



A MEANS FOR INSIGHT INTO THE NONEQUILIBRIUM ELECTRONIC PROCESSES DURING HETEROGENEOUS CHEMICAL REACTIONS

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Generation of a longitudinal electromotive force (e.m.f.) is observed during the reaction of recombination of hydrogen atoms on selenium planar p-n junction with the thin “top” n-layer (chemo e.m.f. or chemo-valve effect). The effect is caused by production of electron-hole pairs due to exoergicity of the surface chemical reaction and its magnitude is a measure of breaking the equilibrium in the electronic system of the catalyst under the reaction conditions. The chemo e.m.f. and chemicurrent is a new means to observe and examine the nonequilibrium electronic processes during heterogeneous chemical reactions.

INTRODUCTION

The role of the excited states in heterogeneous chemical reactions is in focus for a few decades (see *e.g.*¹⁻³ and references therein). It is owing to the fact that heterogeneous chemical reactions on the solid catalysts are accompanied by a plenty of energy released in the exoergic chemical events, the energy being deposited on the surface atoms or/and on the reaction products. It leads to appearance of excited states of various types on the surface of the catalysts occupying both the vibrational and electronic degrees of freedom of the particles (or groups of atoms) involved.

Relaxation of such excitations is often difficult, *i.e.* the excitations are long-living. As to vibrational excitations it is due to high frequency of oscillations of light atoms (H, C, O, N). As a result, the vibrational quanta $\hbar\omega$ of the new nascent bonds are much greater comparing to even the most energetic vibrations $\hbar\omega_D$ of the catalyst atoms (ω_D – is the Debye frequency of the crystal). So relaxation of the $\hbar\omega$ -oscillations requires participation of a low probability many-quantum process. It is the reason why the life-time of the

surface “chemical vibrations” $\hbar\omega$ sufficiently exceeds the values of $10^{-13} \div 10^{-14}$ s (the typical magnitude of the period of the solid state vibrations) reaching $10^{-9} \div 10^{-10}$ s or more.

As regards electronic excitations, they are long-living by their intrinsic nature in comparison with vibrational excitations: the allowed electronic transitions are characterized by a life-time of the order of 10^{-8} s, whereas the forbidden transitions may live 10^{-3} s or more.

The above reasons lead to the conclusion that the catalytic reactions usually proceed under nonequilibrium conditions. Therefore, the effective “temperature” of the reaction site may exceed by orders of magnitude the general temperature of the catalyst. The situation is especially dramatic for processes including participation of free atoms or radicals particularly of light ones with high exoenergetic potential. For instance, in heterogeneous recombination of hydrogen atoms the energy liberated amounts to a few electron-volts (or some tens of kkal/ mole) per elementary chemical event giving rise to formation of vibrationally excited H_2^v molecules on the surface. Because of the large difference between the vibrational quantum of the

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molecule H_2 ($\sim 0,545\text{eV}$) and phonon energy of the catalyst (usually some hundredth parts of eV), an electronic pathway for energy accommodation is possible in addition to the low-probability many phonon mechanism.

Thus, the reaction of recombination of H-atoms – the lightest atoms in the periodic table – is the most promising candidate to observe nonequilibrium in the chemical reactions. Since there exists coupling between vibrational and electronic degrees of freedom due to nonadiabaticity in nuclei motion one may expect the simultaneous observation of both vibrational and electronic excitations in heterogeneous catalysis.

The excited surface sites and adspecies gain new chemical properties and can provide new paths for a reaction. The role of electronic excitations may be especially important owing to their long lifetimes compared to vibrational excitations. Since any chemical reaction is in its essence a rearrangement of an electronic system of the reagents the concept under consideration gives a new approach to understanding the role of the “electronic factor” in heterogeneous catalysis. In addition the nonequilibrium effects throw a new light on the self-catalytic processes.

A number of methods was developed to observe the electronic excitations in the catalytic reactions including heterogeneous chemiluminescence (HCL) of the surface of the catalyst (see⁴ and references therein), external⁴ and internal⁵ electron emission during a reaction, nonequilibrium electron flows measurements by the “catalytic diodes”,⁶⁻⁷ nonequilibrium chemically induced electro-conductivity of the catalyst⁸ and so on.

Here we report on a new method for insight into the nonequilibrium processes during heterogeneous chemical reactions based on the observation of electron-hole pairs generation in the non-metal catalyst due to exoergicity of the elementary chemical events. The reaction of recombination of hydrogen atoms on selenium is studied.

The idea of the method includes an expectation that during recombination of hydrogen atoms on selenium surface the nonadiabatic electronic transitions would be induced due to chemical energy released, *i.e.* electrons would nonthermally jump from the valence band to the conduction band of selenium (the temperature of the crystal being constant) resulting in appearance of nonequilibrium electron-hole (e-h) pairs in the sample. The e-h pairs would migrate from the surface (the place of their birth) into the bulk

reaching the p-n junction. The electric field of the junction would separate the electron and hole components of the pair giving rise to the electromotive force (e.m.f.) in the longitudinal direction relative to the incident atomic flux, *i.e.* in the normal direction to the surface plane. The effect under consideration can be named chemo-valve effect or chemo e.m.f. by analogy with the photo-valve effect or photo e.m.f. widely used in solar photocells and solar photobatteries. The prefix chemo- here indicates the nonequilibrium nature of the effect similar to prefix photo- in the names of corresponding effects under light illumination.

EXPERIMENTAL

The sample examined was a planar p-n junction of selenium with two types of majority carriers – holes and electrons respectively. The surface area of the sample exposed to hydrogen atoms flux was $\sim 25\text{mm}^2$ or $2,5 \cdot 10^{-5}\text{m}^2$. The thickness of the top Te-doped n-layer was approximately $2\ \mu\text{m}$, and the “bottom” p-layer around $70\ \mu\text{m}$. The concentration of the major carriers for both layers was in the range of $10^{21} \div 10^{22}\text{m}^{-3}$.

The cell for electric measurements was placed in a vacuum chamber made of nonmagnetic stainless steel (the residual pressure in the vacuum setup was $\sim 10^{-5}\ \text{Pa}$). The cell contained a heating unit (microheater of a resistive type with the tungsten filament), the sample holder supplied with the pressed against the sample electric contacts and the Teflon mask to prevent the unwanted recombination of H-atoms on the metallic parts of the cell. The sample was mounted on the carefully polished body of the microheater, the working surface of which was fabricated from the sheet copper with the indium coating. The second contact was in the form of an Ag-plate, pressed to the sample by the thick Teflon sheet. The sample temperature was controlled by a thermocouple (platinum-platinum/rhodium) and a digital thermometer.

The produced chemo e.m.f. (chemicurrent) signal was registered by the measurement circuit composed of the electrometric direct current amplifier U5-11, active filter supplied with the built-in diode detector and an analogue-digital converter (ADC) supplied with the pre-amplifier. The signal from the ADC was displayed on the monitor of a PC and can be then processed and analysed.

The hydrogen atoms were produced using HF-electric discharge (40 MHz) in molecular hydrogen pumped through the Wood's tube. The atomic flux incident on the sample surface was determined by the method of precision isothermal wire microcalorimetry⁹. The measurements were performed with the fluxes of atomic hydrogen of $0,5 \cdot 10^{21} \div 1,5 \cdot 10^{22}\text{m}^{-2}\text{s}^{-1}$, corresponding to the density of H-atoms in the range of $0,8 \cdot 10^{18}\text{m}^{-3} \div 2,3 \cdot 10^{19}\text{m}^{-3}$.

For quantitative interpretation of our experimental results we need in some cases to know the product $\gamma\beta$; where γ – is the coefficient of recombination of H-atoms on Se (the probability of recombination of H-atoms into H_2 -molecule per one collision of H-atom with the surface) and β – the coefficient of

accommodation, *i.e.* the fraction of energy transferred to the surface (in the form of heat) of the total energy released in the reaction. The $\gamma\beta$ -value was determined by microcalorimetric method in which the thermoelectric Peltier module was used (composed of 50 semiconductor thermocouples) to measure the heat power produced by the reaction on the selenium surface.

The thin tungsten film ($\sim 50 \mu\text{m}$) served as a resistive microheater. The Se-layer was deposited on the microheater surface by vacuum thermodeposition using auxiliary vacuum setup (VUP-4). The $\gamma\beta$ -value was calculated as follows: $\gamma\beta = 2\Delta w / j_H S D_g$, where Δw – the chemical (heat) power delivered to the Se-sample ($\text{J} \cdot \text{s}^{-1}$), j_H – the density of the atomic flux on the surface ($\text{m}^{-2}\text{s}^{-1}$), S – the area of the surface, D_g – the heat of dissociation of the H_2 -molecule in the gas phase equal to $7,2 \cdot 10^{-19}\text{J}$ (4,48 eV).

RESULTS AND DISCUSSION

Already the first experiments allowed us to discover the chemo-valve effect on selenium p-n junction structure the surface of which was exposed to atomic hydrogen. Fig. 1 illustrates the kinetics of the chemicurrent through p-n junction while the atoms were “switched on” and “switched off” in the space above the sample surface. The current was rising up during $\sim 30\text{s}$ from its noise level ($\sim 0,015 \mu\text{A}$) to the stationary value $\sim 0,06 \mu\text{A}$.

The signal-to-noise ratio was approximately 4:1, *i.e.* the effect was readily measured. It is evident that the rising branch of the kinetics reflects the process of adsorption of H-atoms on the Se-surface up to steady-state coverage (under the reaction conditions). The chemicurrent reaches its stationary magnitude simultaneously with the achievement of stationary coverage of the surface with hydrogen atoms. When the source of atoms is switched off (switching off the HF discharge) the chemocurrent decays during $\sim 25\text{s}$ (in Fig. 1 the moments of switching on and switching off are indicated by arrows). The photocurrent for the same sample under comparable with chemicurrent level of excitation decays approximately during 1s. The slower decay of chemicurrent is probably due to both gradual decay of H-atoms concentration in the gas phase after stopping the H-atoms generation and slow diffusion of adsorbed atoms along the surface (mechanism of Langmuir-Hinshelwood of atomic recombination). A certain contribution to the slow decay of chemicurrent may bring in catching electrons (holes) by traps on the surface due to surface states and crystal structure defects. It may explain the increase in decay rate with the temperature increase.

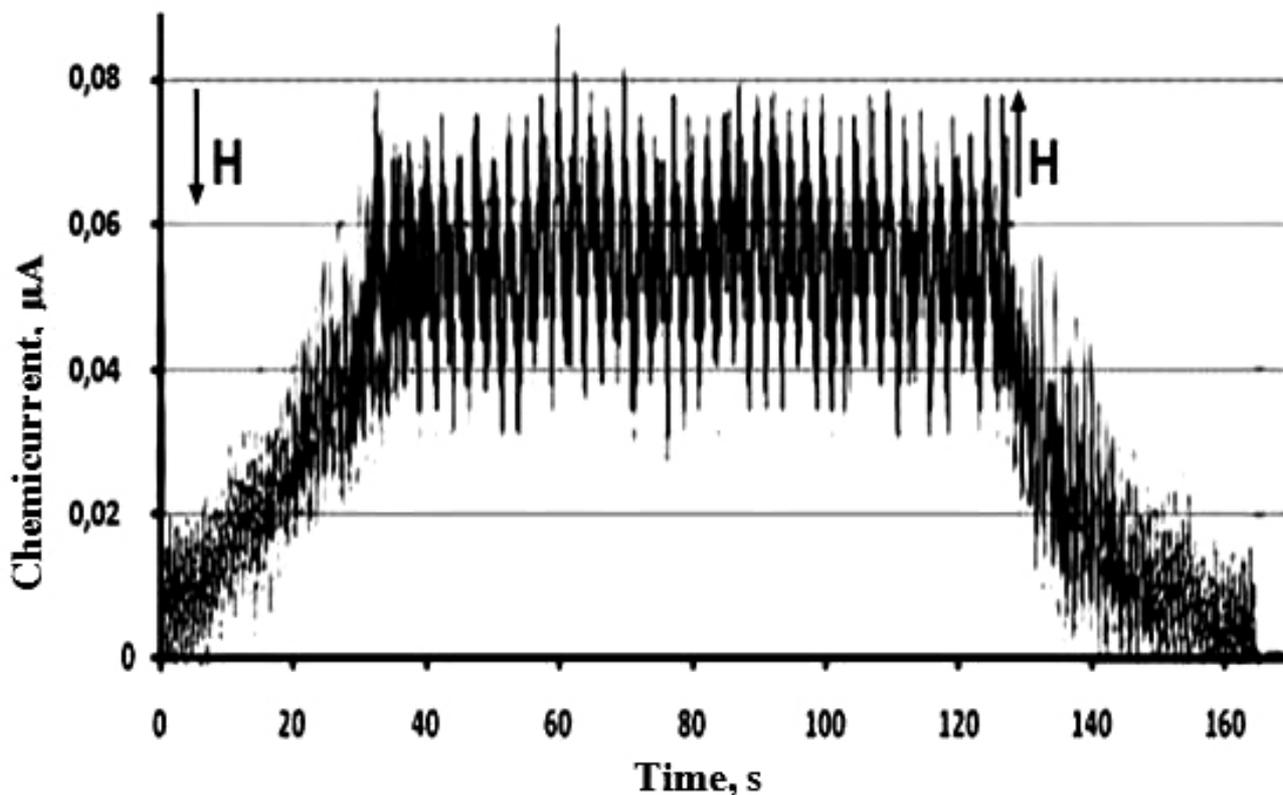


Fig. 1 – Kinetics of the chemicurrent through p-n junction exposed to hydrogen atoms ($j=1.1 \times 10^{22} \text{ m}^{-2}\text{s}^{-1}$; $T=310 \text{ K}$).

Fig. 2 is a plot of the dependence of chemicurrent I on the sample temperature for various densities of atomic fluxes (or various concentrations of atomic hydrogen in the gas phase). The graph can be linearized as a dependence of $\ln I$ vs $1/T$ in the temperature range 300-355K, *i.e.* exponential growth of chemocurrent with temperature takes place. The activation energy of the current increase with the temperature is the same at various j and amounts to ~ 10 kcal/mole (0.43 eV). The most probable cause for this ΔE is the thermal activation of the reaction $2R+L \rightarrow R+RL \rightarrow R_2+L$ (R-atom in the gas phase, L-symbol of the crystal lattice, RL-adatom). The abstraction stage $R+RL \rightarrow R_2+L$ is usually the activation process. One may pay attention that at elevated temperatures (above 355K) the chemicurrent decreases with increasing T . At these temperatures, as we found, there is chemical instability of the selenium surface in the atomic hydrogen atmosphere: gas etching of the surface occurs. It is viewed that the surface after the atomic exposure looks rough. The etching process is accompanied by a dim lighting in the gas phase above the surface probably due to producing electronically excited molecules of

some reaction products that are thrown out of the surface.

In Fig. 3 the dependence of the chemicurrent on the H-atoms concentration in the gas phase is shown. The experimental dots is well lying on the straight line. The line being extrapolated passes through the zero point of coordinates confirming the high precision of measurements. The linear fitting is satisfactory at all temperatures below 355 K if the sample was "fresh", *i.e.* has not been working in atomic hydrogen atmosphere for a long time. All the plots I versus j passed through the zero point of coordinates since no chemicurrent flowed in the absence of atoms in the gas phase.

Thus, the experimental data presented, namely i) appearance of the electrical current through the p-n junction when the heterogeneous chemical reaction begins on its planar surface (n-layer); ii) inertial characteristics of the current which are connected with the adsorption processes; iii) the dependence of the current on the atomic flux value and on the sample temperature, all of them are the solid evidences of the e-h pairs generation in selenium in the course of the surface chemical reaction. As a consequence chemo-valve effect (chemo e.m.f. and chemicurrent) is observed on the p-n junction fabricated of selenium.

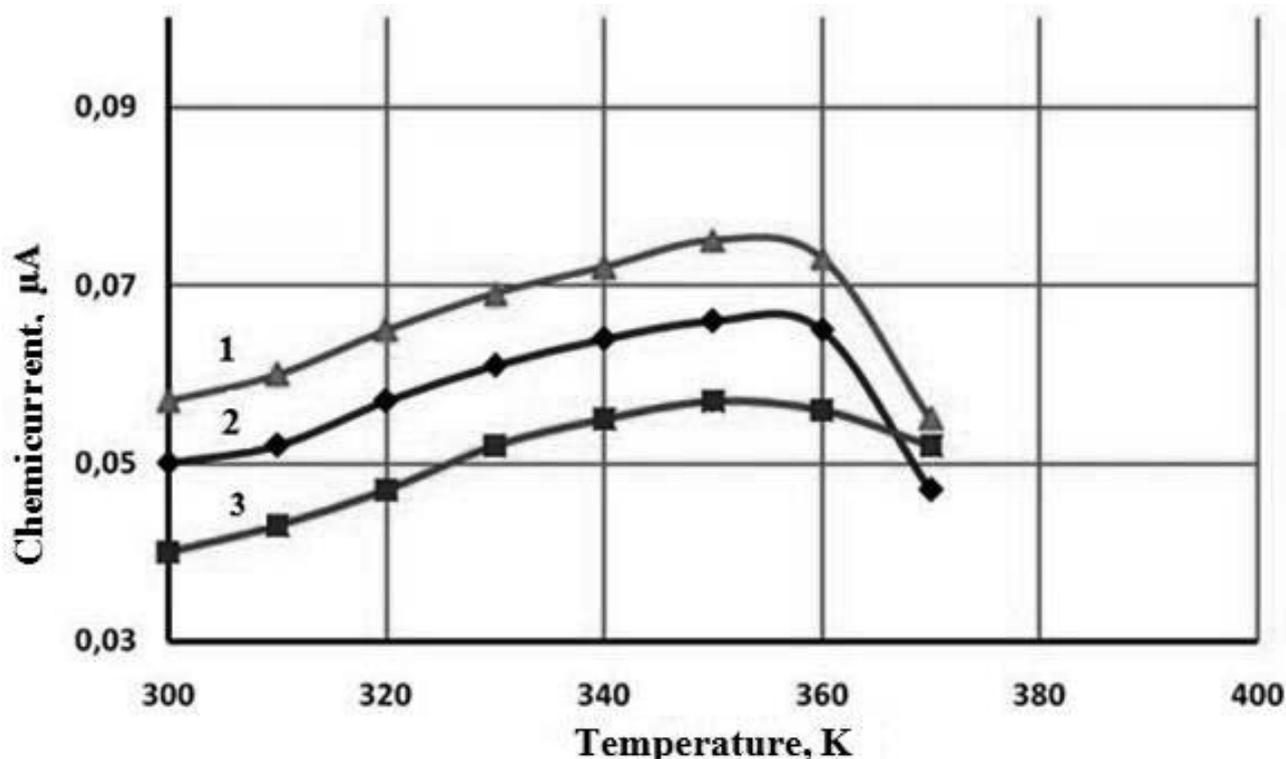


Fig. 2 – Influence of temperature of the sample on the chemicurrent magnitude at different hydrogen fluxes on the surface (1 – $1.4 \times 10^{22} \text{ m}^{-2} \text{ s}^{-1}$; 2 – $1.1 \times 10^{22} \text{ m}^{-2} \text{ s}^{-1}$; 3 – $0.9 \times 10^{22} \text{ m}^{-2} \text{ s}^{-1}$).

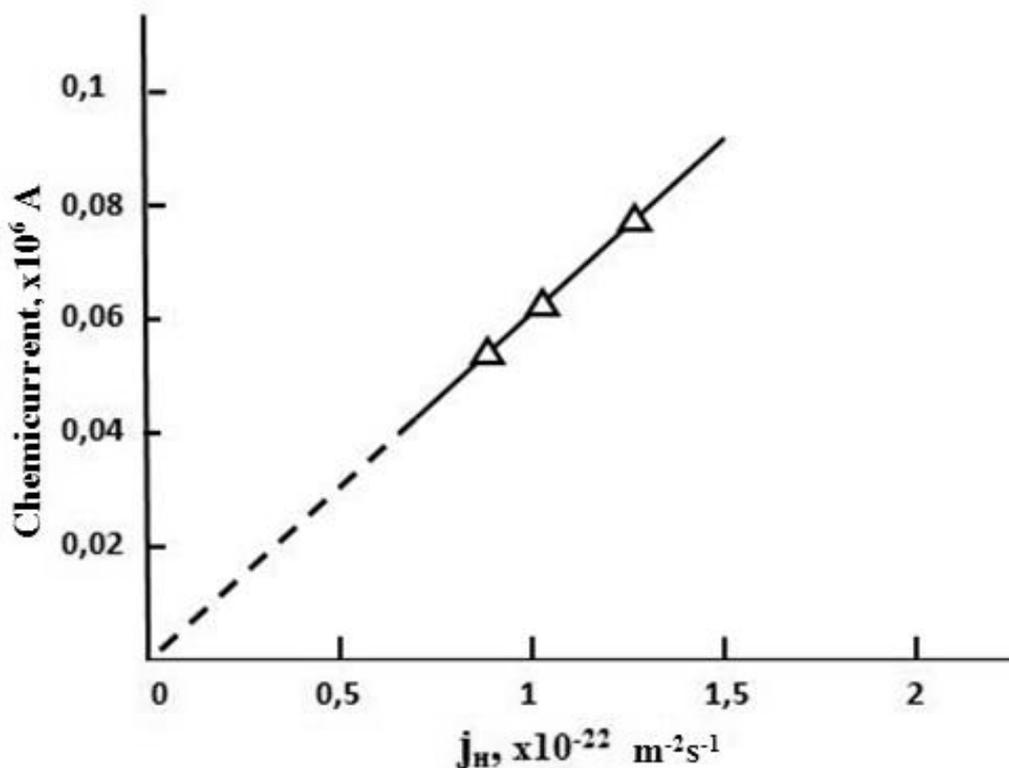


Fig. 3 – Dependence of the chemicurrent on the atomic flux on the selenium p-n junction structure ($T=350 \text{ K}$).

It is interesting to evaluate on the basis of the data presented the probability η_e for generation of the e-h pair per elementary chemical act of recombination of hydrogen atoms on selenium surface (the net-effect manifested itself in the chemicurrent observed). The short circuit chemicurrent is $I = \eta_e \gamma j_e S$ (e – the elementary electrical charge). In one of our experiments we have: $I = 0,06 \mu\text{A}$, $j = 1 \cdot 10^{22} \text{ m}^{-2} \text{ s}^{-1}$ ($S = 2,5 \cdot 10^{-5} \text{ m}^2$, $e = 1,6 \cdot 10^{-19} \text{ C}$). We found calorimetrically that the product $\gamma\beta$ is approximately $1 \cdot 10^{-3}$ (320K). Assuming $\beta \sim 1$ (the typical value for the similar semiconductors) we obtain $\eta_e = 1,5 \cdot 10^{-3}$. By varying the surface treatments prior to measurements we could raise this value up to $2 \cdot 10^{-2}$. For η_e enhancement the prolonged exposure of the selenium surface to atomic hydrogen flux is favorable. The η_e magnitude is increased as the sample is “aged”. The exact origin of this effect is not yet clear. The sample ageing leads eventually to the chemicurrent growth (probably as a consequence of the surface chemical etching accompanied by lowering the sample thickness and improvement of conditions for the nonequilibrium minority carriers collection). The

most great η_e values correspond to the point of the almost entire disappearance of the upper selenium layer. The explanation presented is regarded as the most plausible one, although other interpretations can be advanced.

The values of η_e obtained are large enough, indicating that the sufficient portion of the energy of the reaction is accommodated in a nonequilibrium way by the catalyst through the electronic degrees of freedom of the crystal. The means under consideration based on chemovoltaic effect (chemicurrent) is efficient for studying the channels of disposal of energy in heterogeneous chemical reactions. It may also be used as a method for direct conversion of chemical energy into electricity¹⁰ and as a base for fabrication of sensors to detect hydrogen atoms in a gas phase. Another promising system for this purpose is H-Ge.¹¹

CONCLUSION

We obtained an experimental evidence that in the course of heterogeneous chemical reaction – recombination of atomic hydrogen on selenium – the catalyst passed to the electronically excited state. This state is a collective excitation of the

catalyst in the form of electron-hole pairs (e-h pairs) produced in selenium in a nonequilibrium (nonthermal) way due to exoergicity of the reaction. The e-h pairs were registered by means of chemo e.m.f. (chemicurrent) generated in the planar p-n junction structure on the one side of which the reaction was performed.

The electron-hole pair in selenium is in fact an excess of the negative electric charge on one of the Se-atoms and deficiency of such a charge on the other atom (or excess of positive charge). This excited state of the semiconductor can freely migrate into the lattice and along the surface interacting in the latter case with adspecies. The nature of the interaction may be both "chemical" (changing the electronic state of the reactive "cluster" and, as a consequence, changing the reactivity) and "physical" (e.g. annihilation of e-h pair can provide energy to overcome the energetic barrier of a reaction). The traps (surface defects) may catch the e-h pairs components leading to their very long life-times in the nonequilibrium state. The trap with the trapped electron (or hole) is naturally a new surface site that can take part in the catalytic event on the surface. Its catalytic activity may be grounded upon the same "chemical" and "physical" reasons as in the case of free e-h pairs. It is of importance that the reaction itself can produce the catalytic centers bringing the self-catalytic regime of the reaction.

The probability η_e of generation of e-h pair per elementary chemical event in the system under consideration (in the range of $1, 5 \cdot 10^{-3}$ - $2 \cdot 10^{-2}$) is large enough in order to one should take into account the nonequilibrium state of the catalyst in the course of the reaction.

In fact the degree of the equilibrium breaking in the reaction is on much more level since in addition to electronic excitations vibrational excitations accompany the reaction, the latter being produced with high probability. One may conclude that nonequilibrium is the general feature of any catalytic reaction that may be neglected only under special conditions (e.g. for metal catalyst where electronic and vibrational excitations are extremely short-living). The chemo e.m.f. (chemicurrent) gives a new means for insight into non-equilibrium electronic processes during heterogeneous chemical reactions and catalysis.

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