UDK   541.128:615.014.4

Kinetics of the Bray-Liebhafsky Oscillatory Reaction Perturbed by Polymer Supported Cobalt Catalyst

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Abstract:

The Bray-Liebhafsky (BL) oscillatory reaction generated in the batch reactor at 62-68 ^{o}C was perturbed by cobalt(II)-nitrate, supported on the macroreticular copolymer of poly-4-vinylpyridine with divinylbenzene (Co-PVPDVB). The kinetic data was analyzed of the complex pathways of the hydrogen peroxide decomposition in the examined BL reaction. The obtained results confirm that the kinetics of the BL reaction in the presence Co-PVPDVB comes partially from the Co-catalyst and partially from the macroreticular copolymer support.

Keywords: Co-catalyst; Copolymer of poly-4-vinylpyridine with divinylbenzene; Chemical kinetics; Bray-Liebhafsky reaction; Activation energy.
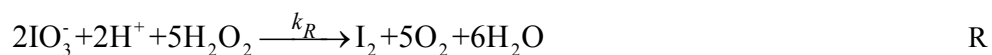
1. Introduction

The oscillatory reactions as analytical matrix were used from about twenty years ago [1-5]. The Bray-Liebhafsky oscillatory reaction [6, 7] has been successfully applied as sensitive matrix for the characterization of catalysts [5, 8-13]. In our previous article [5], it was also shown that this reaction can be used for characterization Co-PVPDVB catalyst.

First, it is necessary to give some data about BL matrix and its net reaction **D**. Namely, BL reaction is the decomposition of hydrogen peroxide into water and oxygen [7, 8] in the presence of iodated and hydrogen ions:

$$2H_2O_2 \xrightarrow[IO_3^-, H^+]{k_D} 2H_2O + O_2, \qquad\qquad D$$

where k_D is the rate constant.

The reaction D is result of two complex consecutive reactions

$$2IO_3^- + 2H^+ + 5H_2O_2 \xrightarrow{k_R} I_2 + 5O_2 + 6H_2O \qquad\qquad R$$

$$I_2 + 5H_2O_2 \xrightarrow{k_O} 2IO_3^- + 2H^+ + 4H_2O . \qquad\qquad O$$

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In closed (or batch) reactor, transient periods alternate with domination of either reaction R or reaction O, and therefore, intermediate concentrations oscillate in time. The overall reaction, independent of its complexity, is the pseudo-first order with respect to hydrogen peroxide:

$$-\frac{d[H_2O_2]}{dt} = k_D[H_2O_2].$$ (1)

Also it was found that there is a correspondence between the rate constants k_R and k_O in reactions **R** and **O**, and characteristic kinetic parameters such as τ_1 (preoscillatory period) and τ_{end} (duration of the oscillogram):

$$k_R = C_1\frac{1}{\tau_1} \qquad k_O \cong C_2\frac{1}{\tau_{end}} = k_D$$ (2)

where C_1 and C_2 are constants characteristic for the considered system. It is known too, that the kinetics of the overall reaction **D** is controlled by reaction **O**. [14-18] These relations are useful for the kinetic analysis of the perturbed BL matrix by any small perturbation. [19]

2. Experimental

Catalyst is prepared by wetness impregnation of cobalt(II)-nitrate ($Co(NO_3)_2 \times 6H_2O$) on the macroreticular copolymer of poly-4-vinylpyridine with divinylbenzene as described before.[20, 21]. The procedure used here for catalyst preparation [20, 21] does not change textural properties of the catalyst. (Fig. 1).
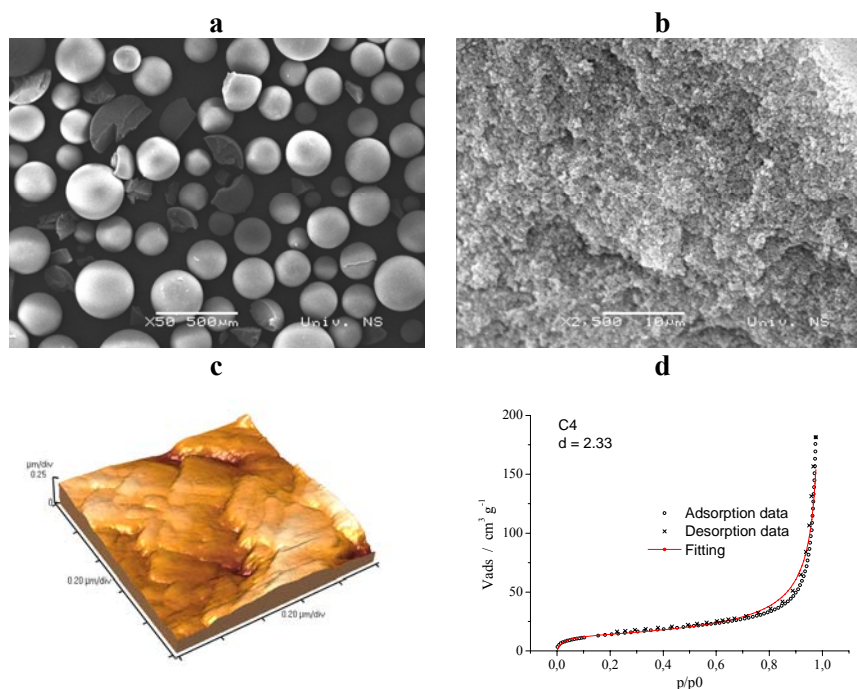

Fig. 1. Textural characterization of the Co-PVPDVB. SEM micrographs of catalyst beads recorded by an automated scanning electron microscope (SEM), JSM-6460LV JOEL with different enlargement: a. ×50 b. ×2500 c. AFM micrograph of the catalyst bead surface obtained by AutoProbe CP Research, TM Microscopes - contact mode. d. Isotherms for N_2 adsorption-desorption with fractal distribution fitting curve

It could be seen from Fig. 1 that Co-PVPDVB catalyst beads are mainly compact spheroids varying in diameter from about 100 μm up to about 300 μm. There is also fraction of fragmented catalyst beads that look roughly compact across the fracture surface, at least with this, the smallest enlargement of SEM. However, fracture surface observed with much higher enlargements, as in Fig. 1 b, clearly shows significant contribution of pores in internal bead structure. This is the macroreticular structure of the PVPDVB support, which remained stable also in the Co-PVPDVB catalyst. Closer look at the surface of the catalyst bead by AFM, Fig. 1 c, gives us an impression of the roughness level, indicating that internal pores are connected with a surface, also. Observed continuous structure of pores is essential for catalytic efficiency, since it enables free transport of both reactants and products from bulk solution to active centers inside catalyst bead. Therefore, detailed structure of pore was studied by physisorption method. Nitrogen adsorption–desorption isotherms were determined on Sorptomatic 1990 Thermo Finnigan automatic system using nitrogen physisorption at −196 ◦C. Before measurement the samples were outgassed at 130 °C for 10 h. Specific surface area of the samples (SBET) was calculated from the nitrogen adsorption isotherms according to the Brunauer, Emmett, and Teller method [22] and it has value of 53 m^2/g for the Co-PVPDVB catalyst, while PVPDVB support has a value of 52 m^2/g. The nitrogen physisorption isotherm for catalyst, Fig. 1 d**,** is very similar to the one of the polymer support. According to the IUPAC recommendations for classification of adsorption isotherms [23] the obtained isotherms, for both samples, correspond to Type II isotherm, characteristic for macroporous materials. Hysteresis loops, which appear in the physisorption isotherms, can be classified as Type H1. Origin of this type of hysteresis is characteristic for solids consisting of grains, crossed by nearly cylindrical channels or made by aggregates or agglomerates of spheroidal particles. Pore size distributions for both samples are in the range of 70–100 nm with a mean pore diameter ~85 nm. The differences in the surface areas of these materials are negligible. The minor decrease in the total pore volume observed with the presence of cobalt on polymer is a consequence of both, the porosity decrease and the bulk density increase. The obtained results confirm that the metal ions on the polymer support do not significantly affect its pore structure and textural properties. Furthermore, the fractal dimension of the polymer internal surfaces was determined by Mahnke and Mögel method and it takes the value of d = 2.33. [24-26] Irregular textural properties with fractal distribution of pores could be optimal for the application of catalyst in liquid environment, where mass transfer could became the limiting factor.

The experiments related to kinetic investigation were carried out in the isothermal ($\pm 0.1^0$C) closed well-stirred (900 rpm) reactor at different temperatures (62, 64, 66 and 68 ^{0}C) in dark. The reaction volume was 52 mL. The initial concentrations the BL matrix species were for $[KIO_3]_0 = 7.2 \cdot 10^{-2}$ mol/dm^3, $[H_2SO_4]_0 = 4.8 \cdot 10^{-2}$ mol/dm^3, and $[H_2O_2]_0 = 4.6 \cdot 10^{-2}$ mol/dm^3. The catalyst was placed in the reactor prior to components of the matrix. The evolution of the indicative BL reaction was followed potentiometrically, by means of iodide ion sensitive electrode connected to the Ag/AgCl reference electrode.

The content of octahedral Co^{2+} coordination on polymer [24, 25] was 5.72 mas.%. The sample of 0.05 g of the catalyst in BL reaction volume of 52 ml is equivalent to $9.32 \cdot 10^{-4}$ mol/dm^3 of cobalt ion and $5.29 \cdot 10^{-3}$ mol/dm^3 of weakly basic pyridine rings.

3. Results and Discussion

In all cases, iodide oscillograms with one preoscillatory period and one row of the relaxations oscillations are obtained (Fig. 2). These type structures of the iodide oscillograms can be analyzed by the relation (2).[18] Generally, increases in amount of catalyst and temperature, both lead to the decrease of number of oscillation.
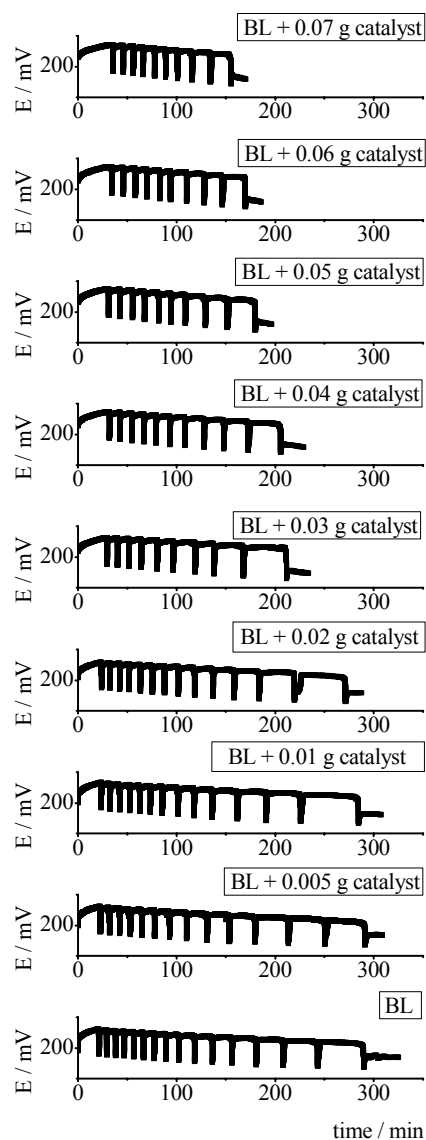
Fig. 2. The typical appearance of the iodide oscillograms of the BL matrix and perturbed BL matrix by different amount of cobalt catalyst (m) at 64 ^{0}C.

The empirical relations between kinetic parameters τ_1 and τ_{end} and the mass of catalyst m have been found to be complex [5]:

$$\ln[\ln(\tau_1^0/\tau_1)] = \ln x + y \ln m \tag{3}$$

$$\ln[\ln(\tau_{end}^0/\tau_{end})] = \ln w + z \ln m \tag{4}$$

where, x, y, w and z are empirical constants, τ_1 and τ_{end} are kinetic parameters related to BL matrix with catalyst, while τ_1^0 and τ_{end}^0 are related to BL matrix only. However, after new investigations we found that the formal relations (3) and (4) don't apply for analysis of the systems at different temperatures and that more natural and simpler relations exist:

$$\frac{1}{\tau_1} = \frac{1}{\tau_1^0} - qm_{cat} \tag{5}$$

$$\frac{1}{\tau_{end}} = \frac{1}{\tau_{end}^0} - pm_{cat} \cdot \tag{6}$$

where q and p are the slopes. In our case the graphics of the relations (5) and (6) are given in the Fig. 3.
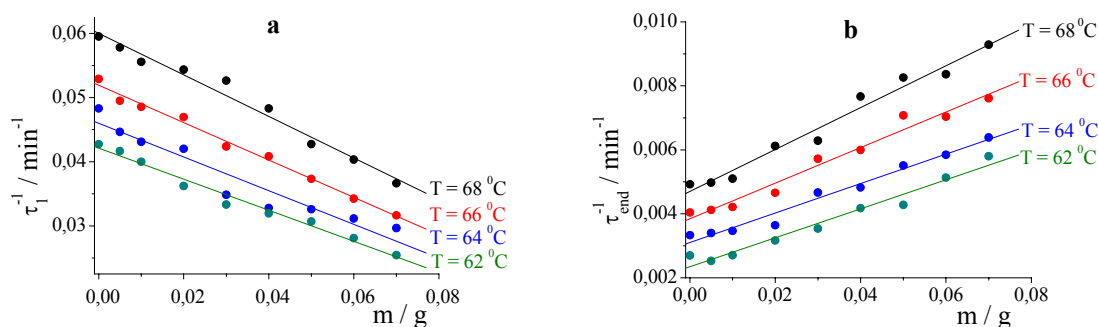

Fig. 3. Dependence of $1/\tau_1$ (a) and $1/\tau_{end}$ (b) on the amount m of catalyst Co-PVPDVB

The reciprocal values of the kinetic parameters τ_1 and τ_{end} are linear functions of the amount of polymer supported cobalt catalyst which have negative and positive slopes respectively (Fig. 3). This is the proof that increase in amount of catalyst accelerates the reaction O and inhibits the reaction R. In other words, it is obvious that k_R decreases and k_O (k_D) increases when the amount of catalysts increases.

Similar conclusion can be found from the values of apparent activation energies $E_a(R)$ and $E_a(O)$ of the reaction R and O (Fig. 4). The values of activation energies were calculated from relations connecting the logarithm of $1/\tau_1$ (Equation (5)), and $1/\tau_{end}$ (Equation (6)), with reciprocal temperatures 1/T for each amount of catalyst.
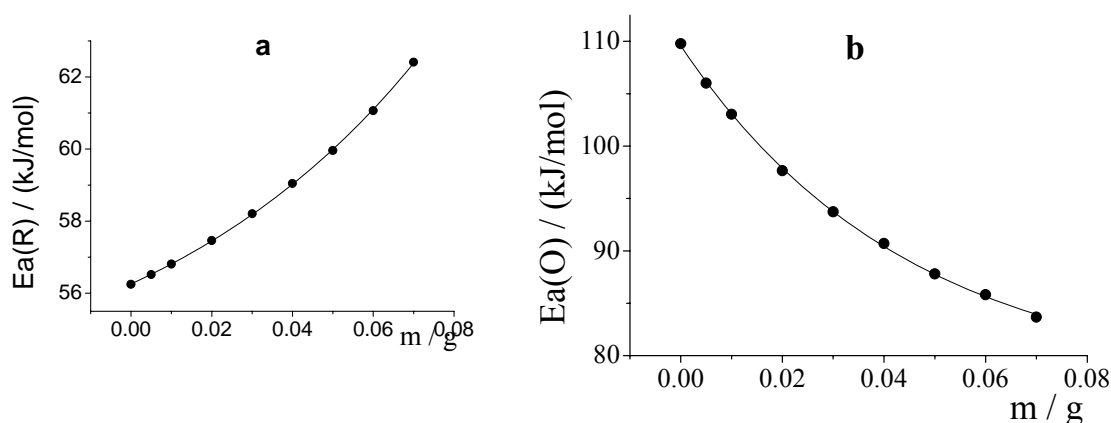

Fig. 4. Apparent activation energies $E_a(R)$ (a) and $E_a(O)$ (b) of the BL matrix and BL matrix perturbed by different amount of Co-catalyst

Now, one would like to know the cause of the observed behavior. It could be in the influence of Co ions supported on the polymer, or maybe influence of the polymer support, itself. Therefore, the perturbation tests were performed with equal amounts m = 0.05g of both, catalyst Co-PVPDVB, and its support PVPDVB (Fig. 5). We found that polymer support has stronger influence on kinetic parameters τ_1 and τ_{end} than the catalyst, and changes were in the same direction. Moreover, experiments at various temperatures show that BL system perturbed with polymer support alone has much higher activation energy for the reaction (R).
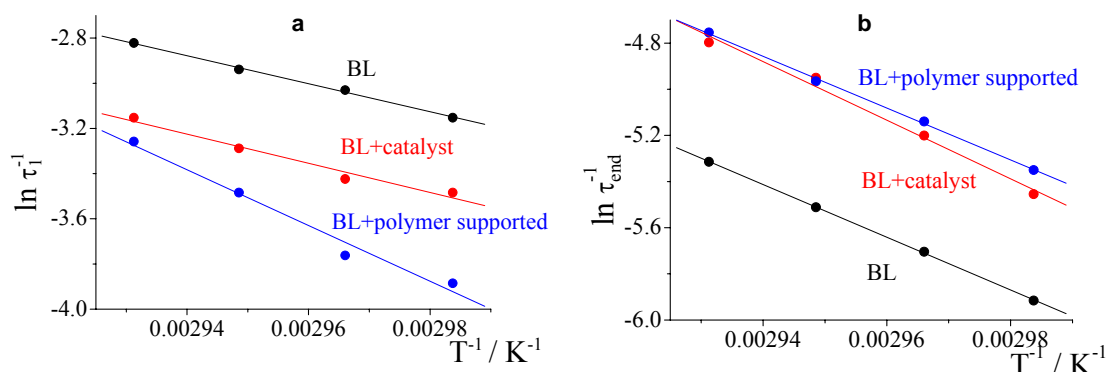
Fig. 5. Correlation between temperature and kinetic parameters τ_1 (left) and τ_{end} (right), for a given amount (m = 0.05 g) of catalyst and polymer support. The apparent activation energies Ea were calculated from the first graphic (left) for reaction R, and from second one (right) for the reaction O. Obtained Ea values for reactions R and O were respectively 51.5 and 94.9 kJ/mol for the BL matrix, then, 53.6 and 105.7 kJ/mol for the BL matrix perturbed by catalyst and finally, (102.5 and 93.2 kJ/mol) for the BL matrix perturbed by polymer support

Nevertheless, results in Fig. 5 indicate complex interaction between polymers supported catalyst Co-PVPDVB and BL matrix. Several complications are possible. Reactive species could be adsorbed from the matrix to the polymer and removed from the liquid reaction phase, or they can even act in adsorbed form with modified activity. Also, cobalt ions could be easily desorbed from the support in acid aqueous medium and continue to interact in homogeneous system. Hence, additional experiments were done, perturbing the BL reaction at 66 ºC with equivalent amount of cobalt nitrate in homogeneous solution, and also with BL matrix filtered from catalyst immediately before the reaction initiation by the hydrogen peroxide addition. Results for the kinetic parameters of all corresponding systems are given in Tab. I.

Both kinetic parameters τ_1 and τ_{end} given in Tab. I show much smaller effects when the BL matrix is perturbed with homogeneous cobalt nitrate and also when catalyst is filtered from the matrix before the reaction initiation. However, the effects made during the induction period are also reflected on the duration of the oscillogram. Therefore, the effects of the support and cobalt ions could not be clearly resolved. But if we observe mean frequency during the oscillating period only, the picture becomes clear. The increase in oscillation frequency when catalyst was filtered before the initiation is equal to those obtained with equal amount of cobalt nitrate. Polymer support contributes to the frequency much more. Moreover, catalyst gives even additional contribution to the frequency which can be identified as simple summation of the support and homogeneous cobalt effects. (See Table I)

Tab. I. Kinetic parameters at 66^0C of BL system, BL system with catalyst, BL filtrate, BL system with $Co(NO_3)_2 \times 6H_2O$, BL system with polymer support. **n** is total number and **v** is the frequency of oscillations.

	τ_1 (min)	τ_{end} (min)	n	v (min^{-1})
1. BL	18.9	247.6	14	0.0612
2. BL + catalyst	26.8	141.3	10	0.0873
3. BL + polymer support	32.6	143.4	9	0.0812
4. BL + Co(NO$_3$)$_2$×6H$_2$O	17.5	225.4	14	0.0673
5. BL filtrate	20.6	213.5	13	0.0674

We can conclude that cobalt ions are leaching from polymer support in acid medium of BL matrix, and they weakly contribute the oxidation reaction during the oscillations. The influence of cobalt ions on dynamic features of the BL matrix is significant during the preoscillatory period. It is interesting that the same catalyst was also active for reaction initiation in cyclohexane oxidation [17]. However, due to high ion-exchange capacity, the polymer support has much stronger effect on the reaction dynamics, through the effects on adsorption-desorption equilibrium of reactive species from BL matrix. Just as in some previous experiments [10] with the same polymer in BL matrix, the iodine is the species which is the most important for the observed influence of the polymer support. Since preoscillatory period is the period of the iodine accumulation, its concentration is the most sensitive parameter on various influences by perturbing materials. However, oscillating dynamics is directed by the limit cycle as the stable attractor of the BL matrix and therefore the mean frequency appears here as more robust kinetic parameter than characteristic periods.

4. Conclusion

Described results confirmed once again that BL reaction is useful matrix for characterization of heterogeneous catalysts. Catalyst activity was identified against oxidation branch of the complex reaction system, while, inhibition effect is observed in reduction part. However, it was also proven that most cobalt ions from catalyst Co-PVPDVB are extracted in acidified aqueous medium of the BL reaction and polymer support, PVPDVB, is itself strongly perturbing agent.

Hence, results of described investigations provoke new ones. One of them should be the search for the model which can describe the interaction between the BL matrix and the catalyst. Also, some research could be related to analytical applications of BL reaction as reaction matrix for quantitative analysis or activity evaluation of polymer supported cobalt catalyst and its polymer support. Finally, it is necessary to carry out new separate examination with aim to define the role of the polymer in the mechanism of the perturbed BL reaction.

5. Acknowledgment

6. References

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Садржај: *Осцилаторна реакција Bray-Liebhafsky (BL) реализована у затвореном реактору на температури* 62-68 ^oC *је пертурбована са кобалт(II)нитратом уграђеним на макроретикуларном кополимеру поли-4-винилпиридина са дивинилбензеном (Co-PVPDVB). Анализирани су кинетички подаци комплексних реакционих путева разлагања водоникпероксида у испитиваној BL реакцији. Добијени резултати потврђују да је у присуству Co-PVPDVB кинетика BL реакције делимично одређена Co–катализатором, а делимично макромолекуларним кополимерним носачем катализатора.*

Кључне речи: *Co-катализатор; кополимер поли-4-винилпиридина са дивинил-бензеном; хемијска кинетика; Bray-Liebhafsky реакција; енергија активације*