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A new idea of the influence of solid materials on kinetics of chemical reactions

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The mechanism of heterogeneous catalysis is still under discussion. There is no clear theory which explains the mechanism of influence of materials on the rate of chemical reactions. All existing theories assume that specific materials, catalysts, decrease activation energy E_a. We hypothesize that for standard and catalyzed heterogeneous reactions the same E_a (real activation energy) is needed to trigger reaction processes. We propose that the difference between E_a and apparent activation energy (E_{app}) can be presented as catalytic reaction activation energy (E_c). This hypothesis is based on the so-called α_i model considering tribochemistry, work function, thermionic emission, and the negative ion–radical action mechanism. The proposed model assumes that mechanical work done on a solid material is accumulated in this material and then emitted as electrons and/or photons to the space in which the reaction takes place. The developed model includes a specific angle γ at which the reaction can be initiated, when the stream of energy e_γ equals some 3–5 eV. Energy emitted by the surface as pulses of 3–5 eV can reach the value of E_a and trigger a heterogeneous catalytic process. The catalyst emits pulses of a high density energy flux and at the angle γ the value of emitted energy is equal to the real activation energy E_a.

Key words: *tribology; heterogeneous catalysis; activation energy*

1. The model

The accepted definition of a catalyst [1] is that it is a substance that increases the rate at which a chemical system approaches equilibrium, without being consumed in the process; catalysis is the phenomenon of a catalyst in action while the catalyst lowers the activation energy. The transition state along a reaction path is the point of maximum free energy, where bond-making and bond-breaking are balanced. Heterogeneous catalysis accelerates the movement of atoms on the passage through the tran-

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sition state; it provides the link between reactants and products on a reaction pathway which involves simultaneous motion of several to very many atoms [2]. It has been emphasized that predictability of the outcome of catalytic reactions depends critically on the understanding of their molecular mechanisms. The mechanism of protective layer formation by lubricants in space near solid materials during a tribological process was recently analyzed by using the so called α_i method [3]. The principle of the α_i method (model) was presented in detail by Kulczycki [4]. The model can be applied to tribological systems in which the mechanical work done can be treated as input and dissipated energy – predominantly heat – as output. The functional input–output relation may also be related to tribochemical reactions which are known to proceed much faster than thermochemical ones. On the other hand, one may compare tribochemical reactions with heterogeneous catalytic reactions [5].

The kinetics of tribochemical reactions depends on conditions of the tribological process, and as a result, it is necessary to find more than one function of the mechanism of a tribochemical reaction. For example, one function can be related to the mechanics of a tribological process, the other one to its chemical reactions. It was assumed that the relationship between these functions makes it possible to analyze the mechanism of a tribological process on a "basic level". Two functions have been taken into account: $f(y)$ and $\phi(y)$. It was assumed that in the both functions y is the only state variable. For transition from a state $y = a$ to a state $y = b$, the following is considered

$$\alpha_i = \frac{\dfrac{f(b)-f(a)}{\phi(b)-\phi(a)}}{\dfrac{f'(b)}{\phi'(b)}} \tag{1}$$

In the above equation, f' and ϕ' are load derivatives of the corresponding functions, and the value of a (describing the initial state) should be constant.

One of the possibilities is to describe the tribological process using thermodynamic relationships. Thus, $f(y)$ can be work L done on a tribological system during the test, up to a critical stage of the tribological system (seizure, weld) and $\phi(y)$ can be internal energy change Δu. Then Eq. (1) can be written as follows:

$$\alpha_i = \frac{L - L_0}{\Delta u - \Delta u_0}\frac{d\Delta u}{dL}, \qquad L = \mu P v t \tag{2}$$

where μ is the friction coefficient, v – speed, t – time, P – a critical value of the applied load (test result: seizure load, weld load) but it is difficult to define Δu. Equation (2) can be rewritten as

$$a_i = \left(L - L_0\right)C, \quad C = \frac{\frac{d\Delta u}{dL}}{\Delta u - \Delta u_0} \tag{3}$$

C is a function of P and for a number of different lubricating additives/reagents (obtained several different values of the critical applied load) its value is constant. Concluding, C should be a harmonic function of P, described by the following equation:

$$C = B\exp\left(\frac{k_1}{P}\right)\cos\left(k_2 P + k_3\right) \tag{4a}$$

or

$$C = Bk_4 P^2 \cos\left(\frac{k_5}{P}\right) \tag{4b}$$

where: k_1, k_2, k_3, k_4, k_5 are constant parameters, B is a function of energy of the dimension [energy]$^{-1}$. The exponential part of the above equation can be connected with the kinetics of chemical/tribochemical reactions by the Arrhenius equation, relating the reaction rate constant k with temperature

$$k = A\exp\left(-\frac{E_a}{RT}\right) \tag{5}$$

where E_a is the activation energy of a given chemical/tribochemical reaction and the average temperature T for the tribological system may be combined with the load P applied in the tribological process and properties of solid materials using the Rowe dependence [6]

$$T = T_b + \mu P^{0.5} D \tag{6}$$

Hence

$$k = A\exp\left(-\frac{E_a}{R\left(T_b + \mu P^{0.5} D\right)}\right) \tag{7}$$

where A is the pre-exponential (frequency) factor, T_b is ambient temperature of lubricant during the tribological process, and D is a constant whose value is characteristic of a given kind of solid material. The trigonometric part of the expression can be connected with emission of energy by metal/solid body (catalyst) surface. The stream of energy emitted by the surface depends on the angle γ related to the normal direction to solid body surface and can be expressed by

$$e_\gamma = e_0 \cos\gamma \tag{8}$$

Consequently

$$B = \frac{e_0 St}{\left(R\left(T_b + \mu P^{0,5} D\right)\right)^2} \tag{9}$$

where S is the area of active sites which emit energy, t stands for time of energy emission by the active sites, and C can be described by the following dependence

$$C = \frac{\left(A\exp\left(\frac{E_a}{R\left(T_b + \mu P^{0.5} D\right)}\right) e_0 \cos\left(k_2 P + k_3\right)\right) St}{R\left(T_b + \mu P^{0.5} D\right)^2} \tag{10}$$

Thus

$$kC = A\exp\left(-\frac{E_a}{R\left(T_b + \mu P^{0.5} D\right)}\right), \quad C = \frac{\left(e_0 \cos\left(k_2 P + k_3\right)\right) St}{R\left(T_b + \mu P^{0.5} D\right)^2} \tag{11}$$

Analysis of the mathematical model in relation to empirical results of studies of tribological processes leads to the conclusion resulting in a new idea of the mechanism of catalytic processes.

The model and, especially, the C value (see Fig. 1), combines the energy E_a delivered to molecules from the energy stream (E/t). Considering the energy delivered to molecules for each reaction, should be noted that:

- A critical rate of triboreactions is reached at a temperature or, equivalently, under a load for which the value of E_a is the same for different reactants in the case of the same mechanism of triboreactions; E_a is not a function of T nor P.
- k, under critical conditions, is connected with the energy emitted by the solid at a specific angle γ.
- The critical rate of triboreactions depends on energy emitted by the solid body.
- The distribution of the energy emitted by the solid body (catalyst) is controlled by the angle of emission

$$e_\gamma = e_0 \cos\gamma \tag{12}$$

where γ is a function of P and depends on the stream of energy introduced into the tribological system, e_0 is the density of the energy flux in the perpendicular direction to the solid body surface.

The value of the angle γ depends on the system energy flux. The critical state of a tribological system appears in conditions resulting in destruction of the protective film. As has been observed that for different reactants, the critical rate of reaction leading to protective layer destruction was achieved for different values of energy flux into the system (different values of applied load *P*). The same value of *C* obtained for different reactants and different densities of streams of energy introduced into the system (characteristic of each reactant) leads to the conclusion that the same critical rate of destruction reaction was achieved and thus for each reactant a different angle γ is connected with the critical rate of reaction.

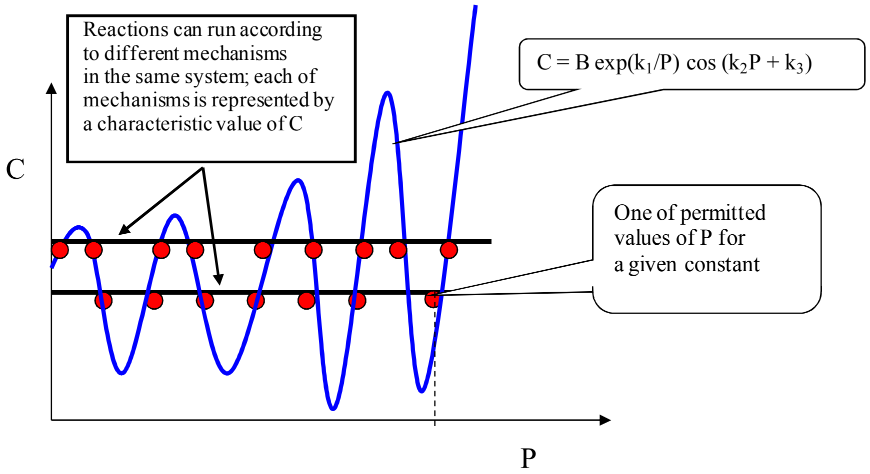

Fig. 1. Relation between the parameter *C* and the applied load *P* characteristic of the critical state of a tribological system (seizure or weld load); a given constant value of *C* can be obtained for a number of *P* values

Consequently, for each reactant there is a specific value of the energy flux density (e_γ) emitted by the solid/catalyst and the value of activation energy E_a is constant. Accordingly, it is possible to say that: (i) E_a is constant for a given type of reaction and the critical rate of reaction depends not only on the energy quantity added to reactants but on the density of the introduced energy stream (time of the tribological process is constant for each load); (ii) the catalyst emits pulses of energy flux of high density and at an angle γ the value of emitted in short time energy is equal to activation energy E_a; (iii) the catalyst collects energy introduced into the system and emits it as pulses of the high energy density flux, thereby initiating the reaction or increasing its rate. Figures 2 and 3 present schematically this approach.

The parameter *C* is constant for a given mechanism of reaction. For different mechanisms, different values of *C* are obtained. Consequently, for each mechanism of reaction (triboreaction) the critical rate of reaction can be achieved only under certain values of energy stream introduced into the system (*T* or *P*). For each of these values, relation between the rate constant calculated for temperature *T* in the friction area and stream of energy emitted by the solid equal to or higher than E_a is constant for a given mechanism of reaction. For another mechanism, this relation changes. It results from analysis of the mathematical model that it is feasible to say that the tribocatalytic effect is observed due to accumulation of energy (introduced into the system as mechanical work) in the solid and the emitted as short time pulses of energy of a high density. Emission of energy by a solid is controlled by the angle of emission.

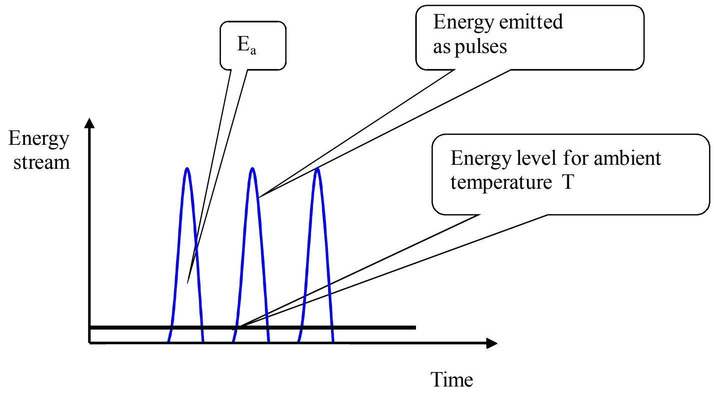

Fig. 2. A general idea of the action mechanism of a heterogeneous catalyst: a part of low energy stream (of the order of *RT*, i.e. less than E_a) , introduced into a solid catalyst is emitted by the catalyst as stream of high energy pulses

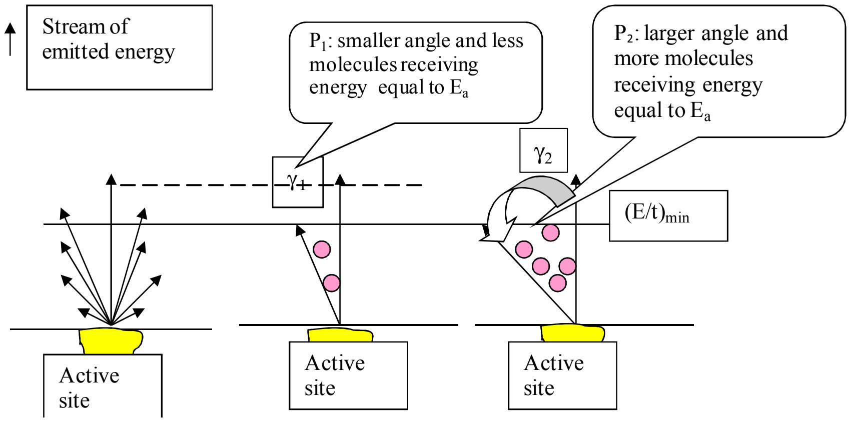

Fig. 3. Illustration of the main concept of the model; stream of the energy emitted by the catalyst depends on the angle γ, hence the number of molecules receiving energy equal to E_a depends on γ

2. Work function and thermionic emission

A promoter chemically modifies a catalyst but is not a catalyst itself. Vayenas at al. [7] described the electrochemical modification of metal catalyst surfaces and presented continuous *in situ* variations and monitoring of the amount of the promoter. Theoretical studies performed by Joyner and Pendry [8] demonstrate that short-range effects dominate, significantly affecting bonding to surface atoms only within a range of less than 0.5 nm, in contrast with the new results of Vayenas et al. [7]. The short range effect, depending on the character of specific surface sites, and long-range electronic interactions, were recently discussed by Pittchard [9, 10]. It has been shown that both sodium and potassium, used as promoters, significantly decrease work functions of catalysts.

Given a small temperature range in which kinetic studies are carried out, it is reasonable to assume the activation energy as being independent of temperature [11]. Similarly, under a wide range of practical conditions, the weak temperature dependence of the pre-exponential factor is negligible compared to the temperature dependence of the exponential term. A thermal model of temperature rise developed by Vick et al. [12] for sliding contact was used to predict the temperature rise over the surface. The predicted temperature rise [13] along with the bulk temperature of the material was used in the Richardson–Dushman equation:

$$J = AT^2 \exp\left(-\frac{\phi}{k_B T}\right) \tag{13}$$

where J is the current density, $A = 4\pi mek_b^2/h^3 = 120$ A/(cm^2·K^2) is the Richardson constant, ϕ is the work function, m and e are the electron mass and electro charge, respectively, h and k_B are the Planck constant and Boltzmann constant, respectively.

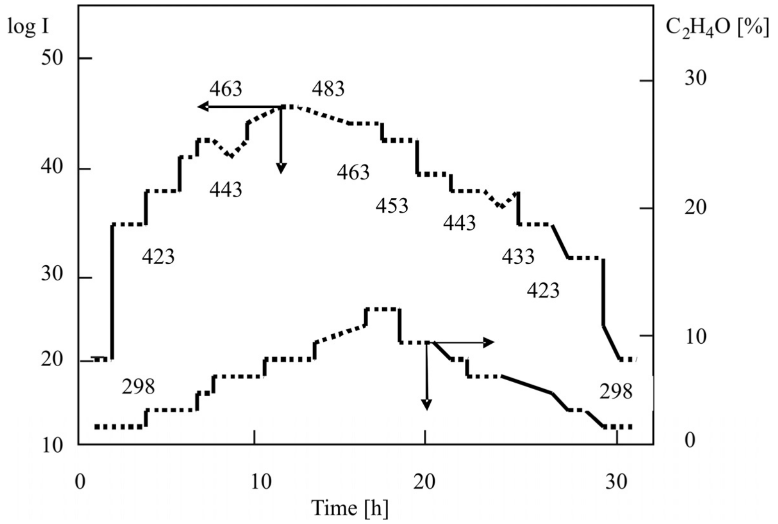

Fig. 4. Effect of temperature on the exoelectron emission rate (emission intensity, expressed in the logarithmic scale) and the formation rate of ethylene oxide (proportional to its amount in the product mixture, expressed in mol. %). The numbers near the upper curve denote temperatures of the system, expressed in K; after Ref. [15]

Park and Somorjai [14] demonstrated that exothermic catalytic reactions induce electronic excitation at metal surfaces, leading to the production of energetic hot electrons. They monitored the flow of hot electrons for several hours using two types of metal –semiconductor Schottky diodes, Pt/TiO_2 or Pt/GaN, during the platinum catalyzed oxidation of carbon monoxide. The thickness of the Pt film used as the catalyst was 5 nm, less than the electron mean free path, resulting in the ballistic transport of hot electrons through the metal. The experiments indicated that chemical energy of the exothermic catalytic reaction was directly converted into hot electron flux in the catalytic nanodiode. Recently, Vick et al. [13] evidenced that high local temperatures generated by friction of the contacts between rubbing surfaces can activate the emission of electrons.

Actually, it is well known and acknowledged that heterogeneous catalytic reactions take place at centres where the electron exchange in the catalyst–substrate system is favoured and that electron emission arises from centres at the surface where electrons are weakly bound. At this point, it is to emphasize that thermally stimulated electron emission occurs in the same range of temperatures as that typical of heterogeneous catalysis [15], as depicted in Fig. 4.

3. The negative ion–radical action mechanism (NIRAM) applied to specific tribochemical and catalytic reactions

The kinetics of tribochemical reactions is different from the kinetics of thermochemical ones. Similar differences arise from the comparison of regular thermochemical heterogeneous reactions and heterogeneous catalytic reactions The difference relates to the initiation steps of these reactions. The NIRAM approach was put forward in order to explain the mechanism of tribochemical reactions and has been successfully applied to account for specific tribochemical reactions [16]. Reactions are said to be initiated by low-energy electrons (exoelectrons) emitted under boundary friction conditions [16]. The emitted electrons interact with molecules in the contact area, which then dissociate forming negative ions and radicals or a negative ion–radicals. Considering the NIRAM approach and the NIRAM-HSAB (hard and soft acids and bases) concept [17] it is possible to look for similarities and differences between tribochemistry and catalysis [5].

Typical physical phenomena evolving from wear processes comprise increased contact temperature and triboemission. Emitted low energy electrons can initiate tribochemical reactions which govern tribological processes by forming anti-wear films. Important research in the field of triboemission was carried out by Nakayama et al. [18] who used a Faraday-cup type assembly to detect bursts of electric current – either charged particle emission or surface charge variation – from scratching diamonds on metals and insulators. Kim et al. [19] investigated photon emission, electron emission intensities, and electron kinetic energy from reciprocating scratching of MgO with diamond. Molina et al. [21, 22] characterised triboemission of electrons from several solids. For the cases of diamond-on-alumina and diamond-on-sapphire, energy spectrometry showed that a large fraction of the triboemitted negative charges were of low energy (e.g., 1–5 eV). This finding was of importance because in the NIRAM approach it was hypothesized that the energy of triboelectrons to initiate tribochemical reaction should be 1–4 eV [16].

NIRAM comprises the following major stages:

(i) low-energy electron emission and creation of positively charged spots, generally on the top of asperities;

(ii) action of the emitted electrons with the lubricant molecules causing the formation of negative ions and radicals on the rubbing surfaces;

(iii) reaction of negative ions with metal surfaces, and other reactions such as free radical reactions, forming an organometallic (or inorganic) film which protects the rubbing surfaces from wear;

(iv) if the shear strength is high, chemical bonds of organometallic compounds are cleaved resulting in formation of inorganic films and further radicals.

(v) eventual destruction of protective layer caused by wear, followed by electron emission and subsequent formation of a new protective film according to the stages (i) through (iv).

In summary, the initiation reaction process is due to tribo-emitted low-energy electrons combined with temperature flash. Specific intermediate reactive species for both tribochemical reactions and some heterogeneous catalytic reactions are formed by the same mechanism mostly governed by the NIRAM approach. The same is due to catalysis and tribocatalysis [5]. The chemically stimulated exoelectron emission occurs continuously from silver catalyst during partial oxidation of ethylene and the emission rate is proportional to the rate of ethylene oxide formation [15]. Generation of fresh surface sites forms a real bridge between physics and chemistry of the wear processes leading to microscopic aspects of a wide variety of wear mechanisms. These mechanisms are often connected with tribochemical reactions that are initiated by the surface enlargement effects. Experimental details on wear and chemical reactions are presented in Ref. [22]. Typical physical phenomena initiated by wear processes include high temperature and triboemission.

4. Conclusions

The model put forward in this paper attempts to correlate mechanical work performed on a solid with its catalytic activity. The tribological system contains fluid reagents and a solid (a specific material). The material plays the role of catalyst (tribocatalyst). The mechanical work done on the system is transformed to internal energy increase. The internal energy is distributed into a liquid/fluid phase bringing about ambient temperature increase (T_b), and is accumulated in the solid. The energy accumulated in the solid is emitted from its surface as pulses of electrons and/or photons. There is a specific angle γ at which the reaction can reach a critical rate or may be initiated, e.g., when e_γ equals some 3–5 eV. The energy accumulated in the liquid phase is insufficient to overcome the threshold of the real activation energy E_a. The energy emitted by surface as pulses of 3–5 eV can reach the value of E_a and the triboreaction process starts to proceed or reaches the critical rate. Based on the discussion concerning the α_i model, thermionic emission, and the NIRAM approach we conclude that for both thermochemical heterogeneous reactions and catalyzed heterogeneous processes, the same activation energy (E_a value) is needed to initiate the reaction process. The fact that triboreactions take place and the critical rate of triboreactions is reached under different conditions (load, temperature) for different reactants cannot be explained by decreasing of activation energy (E_a) by the solid catalyst because E_a is not a function of P.

In summary, it should be emphasized that the activation energy is constant for a given type of reaction and the reaction onset depends not only on the energy quantity added to reactants but on density of the introduced energy stream. The catalyst emits pulses of energy flux of high density and at an angle γ the value of emitted energy is equal to real activation energy E_a.

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