat_{act1}$ and $Cat_{act1}S$ species are active in the formation of product P1 but inactive in the formation of product P2, and *vice versa*. The catalyst precursor $Cat_{prec}$ is inactive species in the routes of formation of both products P1 and P2. The processes marked as "deactivation" and "reactivation" are such with respect to the active species of the main catalytic cycle of the product P1 formation, while they are the processes of formation and deactivation, respectively, of the active species of the catalytic cycle of the product P2 formation.

Integral and differential kinetic relationships hereinafter were simulated using the Gepasi 3.10 program[11,12]. The following values of the rate constants were used for the simulation:

$Cat_{prec}+S \rightarrow Cat_{act1}$ – 10 (l $mol^{-1}$ $min^{-1}$)

$Cat_{act1} \rightarrow Cat_{act2}$ – 5 ($min^{-1}$)

$Cat_{act2} \rightarrow Cat_{prec}$ – 2 ($min^{-1}$)

$Cat_{act1}+S \rightarrow Cat_{act1}S$ – 100 (l $mol^{-1}$ $min^{-1}$)

$Cat_{act1}+S \leftarrow Cat_{act1}S$ – 100 ($min^{-1}$)

$Cat_{act1}S \rightarrow Cat_{act1}+P1$ – 100 ($min^{-1}$)

$Cat_{act2}+S \rightarrow Cat_{act2}S$ – 50 (l $mol^{-1}$ $min^{-1}$)

$Cat_{act2}+S \leftarrow Cat_{act2}S$ – 50 ($min^{-1}$)

$Cat_{act2}S \rightarrow Cat_{act2}+P2$ – 50 ($min^{-1}$)

The initial concentrations used were the follows:

[S]= 1 mol/l; [$Cat_{prec}$]= 0.01; 0.02; 0.03; 0.04 mol/l.

$[Cat_{act1}]=[Cat_{act1}S]=[Cat_{act2}]=[Cat_{act2}S]= 0$ mol/l;

***S5. The homo- and cross-coupling reactions of aryl halides with different reagents using ligand-free catalytic systems***

To study the reactions kinetics, samples for UV-vis and GC-MS analyses were collected at different reaction time points. To estimate the reproducibility of the data, each experiment was performed three times.

The UV-vis spectra of the samples were recorded on an SF-2000 spectrophotometer (Russia) in the 190–600 nm range using quartz cells with an optical path of 0.01 cm.

The concentration of $[PdBr_4]^{2-}$ was measured as the absorbance at 350 nm taking into account the absorbance from stilbene and chalcone (the latter was formed in the Heck reaction when benzoic anhydride was used as a coupling partner for styrene), whose concentration were measured by GC-MS. The calibration curve for the $[PdBr_4]^{2-}$ was constructed using the complex obtained by the interaction of $PdBr_2$ with 20 equiv. of NaBr in DMF. The samples were placed in the cell without any dilution.

The concentration of $[PdI_4]^{2-}$ was measured as the absorbance at 340 nm. The calibration curve for the $[PdI_4]^{2-}$ was constructed using the complex obtained by the interaction of $PdI_2$ with 20 equiv. of NaI in DMF. The samples were placed in the cell diluted with DMF two times.

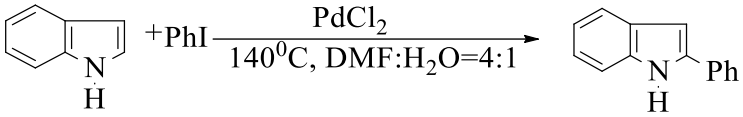
The concentration of $Pd(acac)_2$ was measured as the absorbance at 330 nm using the calibration curve. The samples were placed in the cell without any dilution.

The quantitative compositions of the samples were determined using gas chromatography /mass spectrometry (GC-MS) (Shimadzu GC-MS QP-2010 Ultra, ionization energy of 70 eV, 0.25 μm × 0.25 mm × 30 m GsBP-5MS column, He as the carrier gas) analysis. The recorded mass spectra were compared with those available in the literature (Wiley, NIST, and NIST05 comparison

libraries). The quantitative composition of the samples was determined using naphthalene as the internal standard and calibration against authentic samples.

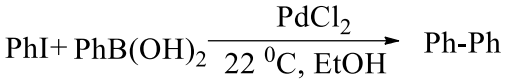
The instantaneous rates of the reactions were estimated from the difference between the substrate concentrations in successive samples of the reaction mixture.

**Direct arylation of indole by iodobenzene**



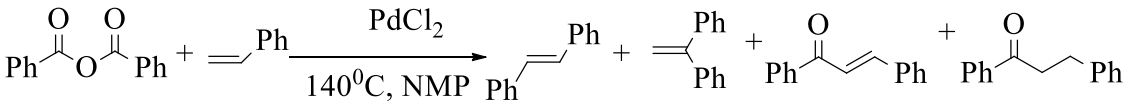

Iodobenzene (5 mmol), indole (5 mmol), NaOAc as a base (0.65 mmol), $PdCl_2$ (0.08 or 0.16 mmol, 1.6 and 3.2 mol%, respectively) and naphthalene (1 mmol) as an internal standard for GC-MS analysis were added to 5 mL of *N*,*N*-dimethyl formamide (DMF) - water mixture (4/1) in a glass reactor equipped with a magnetic stir bar and a septum inlet. The reactor was placed into a pre-heated oil bath (140ºC), and the reaction mixture was stirred.

**Suzuki reaction**




Iodobenzene (5 mmol), phenyl boronic acid (5 mmol), NaOAc as a base (0.65 mmol), $PdCl_2$ (0.08 mmol, 1.6 mol%) and naphthalene (1 mmol) as an internal standard for GC-MS analysis were added to 5 mL of ethanol in a glass reactor equipped with a magnetic stir bar and a septum inlet. The reactor was placed into a thermostatted water bath (22ºC), and the reaction mixture was stirred.

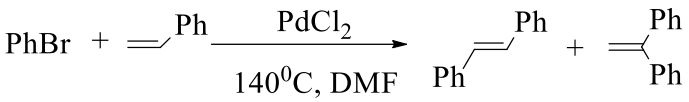
**Heck reaction with benzoic anhydride**




Styrene (5 mmol), benzoic anhydride (5 mmol), $PdCl_2$ (or $PdBr_2$ of $Na_2PdBr_4$) (0.08 mmol, 1.6 mol%), LiCl (0.5 mmol), NaBr or $NBu_4Br$ (1.6 mmol) and naphthalene (1 mmol) as an internal standard for GC-MS analysis were added to 5 mL of *N*-methyl-2-pyrrolidone (NMP) in a glass

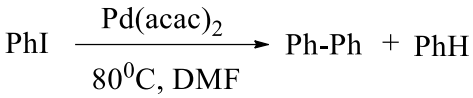
reactor equipped with a magnetic stir bar and a septum inlet. The reactor was placed into a pre-heated oil bath (140ºC), and the reaction mixture was stirred.

**Heck reaction with bromobenzene**




Styrene (5 mmol), bromobenzene (30 mmol), $PdCl_2$ (0.04 or 0.08 mmol, 0.8 and 1.6 mol%, respectively), NaOAc (6.5 mmol) and naphthalene (1 mmol) as an internal standard for GC-MS analysis were added to 5 mL of DMF in a glass reactor equipped with a magnetic stir bar and a septum inlet. The reactor was placed into a pre-heated oil bath (140ºC), and the reaction mixture was stirred.

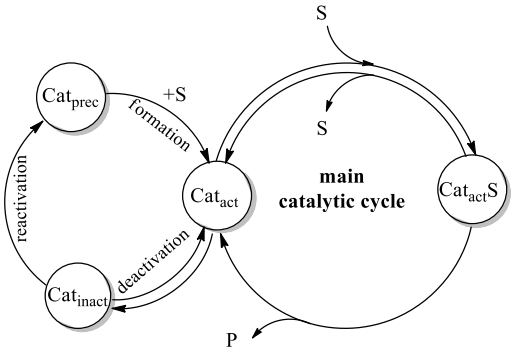
**Reductive homocoupling of iodobenzene**




Iodobenzene (5 mmol), $Pd(acac)_2$ (0.08 mmol, 1.6 mol%), HCOONa (0.65 mmol) and naphthalene (1 mmol) as an internal standard for GC-MS analysis were added to 5 mL of DMF in a glass reactor equipped with a magnetic stir bar and a septum inlet. The reactor was placed into a pre-heated oil bath (80ºC), and the reaction mixture was stirred.

## *S6. The simulation of the [species amount]-[product amount] dependences. The observable inactive species*

For the simulation the [species amount]-[product amount] dependences the mechanism of the catalytic reaction was used where in the catalytic cycle of the Michaelis-Menten type the product P is formed through the active species $Cat_{act}$ and $Cat_{act}S$ formed from inactive catalyst precursor $Cat_{prec}$:




Note, that the species $Cat_{act}$ and $Cat_{act}S$ are the active in the formation of product P, and $Cat_{prec}$ and $Cat_{inact}$ are inactive species participating in the formation/deactivation/reactivation of a catalyst.

For all the simulations depicted at the Figure 6 in the paper the same rate constants of the catalytic cycle as well as initial concentration of the component were used:

$Cat_{act}+S \rightarrow Cat_{act}S$ – 100 (l $mol^{-1}$ $min^{-1}$)

$Cat_{act}+S \leftarrow Cat_{act}S$ – 100 ($min^{-1}$)

$Cat_{act}S \rightarrow Cat_{act}+P$ – 100 ($min^{-1}$)

[S]= 1 mol/l; $[Cat_{act}]=[Cat_{act}S]$ = 0 mol/l;

$[Cat_{prec}]$ = 0.01; 0.02; 0.03; 0.04 mol/l

For the simulation depicted at the Figure 6(*a*) (species observed is inactive and is formed directly from the active one as a result of irreversible deactivation) the following rate constants were used:

$Cat_{prec}+S \rightarrow Cat_{act}$ – 10 (l $mol^{-1}$ $min^{-1}$)

$Cat_{act} \rightarrow Cat_{inact}$ – 5 ($min^{-1}$)

$Cat_{act} \leftarrow Cat_{inact}$ – 0 ($min^{-1}$)

$Cat_{inact} \rightarrow Cat_{prec}$ – 0 ($min^{-1}$)

For the simulation depicted at the Figure 6(*b*) (the observed species is inactive, but its deactivation is reversible) the following rate constants were used:

$Cat_{prec}+S \rightarrow Cat_{act}$ – 10 (l $mol^{-1}$ $min^{-1}$)

$Cat_{act} \rightarrow Cat_{inact}$ – 5 ($min^{-1}$)

$Cat_{act} \leftarrow Cat_{inact}$ – 1 ($min^{-1}$)

$Cat_{inact} \rightarrow Cat_{prec}$ – 0 ($min^{-1}$)

For the simulation depicted at the Figure 6(*c*) (the observed species is inactive, its formation (i.e. the deactivation of active species) is irreversible, but the active species reactivation is possible) the following rate constants were used:

$Cat_{prec} + S \rightarrow Cat_{act}$ – 10 ($l\ mol^{-1}\ min^{-1}$)

$Cat_{act} \rightarrow Cat_{inact}$ – 5 ($min^{-1}$)

$Cat_{act} \leftarrow Cat_{inact}$ – 0 ($min^{-1}$)

$Cat_{inact} \rightarrow Cat_{prec}$ – 2 ($min^{-1}$)

For the simulation depicted at the Figure 6(*d*) (the observed inactive species is formed from the active one indirectly) the following rate constants were used:

$Cat_{prec} + S \rightarrow Cat_{act}$ – 0 ($l\ mol^{-1}\ min^{-1}$)

$Cat_{act} \rightarrow Cat_{inact}$ – 0.5 ($min^{-1}$)

$Cat_{act} \leftarrow Cat_{inact}$ – 0 ($min^{-1}$)

$Cat_{inact} \rightarrow Cat_{prec}$ – 0.2 ($min^{-1}$)

Note, that in this case the initial concentrations of catalyst species were different:

$[Cat_{prec}]=[Cat_{act}S]$ = 0 mol/l;

$[Cat_{act}]$ = 0.01; 0.02; 0.03; 0.04 mol/l

***S7. The simulation of the [species amount]-[product amount] dependences. The observed active species***

For the simulation the [species amount]-[product amount] dependences the mechanism of the catalytic reaction was used where in the catalytic cycle of the Michaelis-Menten type the product P is formed through the active species $Cat_{act}$ and $Cat_{act}S$ formed from inactive catalyst precursor $Cat_{prec}$ (see section S6).

For all the simulations depicted at the Figure 9 in the paper the same rate constants of the catalytic cycle as well as the initial concentrations of the components were used:

$Cat_{act}+S \rightarrow Cat_{act}S$ – 100 (l $mol^{-1}$ $min^{-1}$)

$Cat_{act}+S \leftarrow Cat_{act}S$ – 100 ($min^{-1}$)

$Cat_{act}S \rightarrow Cat_{act}+P$ – 100 ($min^{-1}$)

[S]= 1 mol/l; $[Cat_{act}]=[Cat_{act}S]$ = 0 mol/l;

$[Cat_{prec}]$ = 0.01; 0.02; 0.03; 0.04 mol/l

For the simulations depicted at the Figure 9(*a*) (species observed is active and is subjected to the irreversible deactivation) the following rate constants were used:

$Cat_{prec}+S \rightarrow Cat_{act}$ – 10 (l $mol^{-1}$ $min^{-1}$)

$Cat_{act} \rightarrow Cat_{inact}$ – 5 ($min^{-1}$)

$Cat_{act} \leftarrow Cat_{inact}$ – 0 ($min^{-1}$)

$Cat_{inact} \rightarrow Cat_{prec}$ – 0 ($min^{-1}$)

For the simulations depicted at the Figure 9(*b*) (species observed is active and is subjected to the reversible deactivation) the following rate constants were used:

$Cat_{prec}+S \rightarrow Cat_{act}$ – 10 (l $mol^{-1}$ $min^{-1}$)

$Cat_{act} \rightarrow Cat_{inact}$ – 5 ($min^{-1}$)

$Cat_{act} \leftarrow Cat_{inact}$ – 1 ($min^{-1}$)

$Cat_{inact} \rightarrow Cat_{prec}$ – 0 ($min^{-1}$)

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