

## Activation energy of tribochemical and heterogeneous catalytic reactions

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The relationship between the activation energy and enthalpy, either in the presence or absence of a catalyst, is of particular importance. If a catalyst is present, the energy required for a given chemical reaction to go into transition state decreases, thereby decreasing the energy required to initiate the reaction. The dynamics of heterogeneous catalysis is still under discussion. The same applies to tribochemistry and/or tribocatalysis. It has been assumed that heterogeneous solid catalysts decrease the activation energy, reflected as apparent activation energy. The model presented elsewhere has been theoretically evidenced for the first time by reviewing the existing literature data concerning anisotropy features of the angular distribution of exoelectrons emitted from perturbed surfaces. Metal–insulator–metal thin film sandwich structures are of particular interest in this paper. Other evidence supporting the model is also discussed such as the anisotropic desorption emission from a surface during catalytic processes. The conclusions of this work have been applied in practice to design specific measurement techniques and devices for estimating the angular distribution of electrons triboemitted from solid catalyst materials under sliding contact in a high-vacuum tribometer.

Keywords: *triboemission; tribochemical reaction; catalyst*

### 1. Introduction

A catalyst is a substance that increases the rate at which a chemical system approaches equilibrium, without itself being consumed in the process; catalysis is the action which occurs as a direct result of the presence of a catalyst. A catalyst lowers

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the activation energy [1]. In chemical kinetics,  $E_a$  is the height of the potential barrier separating the products and reactants. It determines the temperature dependence of the reaction rate. When regular solid catalysts such as those applied in industry (for instance, nano-dispersed metals on amorphous aluminosilicates) are considered, the effect of this type of material might be compared with the action of mechanically activated solids such as in tribocatalysis [2]. Heterogeneous catalysis accelerates the movement of atoms on their passage through the transition state; it provides the link between reactants and products on a reaction pathway which involves simultaneous motion from several to numerous atoms [3]. Friction processes enhance the energy of the mating elements by, for instance, dislocation defects. The mechanism by which lubricants form a protective layer, in the space near solid materials, during a tribological process was recently analyzed by the so called  $\alpha_i$  method [4]. The principle of the  $\alpha_i$  model was presented by Kulczycki [5, 6]. Analysis of the model with regard to empirical data of tribological processes leads to conclusions regarding the mechanisms of catalytic processes. Assumptions of the model are as follows: (i)  $E_a$  is constant for a given type of reaction, and the initiation of the reaction depends not only on the energy ( $E_a$ ) delivered to the substrates but also on the density of the energy stream introduced; (ii) a catalyst collects energy introduced into the system and emits it as impulses of a high density flux of energy, thereby triggering the reaction or increasing its rate, (iii) the catalyst emits impulses of energy flux of high density; at some angle  $\gamma$ , the energy emitted in a short time is equal to the activation energy  $E_a$ .

The model can be applied to tribological systems: the mechanical work done can be treated as the input, and the dissipated energy – predominantly heat – can be treated as the output. The functional input–output relationship may also be applied to tribochemical reactions which are known to proceed much faster than thermochemical ones. One further extension of the model, tribochemical reactions with heterogeneous catalytic reactions are compared [5, 7]. The energy accumulated in a solid increases the enthalpy of the system. Tkacova et al. [8] show that the dislocation concentrations with the specific energy of defect structures are of particular meaning for the energetic condition of the energy contributions. It relates to changes in both structure and enthalpy, and it is consistent with the statement that tribochemical reactions are mostly stimulated by triboelectrons emitted under friction conditions. This work proposes that both heterogeneous catalytic and tribochemical processes are controlled by triboelectrons [9]. A direct correlation between catalytic activity and the EEE intensity, for various deposited and promoted catalysts, was clearly shown by Sato and Seo [10]. Biernacki et al. [11] demonstrated the temperature dependence of the intensity of photostimulated EEE from Raney nickel, and cobalt alloys.

While theoretical friction dissipation models and computer simulations have significantly improved in sophistication over the past decade, their applicability is hampered by a lack of empirical data. Most of these models are either of a phenomenological nature only or they consider friction solely at the skin of rigid corrugated surface potentials.

The fact that friction also involves intrinsic activation modes, e.g., relaxation modes in organic solid materials, has only been recognized in a few isolated studies. Knorr et al. [12] provide direct insight into the basic material intrinsic mechanism for frictional dissipation at the submolecular scale of amorphous organic systems. They demonstrated that at low pressures and temperatures below the glass transition point, the phenyl pendant side groups of polystyrene, known for their preferential orientation at the free surface, were the primary channel by which the kinetic sliding-energy is dissipated. This process was found to be truly enthalpic, having an activation energy of 8 kcal/mol. The energy dissipation was shown to possess both enthalpic and cooperative entropic contributions above the loading capacity of the surface phenyl groups. They also found “apparent Arrhenius activation energies of frictional dissipation of 22 kcal/mol and 90 kcal/mol, respectively, and cooperative contributions up to 80% [12].” As such, the study highlighted issues critical to organic lubricant design, i.e., the intrinsic enthalpic activation barriers of mobile linker groups, the evaluation of cooperative mobility phenomena, and critical tribological parameters that permit or prevent coupling between shear disturbances and molecular actuators.

In the paper, activation energy types with respect to the EEE process have been analysed. The primary goal of the present work is to provide the first theoretical evidence for the model presented in [5] by exploiting relevant data in the existing literature about the anisotropy on angular distribution of exoelectrons (EE) emitted from perturbed surfaces, in particular from metal–insulator–metal thin film sandwich structures. The other goal of the paper is the design of specific measurement techniques and devices for use in a high vacuum tribometer [13] for estimating the angular distribution of triboelectrons emitted from solid catalyst materials under a sliding contact.

## 2. Direct background

Kajdas and Kulczycki [5] hypothesized that for standard and catalyzed heterogeneous reactions the same real activation energy  $E_a$  is needed to initiate reaction processes. It is proposed that energy introduced into a tribological system as a mechanical work, performed on a solid material, is accumulated in this material and then emitted as electrons and/or photons to the space in which reactions take place. The developed model includes the specific angle  $\gamma$  at which the stream of emitted energy  $e_\gamma$ , lying in the 3–5 eV range, is emitted and the reaction can be initiated [5].

The distribution of the energy emitted by the solid body (e.g., by the catalyst) is controlled by the angle of emission

$$e_\gamma = e_0 \cos \gamma$$

where  $\gamma$  is a function of loading  $P$  and depends on the stream of energy introduced into the tribological system,  $e_0$  is the density of the energy flux in the direction perpendicular to the solid body surface [5]. Figure 1 shows the process by which the energy emitted from the surface as pulses can reach the value of  $E_a$ , and the heterogeneous catalytic process starts.

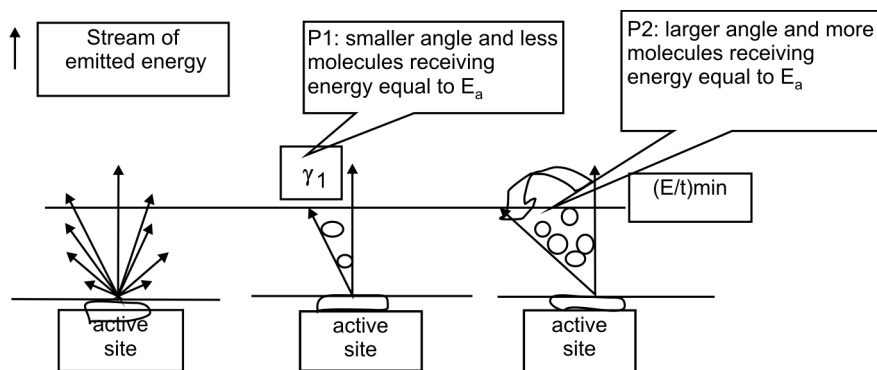


Fig. 1. Main concept of the model: the stream of energy emitted by the catalyst depends on the angle  $\gamma$ , hence the number of molecules receiving energy equal to  $E_a$  depends on  $\gamma$

### 3. Electron and photon emission anisotropy

An exhaustive literature search did not reveal any available data on the angular distribution of triboemitted electrons but the published papers on electron emission from cathodes consistently report that the distributions are anisotropic [14–17]. Highly anisotropic distributions, having a maximum in the direction normal to the emitting surface, were measured.

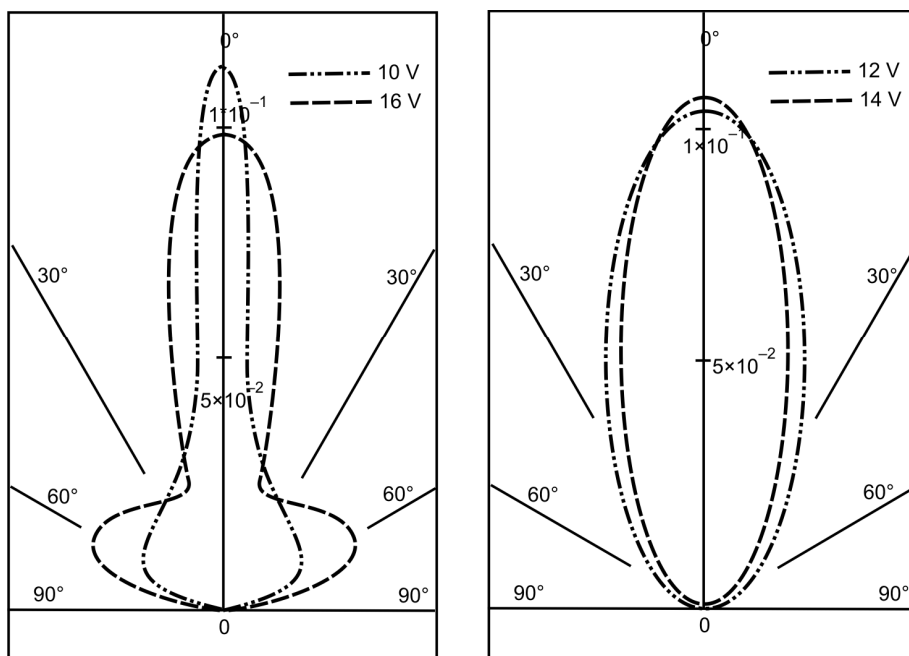


Fig. 2. Examples of EE from sandwich cathodes. The EE is highly anisotropic, and the maxima occur in the direction normal to the emitting surface [16, 17]

Figure 2 shows an example of anisotropic electron emission from sandwich cathodes, from the work of Hrach [16, 17]. At the emission temperature of 300 K, the measured electrons exhibit quasi-isotropic behaviour. But at a lower temperature of 80 K, the isotropic component vanishes. Furthermore, at room temperature approximately 1/3 of the total emission is located in a narrow region around the maximum [14, 15], oriented in the direction normal to the emitting surface. Hrach et al. [16, 17] recorded the energy characteristics of emitted electrons at various angles by means of a hemispherical collector and the retarding-grid technique. They found that at 300 K the anisotropic energy spectra of emitted electrons were in the 0–7 eV range but for emission angles closer to the normal to the surface the measured energy was between zero and 4 eV. In Figure 3, some of these findings are shown.

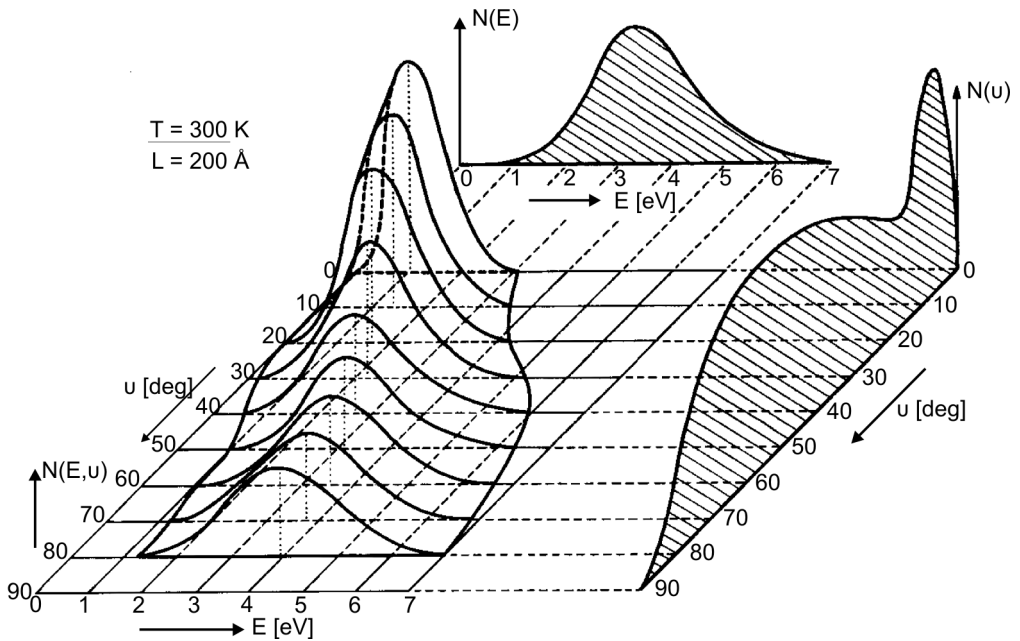


Fig. 3. Typical experimental angular and energy distributions of electrons emitted from Al–Al<sub>2</sub>O<sub>3</sub>–Au sandwich cathode structures. Applied voltage – 10 V [17]

A more recent study was presented by Fitting et al. [18] on the angular distribution of thermostimulated exoelectron emission (TSEE) from  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. They found anisotropic angular distributions to be mainly oriented in the direction normal the surface; the energy of the emitted electrons was in the range 0–4 eV. Thus, the literature review provided strong evidence that low energy electrons are typically emitted according to highly anisotropic distributions, with maxima occurring in the direction normal to the surface. Interestingly, model calculations are consistent with the experimental data and the work of Kortov and Zolnikov [19], who predicted that the angular distri-

bution from an Auger type emission would not be influenced by roughness in homogeneous samples.

The available data on the measurement of the angular distribution of electron emissions is limited to cathode emission [14, 16, 17], TSEE [18] and backscattered emission [20] from electron bombardment of the emitting surfaces. The angular distributions of photoelectrons and emitted photons were also extensively studied; Jablonski and Zemek [21] found a highly anisotropic distribution, similar to the one of electron type, for photon emission from X-ray-irradiated thin polycrystalline aluminum foils. Hucek et al. [22] found similar anisotropy for irradiated Cu, Ag and Au foils, and that the isotropic component is attributable to elastic collisions that photoelectrons experience on their way out of the target. Anisotropy also occurs for other spectral lines.

#### 4. Low energy electron triboemission

The emission of electrons, ions, neutral particles, photons, and acoustic emission under conditions of tribological contact and damage is called triboemission [23]. Triboemitted electrons, which make up the major part of the charged triboemission stream associated with insulators and semiconductors are known to be related to exoemission (including chemical exoemission and fractoemission). Furthermore, it has been postulated that triboemitted electrons are key factors in the initiation and control of tribochemical reactions [24]. For examinations of triboemission of charged particles a high vacuum tribometer [25] was used, but there is evidence that triboemission occurs not only under high vacuum [26, 27]. Molina et al. characterized burst-type electron triboemission for diamond scratching under a constant load and constant scratch-speed. They tested insulators such as alumina, sapphire [23], silicon nitride [28], as well as semiconductors Si and Ge [29]. They also made tests on an alumina ball sliding on an alumina disk [30]. It is of note that positively charged emission from insulators was negligible, regardless of the specific choice of insulator material or the atmospheric conditions. Aluminum was found to produce much lower electron triboemission. Molina et al. [25] also found large fractions of low energy triboelectrons (e.g., 1–5 eV) arising from alumina and sapphire scratching, and spectra extending beyond the largest set potential (i.e., 48 eV). In Figure 4, a typical electron triboemission count (in the 100 msec acquisition window) is shown, obtained from diamond sliding on a silicon nitride disk. Low energy electron emission is clearly associated with, and initiated by, the process of sliding contact.

Some relevant electrical phenomena are well-known, such as triboelectrification on dielectric surfaces, even though their precise mechanisms have not yet been fully clarified. Electron triboemission is affected by surface charge and it may have an effect on the energy of emitted electrons. Figure 5 shows the results of measurement of negatively charged triboemission (CEM-count) when no grounded grid is placed between the emitting surface (a diamond scratching of an alumina disk) and the detector,

making apparent the higher rate of emission that can be attributed to the acceleration of electrons to higher energy levels caused by the surface charge.

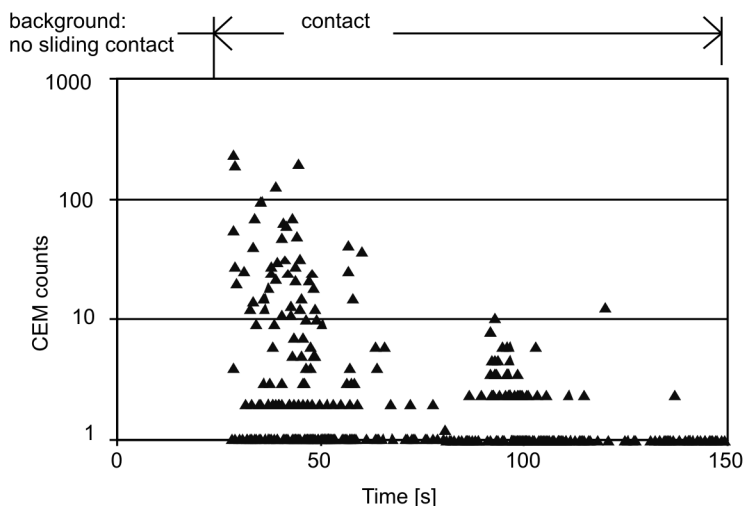


Fig. 4. Negatively charged triboemission (recorded with a channel electron multiplier (CEM) in the count mode) for diamond on  $\text{Si}_3\text{N}_4$ ; acquisition window – 100 msec, load – 5 N, speed – 1.0 mm/s

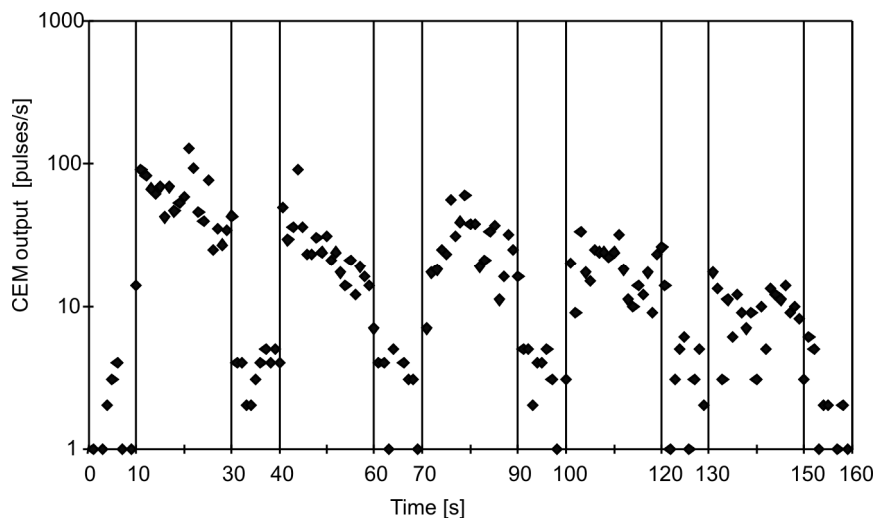


Fig. 5. Negatively-charged triboemission (CEM count for a non-grounded grid) for diamond on alumina sliding contact. 20s periods of sliding contact are followed by 10 s periods of no contact; load – 2N, speed – 0.14 cm/s, acquisition window – 10 ms

Figure 5 also shows that electron emission proceeds after the contact is arrested (e.g., during periods of no-sliding contact); it is attributed to the effect of activated sites on the surface, and has been experimentally shown to last for long periods after

tribological contact has stopped. Precise details of the mechanism by which triboelectron emission occurs still remain however unclear.

Molina et al. [24] have recently proposed that electron triboemission can be the result of non-adiabatic surface reactions according to the Kasemo model [31]. This model is based on the Auger decay process, in which an impinging gas particle provides an empty level that is filled by an electron from the solid, while energy is transferred to another emitted electron. The probability of such an event is very low, of ca.  $10^{-4}$  per impinging molecule but is consistent with the observed exoemission processes.

Chemical reactions may dissipate part of their energy to electron–hole pairs in the surface region: part of the impinging molecule energy may be transferred to electronic states which are lower by several eV from the ground state potential of the surface. A low energy electron would then be emitted in a non-adiabatic process; this phenomenon of low energy “chemi-emission” has been extensively observed. Although classical mathematical models of surface chemistry processes (i.e., quantum or first principle descriptions of the atomic interactions) assume that such deviations from adiabatic behaviour are small and of no practical importance, recent experimental works [32–34] have shown that exoelectron emission is just a fraction of the total electronic excitation on the surface. The majority of non-adiabatic excitations would not be typical exoemissions but they are detectable as “chemicurrents” which are due to chemically generated hot carriers, and stay in the solid. Nienhaus et al. [33] detected such chemicurrents by using thin film electronic devices that allow non-emitted excited electrons to traverse their Schottky barrier (of only about 0.7 eV) as “internal exoemissions”. By this method they estimated that, for instance, for the oxidation of Mg surfaces approximately 10% of the chemical reaction energy is dissipated by non-adiabatic electronic excitation.

Bottcher et al. [35] identified the profile of the electron work function (WF) and the intensity of the exoemission that occurs when Cs is exposed to O<sub>2</sub>. They found that no electron emission was detected during clean surface exposure to increasing quantities of O<sub>2</sub>, until the pressure of ca.  $10^{-6}$  Torr was reached, i.e., until partial oxidation would be needed for this chemi-emission to occur. A decrease in the WF also was observed, but its minimum was reached for lower O<sub>2</sub> exposure than that of the electronic peak. This result suggests that the electronic excitation occurring through chemical reaction may govern exoemission, rather than the lowering of the WF being the dominant factor. The mechanism for this emission can be interpreted by the model of Kasemo et al. [31]. Bottcher et al. [35] also demonstrated that, according to this model, the probability of emission decreases monotonically as the formation of the oxide layer approaches completion.

Nonadiabatic reactions may facilitate explanation of some features of the surface catalytic processes where internal vibrational modes are highly excited and not in equilibrium with each other [36, 37] as in, for instance, the catalytic oxidation of CO on Pt. Interesting enough, product desorption from such catalytic reaction occurs in



a narrow angular cone. Becker et al. [38] established experimentally that the most probable CO<sub>2</sub> desorption energy is 3560 K, which occurs perpendicular to the Pt-emitting surface at 880 K. This is an important characteristic of desorption emissions that arise from surface catalytic processes. It provides further evidence supporting the predicted direction of anisotropy of the model [5] discussed in the paper.

## 5. Current research plans

Data on the angular distribution of triboemitted electrons are not available. Such measurements pose additional challenges when compared with cathode emission measurements, the two most important being: (i) the emitting surface is in motion (as either pin-on-disk or a reciprocating contact) and it will be a ring- or segment-wear-track; and (ii) the pin geometry would interfere with the path of triboelectrons emitted during and immediately after contact.



Fig. 6. High vacuum tribometer  
(photograph by Molina et al. [2, 25])

Based on the conclusions of this work, the following experiments have been planned using high vacuum tribometer [13, 25] shown in Fig. 6:

- The design of a voltage-biased grid-filter with two openings at angles; one opening will maximize the collection of electrons in the direction normal to the emitting-surface, while the other will mostly collect emission for angles greater than about 30 degrees. The two grid-openings will be alternatively biased in a sequence (i.e., one for

negative potential while the other for zero one) that will be synchronized to the electron detection and counting.

- The use of an electron sensitive film (i.e., electron microscopy film), semispherical ring detector on top of a circular shield with a hole and the scratching pin.

- The use of cooled CCD camera for detection of electrons at various angles. However, this option may have a limitation with sensitivity for electrons of energy lower than 700 eV.

- The use of a hemispherical collector divided into concentric annular segments connected to a picoammeter which can be placed above a circular shield with a hole and the scratching pin as in the figure above.

- Alternatively, the measurement of triboemitted photons at various angles; the assumption could be made that photon angular distribution would be similar to that of triboelectrons. In this, the authors develop a setup for counting of triboemitted photons based on a solid state photon detector and a counter, and fibre optics to collect signals from the emitting surfaces.

## 6. Conclusions

This paper demonstrates that heterogeneous catalysis is controlled by low energy electrons, similarly to the way tribochemistry is controlled by triboelectrons. The data under review in this paper confirm the anisotropy of the angular distribution of exoelectrons emitted from perturbed surfaces, and thereby provide the first empirical evidence for the the  $\alpha_i$  mathematical model [5]. The model discussed in this paper provides a new approach to investigate the activation energy and leads to better understanding of heterogeneous catalysis. Although the discussed anisotropic EE relates to metal–insulator–metal thin film sandwich structures, we consider this fact as a first evidence for the proposed model, which predicts such a distribution of triboelectrons. Devices and methods are designed for an updated high-vacuum tribometer [13], for the purpose of providing experimental evidence for the predicted angular distribution of electrons that are triboemitted from solid catalyst materials under sliding contact.

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