Short Communication ___________________________________ *Thematic Section:* Theoretical Research.
Reference Object Identifier – ROI: jbc-01/17-50-6-30 *Subsection:* Physical Chemistry.
The Digital Object Identifier – DOI: 10.37952/ROI-jbc-01/17-50-6-30
Submitted on June 3, 2017.

Chaotic oscillations in a simple heterogeneous catalytic reaction

© **Nikolay I. Koltsov**,*+ and **Vladislav Kh. Fedotov**
Department of Physical Chemistry and Macromolecular Compounds.
Chuvash State University Named after I.N. Ulyanov. Moskovsky Ave., 15. Cheboksary, 428015.
Chuvash Republic. Russia. Phone: +7 (8352) 45-24-68. E-mail: koltsovni@mail.ru

*Supervising author; +Corresponding author

***Keywords**:* heterogeneous catalytic reaction, mechanism, stage scheme, law of acting masses, nonstationary kinetics, chaotic oscillations.

Abstract

For heterogeneous catalytic reactions irregular and chaotic oscillations of reagent concentrations and reaction rates in time have been experimentally observed for heterogeneous catalytic reactions of hydrogen oxidation, carbon monoxide and other reactions. Various approaches and mechanisms are used, applying more complicated assumptions: different various variants of nonideal kinetics different from the law of effective masses; mechanisms of multicenter adsorption involving several types of active catalyst centers; mechanisms including "buffer" stages; mechanisms taking into account the interaction of substances in the adsorbed state and their dissolution in the near-surface layer of the catalyst; parallel reaction of different catalytic oscillators on different types of catalyst centers (superposition of oscillations); mechanisms that allow for random perturbations (noise-induced chaos); phenomenological models using non-standard kinetic laws and unusual model constructions ("reservoirs"); various combinations of these approaches to describe chaotic oscillations in heterogeneous catalytic reactions. Thus, nowadays no mechanisms have been found so far that can describe chaotic oscillations of heterogeneous catalytic reactions in gradient chemical reactors within the framework of models of an ideal adsorbed layer and the law of acting masses. Due to this it is necessary to describe the complex dynamic behavior of heterogeneous catalytic reactions by simple mechanisms without complicating assumptions. A special role in the origin of oscillatory processes is played by autocatalytic stages capable of generating unstable regimes in simple dynamical systems with minimal molecularity. This article presents a simple four-stage scheme with two autocatalytic stages and establishes the possibility of describing it with the help of its chaotic oscillations in heterogeneous catalytic reactions within the framework of an ideal adsorbed layer and the law of acting masses. The randomness of oscillations is confirmed by numerical calculations of the kinetic model and the Lyapunov's exponent.

References

[1] J.E. Zuniga, D. Luss. Kinetic oscillations during the isotherma1 oxidation of hydrogen on platinum wires. *J. Catal*. **1978**. Vol.53. No.3. P.312-320.
[2] Z. Kurtanjek, M. Sheintuch, D. Luss. Surface state and kinetic oscillation in the oxidation of hydrogen on nickel. *Ibid*. **1980**. Vol.66. No.1. P.11-27.
[3] R.A. Schmitz, G.T. Renola, P.C. Garrigan. Observations of complex dynamic behaviour in the H_2-O_2 reaction in nickel. *Ann. N. Y. Acad. Sci*. **1979**. Vol.316. P.638-651.
[4] H. Arif, M. Stoukides. Rate and oxygen activity oscillations during hydrogen oxidation on nickel films in a CSTR. *Chem. Eng. Sci*. **1986**. Vol.41. No.4. P.945-952.
[5] V. Hlavacek, J. Rathousky. Oscillatory behaviour of metallic honeycomb catalysts. *Ibid*. **1982**. Vol.37. No.3. P.375-380.
[6] L.F. Razon, S.M. Chang, R.A. Schmitz. Chaos during the oxidation of carbon monoxide on platinum-experiments and analysis. *Ibid*. **1986**. Vol.41. No.6. P.1561-1576.
[7] R.J. Schwanker, M. Eiswirth, P. Holler et. al. Kinetic oscillations in the catalytic CO oxidation on Pt (100): periodic perturbations. *J. Chem. Phys*. **1987**. Vol.87. No.1. P.742-749.
[8] M. Sheintuch, M. Luss. Reaction rate oscillations during propylene oxidation on platinum. *J. Catal*. **1981**. Vol.68. No.1. P.245-248.
[9] M. Sheintuch, M. Schmidt. Bifurcations to periodic and aperiodic solutions during ammonia oxidation on a Pt wire. *Ibid*. **1988**. Vol.92. No.12. P.3404-3411.

[10] V.I. Bykov, G.S. Yablonskii. Steady state and dynamic characteristics of two-center mechanisms of catalytic reactions. *React. Kinet. Catal. Lett*. **1981**. Vol.17. No.1-2. P.29-34.

[11] V.I. Bykov. On simple models of oscillating simple reactions. *Jour. Fiz. Chemistry.* **1985**. Vol.59. No.11. P.2712-2716.

[12] A.N. Ivanova. Critical phenomena in complex chemical systems: Thesis Phd of physical and mathematical sciences. *Chernogolovka: Institute of Chemical Physics.* **1984**. 274p. (russian)

[13] G.A. Chumakov, M.G. Slinko, V.D. Belyaev. Complex changes in the rate of the heterogeneous catalytic reaction. *Reports. Academy of Sciences of the USSR*. **1980**. Vol.253. No.3. P.653-658. (russian)

[14] G.A. Chumakov, M.G. Slinko. Kinetic turbulence (chaos) of the reaction rate of hydrogen-oxygen interaction. *Reports. Academy of Sciences of the USSR*. **1982**. Vol.266. No.5. P.1194-1198. (russian)

[15] M.G. Slinko, V.S. Beskov, F.Kh. Zharmakhanbetov. Oscillations in the reaction of ammonia oxidation on a platinum catalyst. *Reports. Academy of Sciences of the USSR*. **1988**. Vol.301. No.2. P.398-401. (russian)

[16] A. Shabunin, V. Astakhov, V. Demidov, A. Provata, F. Baras, G. Nicolis, V. Anishchenko. Modeling of chemical reactions by forced limit-cycle oscillator: synchronization phenomena and transition to chaos. *Chaos, Solitons and Fractals*. **2003**. Vol.15. P.395-495.

[17] V.I. Bykov, L.S. Trotsenko. Kinetic "chaos", induced by noise. *Jour. Physical Chemistry*. **2005**. Vol.79. No.5. P.792-796. (russian)

[18] J.G. Freire, J.A.C. Gallas. Stern-Brocot trees in the periodicity of mixed-mode oscillations. *Phys. Chem. Chem. Phys*. **2011**. Vol.13. P.12191-12198.

[19] I. Bodalea, V.A. Oancea. Chaos control for Willamowski-Rössler model of chemical reactions. *Chaos, Solitons and Fractals*. **2015**. Vol.78. P.1-9.

[20] N.I. Koltsov. Modeling of critical phenomena in the kinetics of heterogeneous catalytic reactions. *Butlerov Communications*. **2011**. Vol.24. No.4. P.10-16. ROI: jbc-02/11-24-4-10

[21] V.Kh. Fedotov, N.I. Koltsov. Invariant kinetic portraits of a linear two-stage reaction. *Butlerov Communications*. **2015**. Vol.42. No.6. P.129-131. DOI: 10.37952/ROI-jbc-01/15-42-6-129

[22] S.P. Kuznetsov. Dynamic chaos. *M oscow: Fizmatlit*. **2006**. 356p. (russian)