



# Statistical approach for theoretical description of catalytic hydrogen processes

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## Abstract

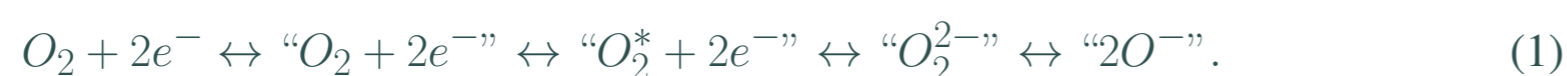
A statistical description for the processes of catalytic hydrogen oxidation is proposed taking into account the reaction-diffusion processes for magnetoactive ions and atoms adsorbed on the metal surface. The basic non-Markov transfer equations are obtained for the abbreviated description parameters of reaction-diffusion processes for magnetoactive ions and atoms adsorbed on the metal surface in the method of nonequilibrium statistical Zubarev operator. Weakly nonequilibrium reaction-diffusion processes are also considered.

## INTRODUCTION

Environmental problems, which have recently become more acute and are largely associated with the negative impact of carbon monoxide ( $CO$ ) on the one hand and significant interest in hydrogen energy on the other, pose the task of finding the latest efficient (nano-, sub-atomic) catalysts containing transition metals [1, 2] for  $CO$  or  $H$  oxidation. Experimental development of such catalysts requires significant financial costs, but the predictability of their effective operation is quite limited. The nature of surface phenomena in catalytic reactions is primarily due to the fact that the catalyst surface is magnetoactive in such reactions.

## REACTION-DIFFUSION PROCESSES FOR MAGNETOACTIVE ATOMS ADSORBED ON THE METAL SURFACE

The processes of dissociation and adsorption of  $O_2$  on  $Pt$  are considered as the following successive processes:



- At  $T \leq 45 K$  there is " $O_2$ " physical adsorption on the surface;
- in the temperature range of  $90 - 135 K$   $O_2$  molecule is converted into superoxide " $O_2^-$ ";
- in the range of  $135 - 150 K$  it is converted into peroxide " $O_2^{2-}$ ", and then at higher temperatures to oxygen ion vapors " $O^- + O^-$ ".

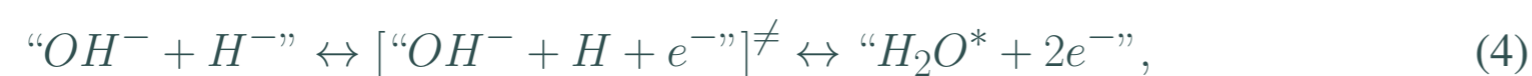
The process of hydrogen molecules adsorption is considered as formation of the bound state hydrogen atom-electron on the surface of platinum:



Then the oxidation process takes place first with formation of  $OH^-$  group and release of the electron



and the next stage – formation of a water molecule and release of two electrons:



Here symbol  $[...]^\ddagger$  denotes the transition state and symbol  $*$  denotes the adsorbed state.

Therefore, from the point of view of model description, there is a system of magnetic dipole particles that fill the volume above the metal surface and can be adsorbed on it, interacting with the electron subsystem of metal surface.

For generality, we consider a system with  $\bar{n}$  different sorts of magnetoactive particles (molecules, atoms, anions, electrons) with  $N_a$  number particles of sort  $a$  ( $a = 1... \bar{n}$ ). The Hamiltonian of the system is given as the sum of classical  $H_L$  and quantum  $\hat{H}_q(t)$  parts:

$$\hat{H}(t) = H_L + \hat{H}_q(t), \quad (5)$$

where

$$H_L = \sum_a \sum_{j=1}^{N_a} \frac{p_j^2}{2m_a} + \frac{1}{2} \sum_{ab} \sum_{j \neq l} \Phi_{ab}(r_{jl}) + V_{ad}$$

is the classical part of Hamiltonian, which describes the system of magnetoactive particles as a simple classical gas, the atoms of sort  $a$  of which can be adsorbed on the magnetoactive surface of metal with an adsorption potential  $V_{ad}$ .  $r_{jl}$  is the distance between  $j$  and  $l$  particles,  $\vec{p}_j$ ,  $m_a$  are the vector momentum and the mass of magnetoactive particle of sort  $a$ ,  $\Phi_{ab}(r_{jl})$  is the pair potential of classical interaction between magnetoactive particles of sort  $a$  and  $b$ , which can be modeled by the Lennard-Jones potential. Values  $a, b, \dots$  in the sums are the indexes of the sort.

The quantum part of the Hamiltonian  $\hat{H}_q(t)$

$$\hat{H}_q(t) = \hat{H}_e(t) + \hat{H}_S(t)$$

contains the contribution of electron subsystem:

$$\hat{H}_e(t) = \sum_{j=1}^{N_e} \frac{(\vec{p}_j - \frac{e}{c} \vec{A}(\vec{r}; t))^2}{2m_e} + V_{ee},$$

with potential of electron-electron interaction  $V_{ee}$  ( $e$  is the electron charge,  $c$  is the speed of light,  $\vec{A}(\vec{r}; t)$  is the vector potential of electromagnetic field generated by electrons and magnetoactive particles in the system) and contribution  $\hat{H}_S(t)$  describing a system of magnetoactive particles with spins  $\vec{S}_j$  in the inhomogeneous magnetic field  $\vec{B}^l(\vec{r}; t)$  and in the field created by  $N_m$  magnetoactive particles of the surface with coordinates  $\vec{R}_f$  and spins.

In order to describe the diffusional and magnetostrictive processes on the metal surface, we choose the average values of particle number density (molecules, atoms, anions, electrons)  $\langle \hat{n}_a(\vec{r}) \rangle^t$  and magnetization  $\langle \vec{M}_a(\vec{r}) \rangle^t$  as parameters (observed values) of the abbreviated description. To study the cluster coverage and correlations, we also include the non-equilibrium structural functions "density-density"  $\langle \hat{g}_{ab}(\vec{r}, \vec{r}') \rangle^t$  and "spin-spin" tensor  $\langle \hat{G}_{ab}(\vec{r}, \vec{r}') \rangle^t$  in the set of observed values, where  $\langle \dots \rangle^t = Sp \dots \rho(t)$ ,  $\rho(t)$  is the nonequilibrium statistical operator of a system.

In order to obtain the transfer equations for parameters of the abbreviated description  $\langle \hat{n}_a(\vec{r}) \rangle^t$ ,  $\langle \vec{M}_a(\vec{r}) \rangle^t$ ,  $\langle \hat{g}_{ab}(\vec{r}, \vec{r}') \rangle^t$ ,  $\langle \hat{G}_{ab}(\vec{r}, \vec{r}') \rangle^t$ , it is necessary to construct the corresponding nonequilibrium statistical operator  $\rho(t)$ , which satisfies the Liouville equation. To obtain  $\rho(t)$ , we use the method of

nonequilibrium statistical Zubarev operator, taking into account the design procedure

$$\begin{aligned} \rho(t) = & \rho_q(t) - \sum_a \int d\vec{r}' \int_{-\infty}^t e^{\varepsilon(t-t')\hat{T}(t,t')} \int_0^1 d\tau (\rho_q(t'))^\tau I_n^a(\vec{r}'; t') (\rho_q(t'))^{1-\tau} \beta \mu_a(\vec{r}', t') dt' \\ & - \sum_a \int d\vec{r}' \int_{-\infty}^t e^{\varepsilon(t-t')\hat{T}(t,t')} \int_0^1 d\tau (\rho_q(t'))^\tau I_M^a(\vec{r}'; t') (\rho_q(t'))^{1-\tau} \beta \vec{\mu}_a(\vec{r}', t') dt' \\ & - \sum_{ab} \int d\vec{r} \int d\vec{r}' \int_{-\infty}^t e^{\varepsilon(t-t')\hat{T}(t,t')} \int_0^1 d\tau (\rho_q(t'))^\tau I_G^{ab}(\vec{r}, \vec{r}'; t') (\rho_q(t'))^{1-\tau} \beta \vec{\mu}_{ba}(\vec{r}, \vec{r}', t') dt' \\ & - \sum_{ab} \int d\vec{r} \int d\vec{r}' \int_{-\infty}^t e^{\varepsilon(t-t')\hat{T}(t,t')} \int_0^1 d\tau (\rho_q(t'))^\tau I_g^{ab}(\vec{r}, \vec{r}'; t') (\rho_q(t'))^{1-\tau} \beta \chi_{ba}(\vec{r}, \vec{r}', t') dt', \end{aligned} \quad (6)$$

where  $\rho_q(t)$  is the relevant statistical operator constructed from the extremum of information entropy of the system at fixed parameters of the abbreviated description;  $\hat{T}(t, t')$  is the evolution operator based on the design;  $I_n^a(\vec{r}'; t')$ ,  $I_M^a(\vec{r}'; t')$ ,  $I_G^{ab}(\vec{r}, \vec{r}'; t')$ ,  $I_g^{ab}(\vec{r}, \vec{r}'; t')$  are the microscopic generalized fluxes describing diffusion, magneto-diffusion and reaction processes in the system and on which there are built the generalized transfer coefficients and functions of reactions between components that describe, in particular, oxidation stages (1)–(4).

Using expression (6) for the nonequilibrium statistical operator  $\rho(t)$ , we obtain the transfer equation to describe the reaction-diffusion, magnetostrictive processes of magnetoactive particles that can be adsorbed on magnetoactive surface of the metal [3].

## WEAKLY NONEQUILIBRIUM CATALYTIC PROCESSES

We consider the reaction-diffusion processes characterized by small fluctuations of nonequilibrium thermodynamic parameters  $\vec{F}_\nu(\vec{r}; t)$  and  $\vec{F}_\eta(\vec{r}, \vec{r}'; t)$

$$\vec{F}_\nu(\vec{r}; t) = (\beta \mu_a(\vec{r}; t), \beta \vec{\mu}_a(\vec{r}; t))^\top,$$

$$\vec{F}_\eta(\vec{r}, \vec{r}'; t) = (\beta \vec{\mu}_{ab}(\vec{r}, \vec{r}'; t), \beta \chi_{ab}(\vec{r}, \vec{r}'; t))^\top.$$

from their locally equilibrium values  $\vec{F}_\nu(\vec{r})$  and  $\vec{F}_\eta(\vec{r}, \vec{r}')$ . In this case, we decompose the relevant statistical operator  $\rho_q(t)$  by fluctuations  $\delta \vec{F}_\nu(\vec{r}; t) = \vec{F}_\nu(\vec{r}; t) - \vec{F}_\nu(\vec{r})$  and  $\delta \vec{F}_\eta(\vec{r}, \vec{r}'; t) = \vec{F}_\eta(\vec{r}, \vec{r}'; t) - \vec{F}_\eta(\vec{r}, \vec{r}')$  into a series and limit ourselves to a linear approximation by these fluctuations.

In this approximation, the fluctuations of parameters in the abbreviated description of nonequilibrium processes have the following structure:  $\delta \hat{n}_a(\vec{r}) = \hat{n}_a(\vec{r}) - \langle \hat{n}_a(\vec{r}) \rangle_0$ ,  $\delta \vec{M}_a(\vec{r}) = \vec{M}_a(\vec{r}) - \langle \vec{M}_a(\vec{r}) \rangle_0$ ,  $\delta \hat{g}_{ab}(\vec{r}, \vec{r}') = \hat{g}_{ab}(\vec{r}, \vec{r}') - \langle \hat{g}_{ab}(\vec{r}, \vec{r}') \rangle_0$ ,  $\delta \hat{G}_{ab}(\vec{r}, \vec{r}') = \hat{G}_{ab}(\vec{r}, \vec{r}') - \langle \hat{G}_{ab}(\vec{r}, \vec{r}') \rangle_0$ ,  $\langle \langle \dots \rangle \rangle_0 = Sp[\langle \dots \rangle \rho_0]$  is the averaging with the equilibrium statistical operator  $\rho_0$  in which  $\vec{M}_a(\vec{r})$ ,  $\hat{g}_{ab}(\vec{r}, \vec{r}')$ ,  $\hat{G}_{ab}(\vec{r}, \vec{r}')$  are the new description parameters

As a result, for the nonequilibrium statistical operator we obtain:

$$\begin{aligned} \rho(t) = & \rho_q^0(t) \\ & - \sum_{ab} \int d\vec{r}' \int d\vec{r}'' \int_{-\infty}^t e^{\varepsilon(t-t')\hat{T}_0(t,t')} \int_0^1 d\tau (\rho_0^\tau I_n^a(\vec{r}'; t') \rho_0^{1-\tau}) [\hat{\Phi}_{nn}^{-1}(\vec{r}', \vec{r}'')]_{ab} \langle \delta \hat{n}_b(\vec{r}'') \rangle^t dt' \\ & - \sum_{ab} \int d\vec{r}' \int d\vec{r}'' \int_{-\infty}^t e^{\varepsilon(t-t')\hat{T}_0(t,t')} \int_0^1 d\tau (\rho_0^\tau I_M^a(\vec{r}'; t') \rho_0^{1-\tau}) [\hat{\Phi}_{MM}^{-1}(\vec{r}', \vec{r}'')]_{ab} \langle \delta \vec{M}_b(\vec{r}'') \rangle^t dt' \\ & - \sum_{abcd} \int d\vec{r}' \int d\vec{r}'' \int d\vec{r}''' \int_{-\infty}^t e^{\varepsilon(t-t')\hat{T}_0(t,t')} \int_0^1 d\tau (\rho_0^\tau I_G^{ab}(\vec{r}, \vec{r}'; t') \rho_0^{1-\tau}) \\ & \quad [\hat{\Phi}_{GG}^{-1}(\vec{r}, \vec{r}', \vec{r}'', \vec{r}''')]_{abcd} \langle \delta \hat{G}_{cd}(\vec{r}'', \vec{r}''') \rangle^t dt' \\ & - \sum_{abcd} \int d\vec{r}' \int d\vec{r}'' \int d\vec{r}''' \int_{-\infty}^t e^{\varepsilon(t-t')\hat{T}_0(t,t')} \int_0^1 d\tau (\rho_0^\tau I_g^{ab}(\vec{r}, \vec{r}'; t') \rho_0^{1-\tau}) \\ & \quad [\hat{\Phi}_{gg}^{-1}(\vec{r}, \vec{r}', \vec{r}'', \vec{r}''')]_{abcd} \langle \delta \hat{g}_{cd}(\vec{r}'', \vec{r}''') \rangle^t dt', \end{aligned} \quad (7)$$

where  $\rho_q^0(t)$  is the relevant statistical operator obtained in this approximation;  $\hat{T}_0(t, t')$  is the evolution operator taking into account the design procedure in the linear approximation by fluctuations.

By structure, the nonequilibrium statistical operator (7) is a linear functional by fluctuations of the abbreviated description parameters  $\langle \delta \hat{n}_b(\vec{r}'') \rangle^t$ ,  $\langle \delta \vec{M}_b(\vec{r}'') \rangle^t$ ,  $\langle \delta \hat{G}_{cd}(\vec{r}'', \vec{r}''') \rangle^t$ ,  $\langle \delta \hat{g}_{cd}(\vec{r}'', \vec{r}''') \rangle^t$ . With the help of it, we obtain a closed system of non-Markov in time integro-differential equations for fluctuations of the abbreviated description parameters [3].

## CONCLUSIONS

In our paper [3] a statistical description for the processes of catalytic hydrogen oxidation is proposed taking into account the reaction-diffusion processes for magnetoactive ions and atoms adsorbed on the metal surface. The basic non-Markov transfer equations are obtained for the abbreviated description parameters of reaction-diffusion processes for magnetoactive ions and atoms adsorbed on the metal surface in the method of nonequilibrium statistical Zubarev operator. Weakly nonequilibrium reaction-diffusion processes are also considered

## References

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