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## ON HYDROGEN GENERATION DURING TRIBO-DEGRADATION OF ORGANIC COMPOUNDS

## GENEROWANIE WODORU PODCZAS TRIBO-DEGRADACJI ZWIĄZKÓW ORGANICZNYCH

### Key-words:

hydrogen generation, formic acid decomposition, friction, tribocatalysis,  
NIRAM approach

### Słowa kluczowe:

generowanie wodoru, rozkład kwasu mrówkowego, tarcie, tribokataliza,  
NIRAM

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## Summary

This paper considers mechanisms of catalytic hydrogen generation from formic acid aiming at developing a new more coherent one. The focus is on better understanding of formic acid decomposition processes from the view-point of both regular catalysis and tribo-catalysis. Basing on a hypothesis that tribocatalytic reaction is enhanced by exoelectron emission, it is assumed that both typical tribochemical reactions and catalytic reactions may be connected with the same driving force. Accordingly, catalytic processes, likewise tribochemical reactions should be governed by the NIRAM – approach. Applying this approach a mechanism is proposed for the reaction of formic acid decomposition, connecting tribochemical and heterogeneous tribocatalytic reactions.

## INTRODUCTION

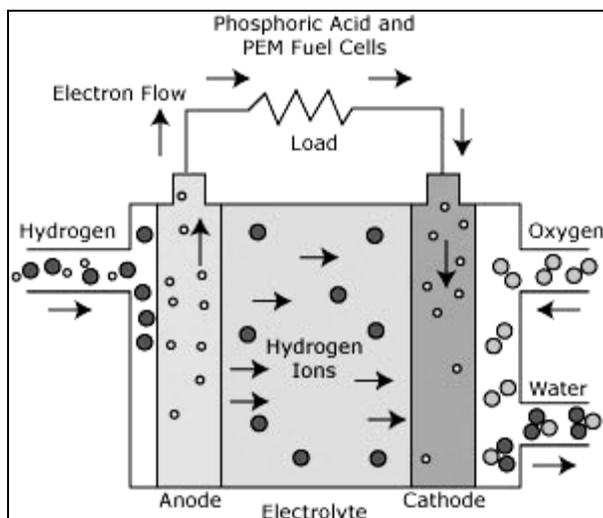
Hydrogen as a pollution free fuel is very attractive for further transportation development. To avoid problems concerning the storage and handling of hydrogen, liquid fuels could be used for on board production of hydrogen. To develop an economical and ecological technology a comprehensive knowledge about the functionality of the catalyst is decisive. In this work the mechanism of hydrogen generation from simple organic compounds is presented on the example of formic acid. It might be a good starting point for the research on hydrogen generation from methanol.

## HYDROGEN FUEL CELLS

In the case of fuel cells at present time for city vehicles only power installations based on proton exchange membrane fuel cells (PEMFC) may find practical application [L. 1]. In the process that goes on inside an individual fuel cell, electrons are removed from H<sub>2</sub> molecules (Fig. 1) and move through a circuit to perform work. H<sub>2</sub> reacts with O<sub>2</sub> from air to produce water- the only by product of hydrogen power.

Absence of hydrogen infrastructure and problems of hydrogen on-board storage may become an obstacle for the commercialization of such vehicles [L. 3]. It should be stressed that at present time only the application of liquid hydrogen or hydrogen at high pressure provides reasonable amount of on-board hydrogen for fuel cells or “hydrogen” internal combustion engines. Liquid fuels with high energy densities (high molecular

ratio of hydrogen to carbon) could be used for on board production of hydrogen. So development of hydrogen production systems is becoming more and more important. The choice of primary fuels (hydrogen precursors) is another important task. Fuels such as gasoline, methanol and ethanol are usually said to be possible hydrogen precursors for this application, however the technologies involved are still imperfect.



**Fig. 1. Proton Exchange Membrane Fuel Cell (PEMFC) [L. 2]**

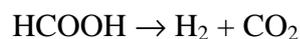
Rys. 1. Ogniwo Paliwowe z Elektrolitem w Postaci Membrany Polimerowej (PEMFC) [L. 2]

## OBJECTIVES OF THE WORK

This paper is focused on better understanding of formic acid decomposition process proceeding on silver to generate  $H_2$  and  $CO_2$  from the viewpoint of both regular catalysis and tribo-catalysis. This study might be a good starting point for the research on hydrogen generation from methanol. To develop an economical and ecological technology a comprehensive knowledge about the functionality of the catalyst is decisive, therefore it is crucial to determine action mechanisms of hydrogen generation reactions from simple organic compounds. Detailed mechanism of catalytic hydrogen generation, even from low-molecular weight organic compounds, is very complex. Tribo-catalytic processes seem to be more entangled.

## FORMIC ACID DECOMPOSITION

Gas phase dehydrogenation of formic acid:



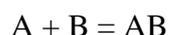
$$\Delta G^\circ = -58.6 \text{ kJ/mol}$$

$$\Delta H^\circ = -31.0 \text{ kJ/mol}$$

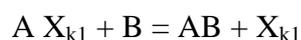
was acknowledged to be suitable for the research carried out to determine an influence of defects and surface structure of a catalyst on the reaction course, because it enables to use a catalyst with well-defined surfaces, proceeds reproducibly and with sufficient speed on rather small surface areas. It can be also carried out using simple experimental set-up and its products are easy to analyse [L. 4–5].

## BASIC INFORMATION ON NIRAM APPROACH

Usually a non-catalytic reaction:

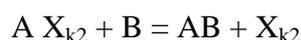
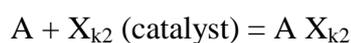


is of rather slow rate. A catalytic reaction:



is faster.

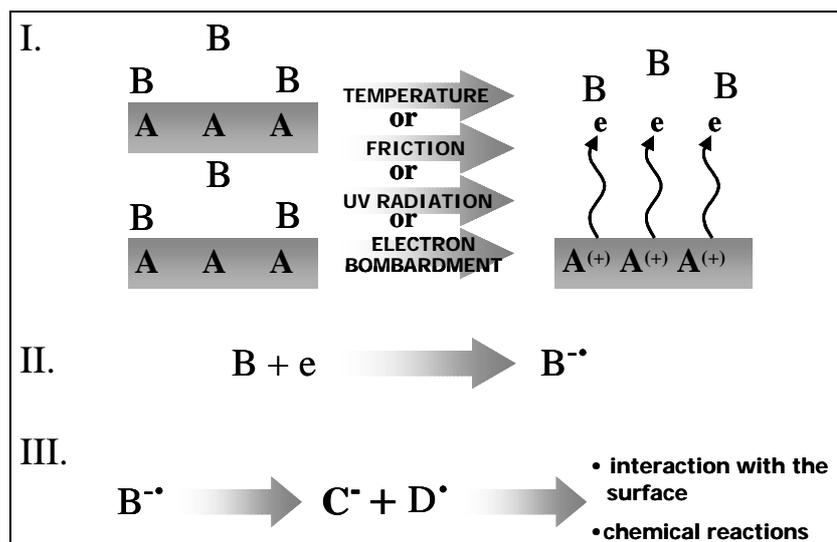
A catalyst under friction conditions ( $\text{X}_{k2}$ ) is known to cause a further rise in the reaction rate [L. 6–8]:



So a question is to be asked: what may be a main reason for which a catalyst under friction conditions ( $\text{X}_{k2}$ ) causes a further rise in the reaction rate?

Kinetics of tribochemical reactions is different from kinetics of thermochemical ones. Similar differences arise from the comparison of chosen regular heterogeneous catalytic reactions and tribocatalytic processes

on the same catalysts. The difference relates to the initiation step of these reactions [L. 9]. Therefore a Negative-Ion-Radical Action Mechanism (NIRAM) was proposed in order to explain the mechanism of tribochemical reactions. Reactions are said to be initiated by low-energy electrons (exoelectrons) emitted under boundary friction conditions [L. 10]. As a result ionisation occurs [L. 11–13]. Emitted electrons interact with molecules present in the contact area, which then dissociate forming a negative ion and a radical or a negative-ion radical. Subsequently, these molecules can induce many chemical reactions (Fig. 2).



**Fig. 2. Diagram of Negative-Ion-Radical Action Mechanism (NIRAM) [L. 14]**

Rys. 2. Schemat mechanizmu NIRAM (Negative-Ion-Radical Action Mechanism) [L. 14]

Considering the NIRAM approach [L. 13] and the NIRAM-HSAB (Hard and Soft Acids and Bases) concept [L. 15] it is possible to look for similarities and differences between tribochemistry and catalysis. Referring to [L. 16] one can say that there is a link between tribochemistry and catalysis and/or tribocatalysis; in both tribochemical and regular heterogeneous catalytic reactions reactive intermediates are produced according to the same mechanism (NIRAM) [L. 17].

The initiation of catalytic and tribocatalytic reactions is connected with thermoelectron and triboelectron emission (Table 1). In both tribocatalytic and regular heterogeneous catalytic reactions increased tempera-

ture is observed, that causes activation energy decrease [L. 18]. In tribo-catalysis it is related to so called flash temperature, which is probably caused by electron emission.

**Table 1. Interdependence between tribochemical reactions and selected reactions of heterogeneous catalysis [L. 16]**

Tabela 1. Współzależność reakcji tribochemicznych z wybranymi reakcjami katalizy heterogenicznej [L. 16]

Reaction type:	Initiation manner:
TRIBOCHEMICAL	TRIBOELECTRONS plus THERMAL ELECTRONS
CATALYTIC (heterogeneous)	THERMAL ELECTRONS
TRIBOCATALYTIC (heterogeneous)	THERMAL ELECTRONS and TRIBOELECTRONS

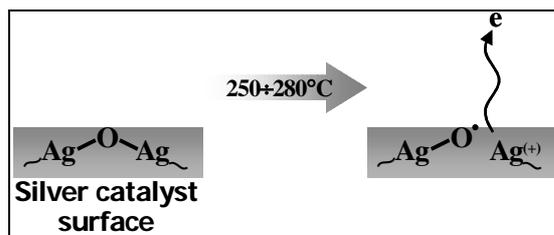
Under friction conditions the active surface area of the catalyst increases, causing a decrease of the value of work function, which concerns electron emission from given material surface. As a result activation energy decreases and a rise in the reaction rate is observed. Moreover as a result of friction process defects and electron gaps (holes) are produced on the surface of given material, in case of the catalysts they are fresh surface active sites, which are very active and cause a significant increase in the reaction rate.

### **PROPOSITION OF MECHANISM OF FORMIC ACID DECOMPOSITION INITIATED BY THERMAL ELECTRONS**

Taking into account experimental findings of various researchers and considering the most recent data concerning model calculations of the emission of thermal electrons [L. 19] we propose the following mechanism of the formic acid decomposition initiated by thermal electrons according to the NIRAM approach [L. 18]. The following 4 stages of formic acid decomposition can be specified:

#### **Stage I: Electron emission (Fig. 3)**

Under increased temperature conditions (250–280°C) low-energy electrons are emitted from silver catalyst surface. Positively charged sites  $\sim\text{Ag}^+$  and radicals  $\sim\text{Ag-O}\cdot$  are formed on the surface.



**Fig. 3. Stage I: Electron emission from silver catalyst surface [L. 18]**

Rys. 3. Etap I: Emisja elektronu z powierzchni katalizatora srebrowego [L. 18]

It is to mention at this point that the transformation of AgO to Ag<sub>2</sub>O occurs with heating in the 373–473 K region, while the product of the reaction is stable to temperature in excess of 623 K [L. 20].

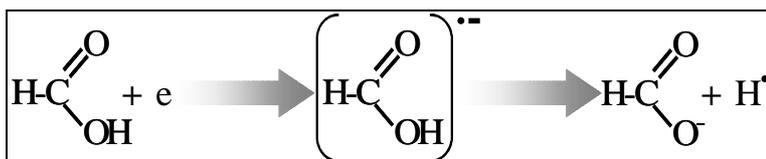
The work function ( $\phi$ ) expresses what work should be performed in order to draw an electron out of the solid. The higher the value of the work function the harder it is to draw out the electron from the solid. For silver the value of work function for thermal excitation is about 4.80 eV. It corresponds to the ionisation energy of isolated atom [L. 21]. As early as in 1960's it was suggested that in formic acid decomposition reaction on a metal catalyst an electron transfer from the catalyst to the adsorbed species might occur [L. 22]. Therefore it is assumed that in the discussed decomposition reaction the silver catalyst provides electrons emitted from the metal in sufficient temperature. It is so because the silver catalyst becomes activated in increased temperatures.

The above listed conclusions allow to understand observations included in [L. 23] namely that on the nascent surfaces of steel two types of active sites can exist [L. 18]:

- small amount of strong active sites which are able to chemisorb and decompose formic acid molecules; for these sites the work function value is lower. They include among others the surface defects formed by scratching,
- relatively large amount of active sites which could only chemisorb formic acid molecules; for these sites the work function value is higher.

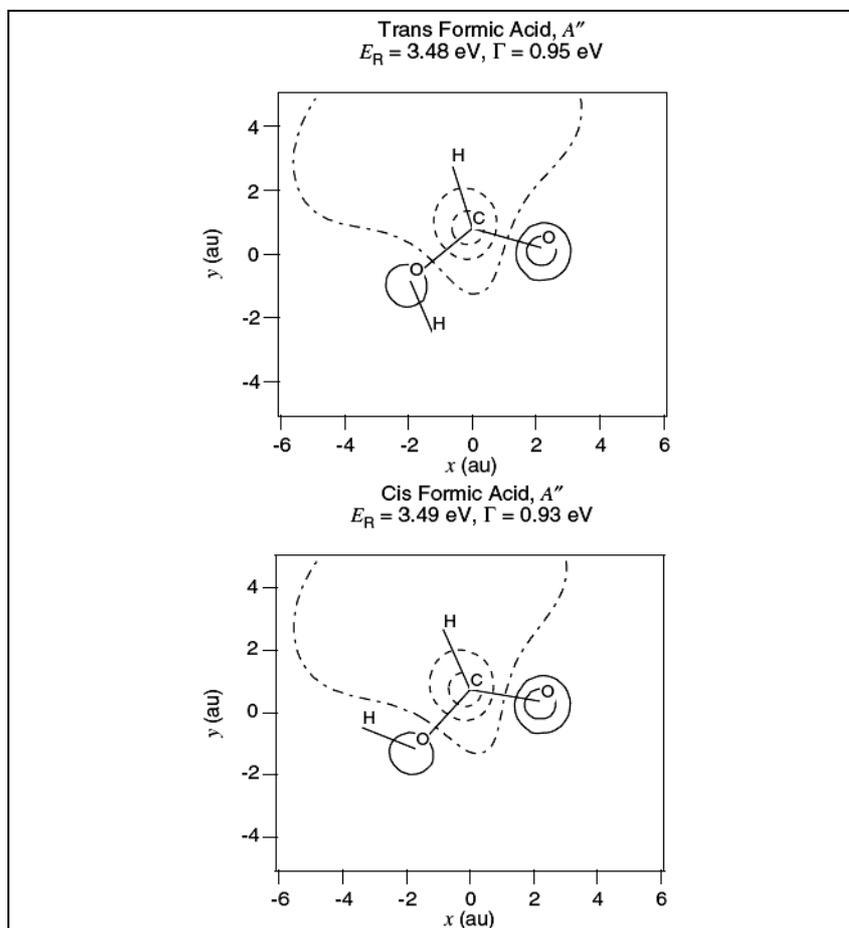
#### **Stage II: Reaction initiation (Fig. 4)**

The emitted electron attaches to the formic acid molecule forming a negative-ion radical (HCOOH)<sup>-</sup>, which subsequently decomposes to generate HCOO<sup>-</sup> anion and H<sup>•</sup> radical.



**Fig. 4. Stage II: Reaction initiation [L. 18]**

Rys. 4. Etap II: Inicjowanie reakcji [L. 18]



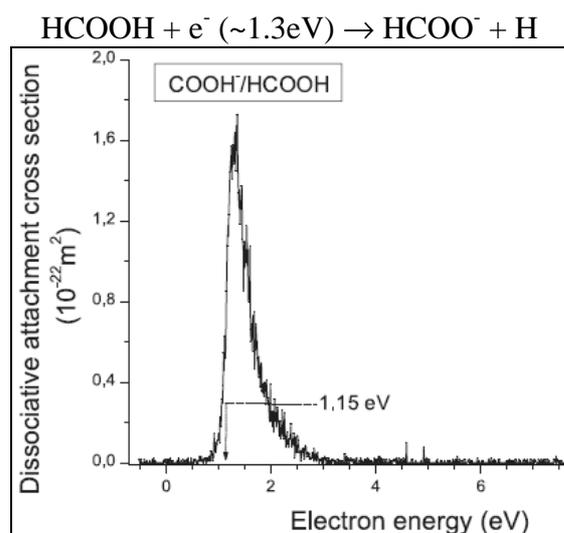
**Fig. 5. The resonant electron wave functions associated to the two resonances of both trans and cis formic acid. Solid lines and dashed lines correspond to regions of positive and negative values, respectively, of the wave functions [L. 26]**

Rys. 5. Elektronowe funkcje falowe związane z dwoma stanami rezonansowymi *trans* i *cis* kwasu mrówkowego. Linie ciągłe i przerywane funkcji falowych odnoszą się, odpowiednio, do obszarów wartości dodatnich i ujemnych [L. 26]

In work [L. 24] it was proposed, that a temporary anion,  $\text{HCOOH}^-$ , is formed and it may subsequently decay by either dissociation to  $\text{HCOO}^-$  or auto-detachment leaving the parent molecule vibrationally excited. In work [L. 25] a fine structure was observed for a resonance state excited at around 1.3 eV. This structure has been attributed to OCO vibrational bending in the temporary parent anion. This may be as well due to  $(\text{HCOOH})^-$  negative-ion-radical formation, according to the mechanism proposed here.

According to [L. 26] no extra electron density is present on the hydrogen atom bound to one of the oxygen atoms, i.e. the general strengthening of the bonds provided by the temporarily trapped electron does not extend to that specific H atom (Fig. 5). The conclusion is simple: the O-H bond in  $\text{HCOOH}$  is the weakest.

In work [L. 24] low energy electron attachment to formic acid has been studied. The major channel obtained in the range of 0-6 eV is  $\text{HCOO}^-$  with anion production observed over a narrow energy range between 1 and 3 eV peaking at about 1.3 eV (Fig. 6). The authors assigned the observed anion signal to the following dissociative electron attachment (DA) reaction:

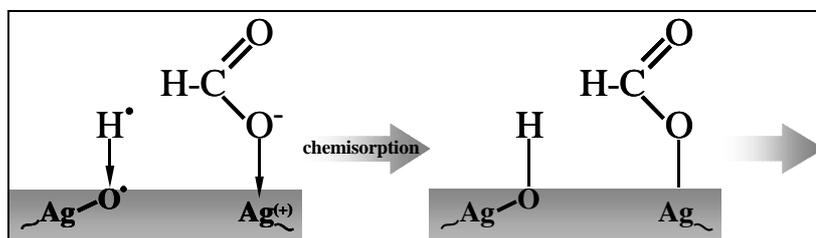


**Fig. 6. Formation of negative ions  $\text{HCOO}^-$  by dissociative electron attachment to formic acid [L. 24]**

Rys. 6. Powstawanie anionów  $\text{HCOO}^-$  w wyniku dysocjatywnego przyłączenia elektronu do kwasu mrówkowego [L. 24]

### Stage III: Chemisorption (Fig. 7)

The chemisorption occurs:  $\text{HCOO}^-$  ion interacts with positively charged spot on the surface and  $\text{H}\cdot$  radical with  $\sim\text{Ag}-\text{O}\cdot$  surface radical.

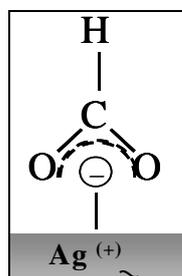


**Fig. 7. Stage III: Chemisorption [L. 18]**

Rys. 7. Etap III: Chemisorpcja [L. 18]

The presence of adsorbed  $\text{HCOO}$  has been confirmed by various authors [L. 17, 27–31].

According to [L. 25] the electronegativity of the OH substituent in  $\text{HCOOH}$  influences the energy, lifetime and excited levels of the  $\pi^*$   $\text{C}=\text{O}$  resonance with the presence of the two lone pairs making the  $\pi^*$   $\text{CO}$  double bond not completely localised but rather involving a charge transfer from the carboxyl and hydroxyl oxygen to the carbon atom. After  $\text{H}$  detachment the double bond can become even more delocalised, so the adsorbed form could be like shown in **Fig. 8**.



**Fig. 8. Proposed structure of adsorbed  $\text{HCOO}^-$  ion [L. 32]**

Rys. 8. Proponowana struktura zaadsorbowanego jonu  $\text{HCOO}^-$  [L. 32]

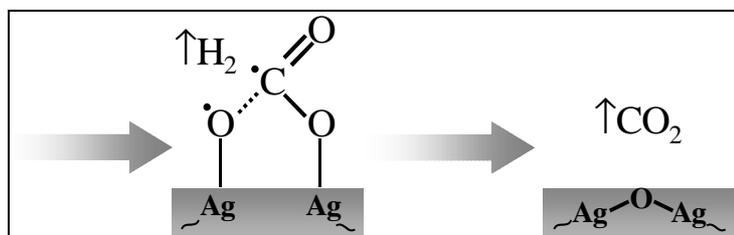
### Stage IV: Desorption of $\text{H}_2$ and $\text{CO}_2$ (Fig. 9)

Hydrogen molecules are desorbed. As a result a transient species attached to the silver catalyst surface is formed. This surface intermediate

decays and  $\text{CO}_2$  is desorbed, regenerating the original structure of the catalyst surface.

According to [L. 4]  $\text{CO}_2$  desorption is the slow step of  $\text{HCOOH}$  decomposition reaction.

There are many unanswered questions considering this stage. Desorption sequence of  $\text{H}_2$  and  $\text{CO}_2$  and the mechanism involved are still to be determined.



**Fig. 9. Stage IV: Desorption of  $\text{H}_2$  and  $\text{CO}_2$  [L. 18]**

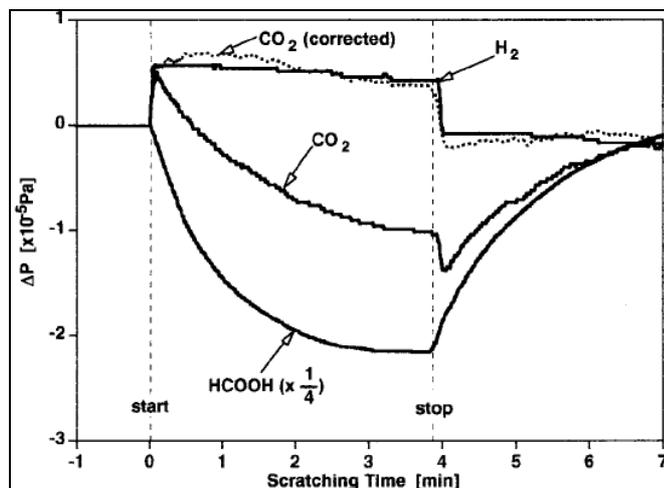
Rys. 9. Etap IV: Desorpcja of  $\text{H}_2$  and  $\text{CO}_2$  [L. 18]

An interesting hypothesis was proposed by Mori et al. [L. 23] in relation to tribochemical formic acid decomposition on the nascent surfaces of steel formed by scratching. Such nascent surfaces show so high activity that the lubricant molecules decompose on them even at room temperature.

It was found that formic acid adsorbed on the nascent surface sites decomposed to  $\text{H}_2$  and  $\text{CO}_2$ , whereas the reaction to  $\text{CO}$  and  $\text{H}_2\text{O}$  did not occur. With starting scratching, the partial pressure of formic acid gradually decreased due to adsorption to the nascent surfaces formed by scratching (Fig. 10). On the other hand, partial pressures of  $\text{H}_2$  and  $\text{CO}_2$  steeply increased and became stable within some seconds. After termination of scratching, the partial pressure of formic acid increased slowly, because surface active sites were covered with adsorbed molecules, whereas the formation of  $\text{H}_2$  and  $\text{CO}_2$  terminated quickly.

It was also demonstrated, that the chemisorption rate of the formic acid increased linearly with its initial pressure, that is, the collision rate of molecules, while the formation rates of  $\text{H}_2$  and  $\text{CO}_2$  increased linearly with the scratching speed, that is, the formation rate of active sites. In the discussed process, chemisorption of  $\text{HCOOH}$  is followed by a surface reaction of decomposition. The rate-determining step of chemisorption is

mass-transfer of formic acid onto the nascent surface. Whereas the decomposition rate is determined by the amount of active sites.



**Fig. 10. Changes of partial pressures of  $H_2$ ,  $CO_2$  and  $HCOOH$  during scratching [L. 23]**

Rys. 10. Zmiany ciśnień cząstkowych  $H_2$ ,  $CO_2$  i  $HCOOH$  podczas rysowania [L. 23]

On the basis of the results obtained it was proposed that two types of active sites might exist on the nascent surfaces. A large amount of active sites could chemisorb formic acid molecules, but only a portion of them decomposed formic acid molecules. Surface defects formed by scratching seem to be one of the strong sites [L. 32].

The above tribocatalytic reaction mechanism has been developed in terms of the NIRAM approach.

### AN ATTEMPT TO CONFIRM THE PROPOSED MECHANISM

Three reactions are presented, towards which attempts have been made to determine the reaction mechanism in terms of the NIRAM approach. Presented mechanism propositions were based on the results of adequate experiments and developed in terms of the NIRAM approach; therefore they can be also considered to be a preliminary confirmation of here proposed mechanism of formic acid decomposition.

### Mechanism of water synthesis [L.10]

This reaction has been examined under static conditions during heating and under friction conditions [L. 10]. It was found that the most important difference in both processes relates to the fact that under friction conditions the reaction is initiated immediately.

The new mechanism of tribocatalytic reaction was proposed based on the fact, that the most of the hydrogen adsorbed in platinum exists in the atomic form and that low-energy electrons are emitted during friction.

### Mechanism of carbon dioxide synthesis

Results of the research on  $\text{CO}_2$  synthesis from carbon oxide and oxygen during rubbing between palladium and aluminum oxide was presented in work [L. 33]. On the basis of obtained results and the NIRAM approach authors of work [L. 33] proposed the mechanism of  $\text{CO}_2$  synthesis.

### Methane oxidation

In work [L. 34] the effect of friction and heating of silver catalyst on methane oxidation have been investigated. Fig. 11 represents the results obtained during rubbing between silver and aluminium oxide.

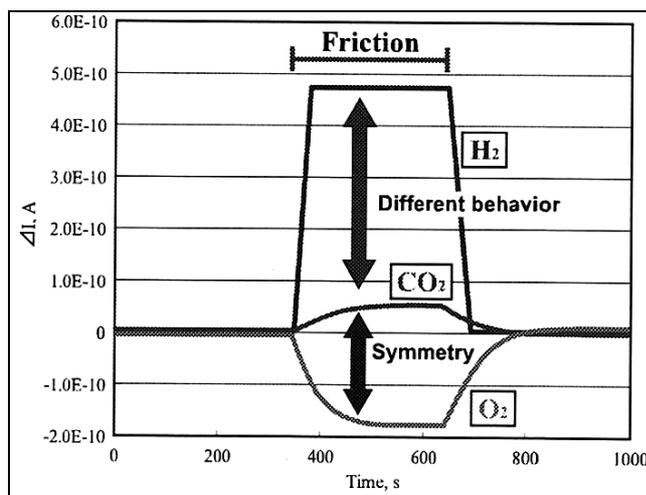


Fig. 11. Ion current change of  $\text{H}_2$ ,  $\text{CO}_2$  and  $\text{O}_2$  ( $\text{Al}_2\text{O}_3/\text{Ag}$ ) [L. 34]

Rys. 11. Zmiana prądu jonowego  $\text{H}_2$ ,  $\text{CO}_2$  i  $\text{O}_2$  ( $\text{Al}_2\text{O}_3/\text{Ag}$ ) [L. 34]

On the basis of obtained results, the authors hypothesized that different behaviour between hydrogen and carbon dioxide during friction is due to the different reaction sites on friction track [L. 34]. As soon as friction commenced, hydrogen was evolved. This reaction could occur at the contact point. On the contrary carbon dioxide was gradually evolved. This means that this reaction occurs after the contact area (Fig. 12). An interesting conclusion is that an important reaction intermediate is water, although no change in its concentration was observed during the process.

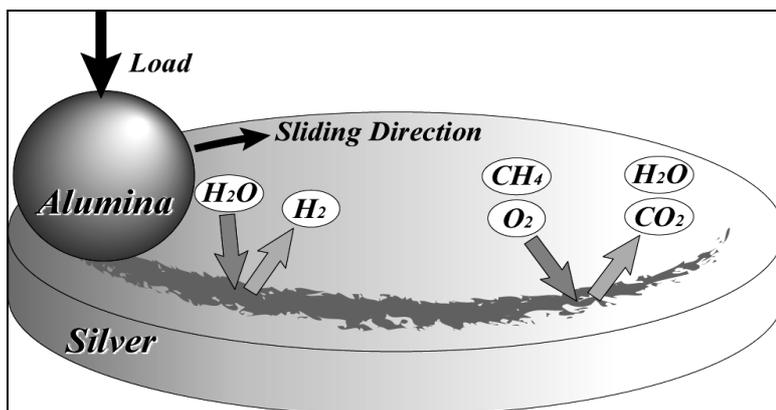


Fig. 12. Reaction model [L. 34]

Rys. 12. Model przebiegu reakcji [L. 34]

On the basis of obtained results [L. 34] authors proposed a new mechanism of the tribocatalytic reaction.

## SUMMARY

A catalyst under friction conditions causes a further rise in the reaction rate. It is supposed that both typical tribochemical reactions and catalytic reactions may be connected with the same driving force related to exoelectron emission. Therefore some catalytic processes, likewise tribochemical reactions can proceed according to the NIRAM-HSAB mechanism.

Using the NIRAM approach a mechanism has been proposed for the reaction of formic acid decomposition, connecting tribochemical and tribocatalytic reactions. In both types of reactions the presence of low-energy electrons is of great importance: triboelectrons and maybe thermal

electrons in tribochemical reaction, thermal electrons in heterogeneous catalytic reaction and thermal and triboelectrons in heterogeneous tribo-catalytic reaction.

This study might initiate further activities aiming at research on hydrogen generation from methanol. Proposed mechanism of formic acid decomposition requires experimental confirmation. Also a comparison needs to be made between catalytic and tribocatalytic reactions on different catalysts. For that purpose further joint research has been planned with Chiba Institute of Technology in Japan.

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### Streszczenie

**Praca rozpatruje mechanizmy katalitycznego generowania wodoru z kwasu mrówkowego w celu opracowania nowego, bardziej spójnego mechanizmu tej reakcji. Uwagę skupiono na lepszym zrozumieniu procesów rozkładu kwasu mrówkowego z punktu widzenia zarówno katalizy, jak i tribokatalizy. Bazując na hipotezie, że emisja egzoelektronów intensyfikuje reakcje tribokatalityczne, zakłada się, że zarówno reakcje tribochemiczne, jak i katalityczne mogą wiązać się z tą samą siłą napędową. Zatem reakcje katalityczne i reakcje tribochemiczne powinny przebiegać zgodnie z tym samym mechanizmem (NIRAM). Wykorzystując koncepcję NIRAM, zaproponowano mechanizm reakcji rozkładu kwasu mrówkowego, wiążący reakcje tribochemiczne i heterogeniczne reakcje tribokatalityczne.**