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TOF AND TON EVOLUTION IN HETEROGENEOUS CATALYSIS

***Abstract.** The review article shows the evolutionary path that turnover frequency (TOF) and turnover number (TON) have passed from “Boreskov’s Rule” to their modern definitions. From the equation catalysis rate, the second method for calculating TOF is obtained using the characteristics of catalyst material. Was proved the possibility of obtaining TOF in two ways - using the characteristics of catalysis process and using the characteristics of the catalyst and reagents. The equivalence of two methods of TOF calculation is proved. It turned out that TOF is not a complete and unambiguous characteristic of the catalyst, as it was usually believed. TOF is only partially dependent on the characteristics of the catalyst material. It turned out that TOF is not a characteristic of a catalyst, but of a “catalyst + reagents” system, and its value directly depends on the state of their oxidation. It is proposed to use the list of oxidation states of chemical elements as the main tool in the selection of catalysts. The Sabatier principle limits the TOF and TON values by limiting the multielectron transitions when the oxidation state of the active sites of the catalyst changes. An explanation for the effect of overcoming the Sabatier prohibition is given, in which external synchronous action on the catalyst makes it possible to achieve a catalytic reaction speed higher than the Sabatier maximum.*

***Keywords:** Turnover frequency (TOF), catalyst redox state, Horiuti numbers, Sabatier maximum, catalytic resonance.*

1. Introduction

When it comes to choosing the best catalyst for a chemical reaction, chemists use a proven method of comparing the effectiveness of different catalysts. In the practice of catalysis, such characteristics as turnover frequency (TOF) and turnover number (TON) [1-8] are widely used for this purpose. They allow a quantitative comparison of the performance of different catalysts if the reaction conditions are properly defined. The importance of TOF and TON for catalysis and their special status in the practice of catalysis have been proven by their long period of use. Without them, a quantitative description and comparison of the activity of catalysts is inconceivable.

TOF is defined as the amount of product N formed in the catalytic reaction divided by the number of active sites of the catalyst n_a and the reaction time t [4, 8-12]:

$$TOF = \frac{N}{t \cdot n_a} ; \quad (1)$$

where: N - the number of reactant converted or product produced; n_a - the number of active sites; t - reaction time.

TOF is considered a universal characteristic for quantitative comparison of catalysts [3, 8-11]. When calculating TOF, it is assumed that all active sites on the catalyst either have the same activity, or one type of active site is dominant and is decisive.

In addition to TOF, the TON characteristic is used for evaluating catalysts, which is an important parameter for evaluating catalyst stability. In homogeneous and heterogeneous catalysis, TON is a dimensionless number, which is defined as the number of molecules formed per one catalytic site before deactivation. Thus, TON characterizes the maximum product yield achieved from the active catalytic site to the decline in activity for a specific reaction [1-8, 12]. The formula for calculating TON is:

$$TON = \frac{N}{n_a} ; \quad (2)$$

Formulas (1) and (2) for calculating TOF and TON are valuable in that they

make it possible to compare the efficiency of catalysts based on the final result of the catalytic reaction, i.e. by the amount of the product received.

The conflict between TOF and TON is that, being the characteristics of the catalyst, they are calculated from the characteristics of the catalysis process, and not from the characteristics of the catalyst substance. Therefore, although the TOF and TON values make it possible to compare catalysts, they do not provide any clue for the correct selection of catalysts in terms of their chemical composition and their chemical structure.

2. The evolutionary path of formation of TOF and TON

TOF and TON have come a long way. TOF and TON originate from the works of G.K. Boreskov [13, 14]. Boreskov believed that the main factor of the catalytic action is the chemical composition of the catalyst. As activity measure of the catalyst, he proposed to relate the rate of the catalytic reaction to a unit surface area and called the obtained value the Specific Catalytic Activity (SCA). He considered this characteristic to be a constant, which should be determined from the chemical composition of the catalyst and its chemical structure. The principle of the SCA constancy went to the science of catalysis called "*Boreskov's rule*" [15].

Boreskov considered SCA as a basis for the selection of optimal catalysts and their comparison [16]. Later, Boreskov proposed to switch from SCA to atomic catalytic activity (ACA), referring the value of catalytic activity to the surface concentration of those atoms that determine this activity [16, 17].

M. Boudart, who first used a characteristic with the name "turnover number" to compare catalysts by analogy with enzymatic catalysis [18], carried out in-depth studies to find a measure of the activity of catalysts. Then he introduced the term "turnover rate" [3]. As a result of long-term changes and refinements, the "*Boreskov's rule*" and M. Boudart's terms were finally transformed into a characteristic with the term "*turnover frequency (TOF)*" [2], which was included in the IUPAC Gold Book. TOF has been widely used in catalysis for many decades and even entered textbooks on catalysis [19-21]. The calculated TOF value under a fixed set of reaction conditions has become a reliable way to compare data obtained on catalysts in different laboratories [4, 8-11].

Nevertheless, the problems associated with the determination of TOF and TON in various types of catalysis and their calculation still remain unresolved. If the researcher gives the values of TOF and TON, then additional information is needed about the conditions under which their values were obtained [22]. In recent years, the problems of TOF and TON have been studied in most detail in [8-10, 23]. In [8, 23], an attempt was made to clarify the concepts of TOF and TON, it was proposed to give them new definitions and normalize their values in order to avoid confusion when using them. The standard TOF^0 and standard TON^0 are received. An energy method for calculating TOF has been proposed. The problem of TOF was also identified, which is that this characteristic is determined from the characteristics of the catalysis process, but should be determined from the characteristics of the catalyst substance. In [8], Kozuch and Martin even a bold assumption was made that someday the catalysts will be listed in a standard table in accordance with their kinetic behavior, and this standard table can be used when choosing catalysts.

Until now, those important characteristics of the catalyst substance, which would make it possible to compare different catalysts, remain unknown. At present, TOF as a characteristic of catalysts is determined not from the characteristics of the catalyst substance, but from the characteristics of the catalysis process (formula (1)). Formula (1) allows you to get the TOF value, but does not reveal its essence. It is possible that the main result of the theory of catalysis should not be the indirect calculation of TOF from the catalysis process, but its direct calculation from the characteristics of the catalyst substance. The ideal conclusion to the TOF story would be a standard table of catalysts according to their kinetic behavior, as it was suggested in [8].

As you can see, TOF and TON have not yet fully completed the path of their formation, both in the content part and in the methods of obtaining [8, 11, 22]. Their formulations differ in various types of catalysis; the characteristics of the catalyst substance suitable for their calculation remain unknown. Probably, these should be such characteristics of a substance that directly affect the mechanism of catalysis itself. Revealing such characteristics of catalysts would make it possible to obtain

not only the TOF and TON values, but also to reveal the secrets of the mechanisms of catalytic reactions.

3. Problems of calculating TOF and TON values

It is desirable that TOF and TON, as characteristics of the activity of catalysts, can be calculated based on the chemical composition and structure of the catalyst, and not only from the catalysis process according to formulas (1) and (2). Let us consider how reasonable is the determination of TOF and TON using the characteristics of the catalysis process instead of the characteristics of the substance. This state of affairs with TOF and TON resembles the situation with Ohm's law: $I = U/R$, where: I - electric current, U - voltage, R - resistance. From Ohm's law, it follows that $R=U/I$. This formula gives only the value of R , but does not reveal the essence of this characteristic. It is not entirely correct to determine that resistance is the ratio of voltage to current. This formulation would seem to be confusing, since the resistance R is a constant in Ohm's law, it does not depend on voltage or current, but is exclusively a characteristic of the substance from which the resistor is made. There is the second formula for determining R from the characteristics of a substance, it is well known ($R = \frac{\rho \cdot l}{S}$). Thus, there are two ways of calculating R in Ohm's law. The second formula, besides the R value, gives a lot of other useful information about this constant. This formula is more important and more informative than $R = U/I$. But this does not mean that the resistance value cannot be calculated as the ratio of the measured voltage to the value of the measured current. This is what they do in practice, when instead of directly determining the value of resistance from the characteristics of a substance, an indirect method is used and the characteristics of the process are used to calculate it. This is an example of how a quantity that is determined only by the characteristics of a substance can be obtained by calculation from the characteristics of the process. This is not the only example in science where the accepted formulation of something, or even the absence of formulation, is not an obstacle to practice. Nobody knows what gravity is, but this does not interfere with the application of the law of gravity in practice and determining the value of the gravitational constant from the force formula, since

there is no direct formula for calculating the gravitational constant from the characteristics of space-time [24].

We have considered an example of calculating the value of resistance in Ohm's law in order to demonstrate a similar, but more complicated situation with the calculation of TOF in a catalysis phenomenon, which is more complex than Ohm's law. This problem of catalysis was already outlined in the works of Boreskov, where it was pointed out that it was necessary to calculate the SCA from the chemical composition of the catalyst and its chemical structure [13-16]. Until now, this problem remains relevant and is periodically raised in discussions [8, 25]. As noted in [8], this discussion is still far from complete. Problems and misunderstandings associated with the determination and calculation of TOF occur primarily because the performance related to the catalyst is not determined from the catalyst parameters. This raises doubts about the method for calculating TOF without using the characteristics of the catalyst material. The problem will cease to exist if, in addition to formula (1), the second way of calculating TOF from the characteristics of the catalyst substance is found, as is done for R in Ohm's law. In this case, it is necessary to prove that both methods of calculating TOF are equivalent, that we are talking about the same characteristic. This is necessary in order not to get the impression that there is a comparison of "apples and oranges" [8, 25]. Such a second way of calculating TOF, in addition to clarifying its numerical value, would help to reveal the essence of this characteristic and to clarify its relationship with the mechanism of catalysis. But since there is still no such direct method of calculation, it is necessary to calculate its value indirectly from the values available in the process of catalysis - the amount of the produced product, the number of active sites of the catalyst and the time of catalysis.

As you can see, the concept of TOF and TON cannot be considered complete until there are no analytical ratios for their direct calculation using the characteristics of the catalyst substance. This has become one of the problems of catalysis, which still does not find a solution since the appearance of the first works by G.K. Boreskov and M.Boudart [13, 14, 18] . As noted by G. Lente in [25]: "A full characterization of catalytic activity can and should be made by determining the rate

law of the catalyzed process”.

Let us designate the way to solve this problem, which was formulated in [25]. The law of the rate of catalysis, as a tool for calculating TOF, can be obtained only on the basis of knowledge of the real mechanism of catalysis. In the mechanism of catalysis, it is necessary to identify such characteristics of the catalyst substance that are essential for the implementation of this mechanism. These characteristics will be the desired parameters for comparing different catalysts. Therefore, in order to obtain the equation of the rate of catalysis for the analytical calculation of TOF from the characteristics of the catalyst, and not from the characteristics of the catalysis process, an adequate model of the mechanism of heterogeneous catalysis is required. To clarify the mechanism of catalysis, let us consider the role of electrons in heterogeneous catalysis.

4. The role of electrons in heterogeneous catalysis

Ostwald [26] was the first to suggest the important role of electrons in catalysis. Ostwald drew attention to the fact that good catalysts have a common property - they easily emit electrons from their surface. Active catalysts tend to emit significant amounts of electrons, which affects their efficiency [26].

Close ideas about the role of electrons in catalysis were expressed about 85 years ago by L.V. Pisarzhevsky. He put forward a hypothesis about direct transitions of electrons between reactants in catalytic reactions [27].

The mechanism of catalysis, in which an important role is assigned to the transfer of electrons, was pointed out by S.Z. Roginsky. He divided all catalytic processes into groups depending on the presence of free electrons in the catalyst and on the ability of the catalyst to act as an electron donor [28].

It is noted in [29] that the efficiency of the catalyst correlates with its electronic state, and in paperwork [30] it is shown that a change in the electron density of the catalyst directly affects the TOF value.

As noted in [31], the transfer of electrons between a solid catalyst and reagents is one of the important factors of catalysis, which must be taken into account, since it belongs to the rate-limiting stage that determines the rate of the catalytic reaction.

An example showing the decisive role of electrons in catalysis is the discovery

of a new generation of catalysts - metal-free organic catalysts [32, 33]. A new idea has been implemented in design of organocatalysts. Instead of a metal active center, an organic active center was synthesized without the use of metal, which is capable of donating and accepting electrons. The realization of the donor-acceptor function by organocatalyst organic active center is the key reason for its catalytic activity.

In [34–37], the attempts were made to understand the role of electrons in the catalytic reaction and to create an electronic theory of catalysis. Despite the fact that the mechanisms of electron transfer were studied in [34 - 37], they did not pay due attention to the effect of electrons on the oxidation state of the active centers of the catalyst. An important role in the catalysis of the oxidation state of the reactants has not been identified. Changes in their oxidation state during the catalytic reaction and the effect of a change in the oxidation state on the catalytic reaction rate have not been investigated. Therefore, these studies did not lead to the creation of a theory of catalysis and did not allow obtaining the main characteristics of catalysis depending on the characteristics of the catalyst substance.

5. Influence of the oxidation state of catalysts on TOF

There are many catalytic reactions in which catalysts act as electron donors or acceptors. Their activity depends on the oxidation state of the active sites of catalysts. For example, copper in a low oxidation state Cu^+ makes it possible to obtain hydrocarbons by reducing carbon dioxide. Copper in this case plays the role of an electron donor. During the course of the catalysis reaction, there is a change in the oxidation state of copper and, accordingly, a change in the electronic state of the catalyst [38].

In the Fischer – Tropsch process, cyclic changes in the oxidation state of nickel occur. Under the influence of hydrogen, nickel lowers its oxidation state from +2 to 0, that is, it is reduced to nickel. The formed nickel interacts with carbon monoxide to form carbide, where nickel is again oxidized to the +2 degree [39].

In the oxidation reaction of hydrocarbons on a vanadium V_2O_5 catalyst, the transfer of electrons between the reacting molecules and the catalyst is involved in catalysis mechanism. In this case, there is a change in the electronic properties of the catalyst surface and a change in the oxidation state of vanadium [31, 40].

These examples of catalytic reactions indicate that, for all their variety, they have common features. These are the signs: a) cyclic change in the oxidation state of the catalyst; b) change in the oxidation state of the reactants; c) change in the redox state of the reaction medium. The very process of heterogeneous catalysis occurs with the participation of electrons, and the mechanism of catalysis involves the transfer of electrons. This is accompanied by changes in the oxidation states of the active sites of the catalyst. In the course of catalysis, there is a unidirectional change in the oxidation state of the reactants and a cyclic change in the oxidation state of the catalyst due to the transfer of electrons between the catalyst and the reactants.

The fact that the mechanisms of catalysis are somehow connected with atoms' oxidation state on the surface of the catalyst is indicated in his studies by G.A. Somorjai. At the same time, he notes that the oxidation states of surface atoms are important characteristics of catalyst activity [41]. This emphasis on a direct relationship between the oxidation state and catalyst activity is an important clue for finding a way to calculate TOF from catalyst characteristics.

The oxidation state of the catalyst atoms, as well as the cyclic changes in the oxidation states of the active sites of the catalyst during the catalytic reaction, can act as parameters that determine the TOF value. The correct choice of the model of the catalytic reaction mechanism will help us to understand this dependence and identify the factors that determine the TOF value.

6. Choice of the mechanism of heterogeneous catalysis

The question of the nature and features of the interaction between the catalyst and the reagents is central when considering the mechanisms of heterogeneous catalytic reactions. Several models of the mechanism of a heterogeneous catalytic reaction are known. According to the Langmuir – Hinshelwood mechanism, the formation of products occurs as a result of elementary reactions between adsorbed particles [42]. The Eley-Rideal mechanism is a heterogeneous reaction mechanism that includes the stages of interaction between an adsorbed particle and a particle in a homogeneous phase. According to this mechanism, a molecule, without being adsorbed, immediately enters into reaction with an adsorbed molecule or atom

directly from the gas phase [42]. As we can see, the Langmuir – Hinshelwood and Ely – Reedil models do not take into account the electron transfer mechanism and, accordingly, the stages of changing the oxidation state of the catalyst and reagents are completely out of consideration.

A closer mechanism that takes into account the participation of electrons in the catalytic reaction is the Mars – van Krevelen redox mechanism [42, 43], which is used to describe the kinetics of oxidation reactions. This model is based on the fact that an active oxygen form is presented in the catalyst, which is involved in interaction with the oxidizable reagent. As a rule, the limits of applicability of the mechanism and the Mars – van Krevelen equation are associated with the presence of active lattice oxygen in the catalyst, which is understood as oxygen of the oxide. The reactive oxygen form directly participates in the interaction with the oxidizable reagent in the reduction stage and is regenerated in the reoxidation stage. In the Mars – van Krevelen model, both stages are considered practically irreversible; the model is not thermodynamically consistent. This narrows the scope of its application. These disadvantages of the Mars – van Krevelen mechanism are indicated in [44].

The main drawback of the Mars – van Krevelen mechanism is that it does not take into account the depth of change in the oxidation state of the catalyst and this characteristic is not explicitly included in the equation, and the change in the oxidation state of the reactants is completely out of consideration.

7. Donor-acceptor mechanism of heterogeneous catalysis

Thus, in well known models of catalytic mechanisms, the electron exchange stage of the catalytic process is not well represented. The decisive role of the electron exchange stage is that it performs a preparatory function that precedes the direct chemical interaction of the reagents. At this stage, a change in the charge state of the catalyst and reagents occurs, and this affects the adsorption rate, and the dissociation rate, and the desorption rate.

The foregoing forces us to look for a different explanation for the interaction of the catalyst and reagents and to search for such type of interaction in which electrons should play the main role. A new model of the mechanism of the

heterogeneous catalytic reaction is needed, that take into account the presence of an additional electron-exchange stage. The main contender for a new type of interaction in heterogeneous catalysis is the donor-acceptor interaction. Donor-acceptor interaction is a special case of electromagnetic interaction - one of the four fundamental interactions in nature. The donor-acceptor interaction is accompanied by the exchange mechanism of electric charge transfer between the catalyst and the reagents [45]. Let us conditionally call this mechanism of heterogeneous catalysis the electron donor-acceptor mechanism. In it, the staged mechanism of catalysis is supplemented by a cyclic electron-exchange stage. At this stage, the oxidation state of active sites of the catalyst decreases with the capture of electrons from the reagent. This is an acceptor component of the stage. At the same stage, the oxidation state of active sites of the catalyst increases with a transfer of electrons from the catalyst to the reagent. This is the donor component of the stage.

For the first time, the model of donor-acceptor interaction of a catalyst and reagents was considered by Thomas Martin Lowry (1925 - 1928). He formulated the idea of a proton donor-acceptor mechanism as applied to homogeneous catalytic processes. According to Lauri, acid-base catalysis is due to the alternate interaction of the reagent molecule with the catalyst and it consists in the addition of the proton received from the donor catalyst by the reagent molecule and the subsequent release of protons to the acceptor catalyst [46]. Later, at the suggestion of Whitmore F., this mechanism of catalysis was called the ion-carbonium mechanism [47, 48].

The proton donor-acceptor mechanism does not include electron transfer processes and does not take into account the change in the oxidation state of the active centers of the catalyst. Its range of applicability is limited to homogeneous catalysis. This mechanism is not typical for heterogeneous catalysis. In heterogeneous catalysis, the exchange mechanism of electric charge transfer between the catalyst and the reactants is carried out by means of negatively charged elementary particles - electrons.

The electronic donor-acceptor mechanism of heterogeneous catalysis is caused by the alternate interaction of the reactants with the catalyst and consists in the addition of the electrons received from the catalyst by the reactant and the transfer

of electrons from the reactant to the catalyst. In this case, the catalyst undergoes a cyclic change in the oxidation state of active centers. To implement this function, the catalyst must have a special property - it must easily change the oxidation state of cations within wide limits. This is one of the main requirements that must be met when selecting catalysts for heterogeneous catalysis.

In the donor-acceptor mechanism of catalysis, electrons are direct participants in catalysis process and behave as an active factor of heterogeneous catalysis. In this article, we consider the role and place of electrons in the donor-acceptor mechanism of heterogeneous catalysis without detailing the features of electron transfer. The detailed mechanism of electron transfer between reagents and solid catalysts can be found in works on kinetics of electron transfer in donor-acceptor interactions or, for example, in [31].

8. New formula for calculating TOF

Based on the model of the donor-acceptor mechanism of heterogeneous catalysis, an equation for the rate of catalytic reaction was obtained [49]. The mathematical representation of the equation for the rate of catalysis has the form [49]:

$$v = \frac{e \cdot n_a \cdot |k_1 - k_2|}{F \cdot (\tau_D + \tau_A) \cdot |z_1 - z_2|}; \quad (3)$$

where: v is the rate of catalytic reaction (mol/s); n_a - the number of active sites of the catalyst involved in the reaction; F - is the Faraday constant; e - is the electron charge; τ_D - the time of the donor half-cycle of catalysis; τ_A - the time of the acceptor half-cycle of catalysis; k_1 - is the initial degree of catalyst oxidation; k_2 - the final degree of oxidation of the catalyst; z_1 - the oxidation state of the reagent in original product; z_2 - the oxidation state of the reagent in the final product.

In the equation for the rate of catalysis, an electron is present as the main actor in the donor-acceptor interaction of the catalyst with reagents. The electron in the formula is presented in the form of a fundamental physical constant - an elementary charge e . Equation (3) contains the Faraday constant F . It is known that the Faraday

constant is included in the Faraday law and in the Nernst equation. Catalysis turned out to be another phenomenon where in equations this constant is present. Formula (3) takes into account the oxidation states of the active sites of the catalyst k_1 , k_2 and the oxidation states of the reactants z_1 , z_2 . Formula (3) includes the modulus of difference in oxidation states, since the initial oxidation state can be both in the field of high oxidation state values and in the field of low values.

Analysis of formula (3) shows that it includes two combinations of quantities. One combination of quantities is the ratio of total electric charge of the active sites of the catalyst to the Faraday constant:

$$\frac{e \bullet n_a}{F} ; \quad (4)$$

The second combination of quantities has the dimension of frequency and includes the time of donor half-cycle of catalysis τ_D and the time of acceptor half-cycle of catalysis τ_A , as well as the characteristics of the catalyst substance and reagents in the form of difference in their oxidation states:

$$\frac{|k_1 - k_2|}{(\tau_D + \tau_A) \bullet |z_1 - z_2|} ; \quad (5)$$

The second combination of values (5) in formula (3) is nothing but TOF:

$$TOF = \frac{|k_1 - k_2|}{(\tau_D + \tau_A) \bullet |z_1 - z_2|} ; \quad (6)$$

As a result, a new formula for calculating TOF was obtained, in which, instead of the characteristics of catalysis process, the parameters are characteristics of the substance. The proof that Formula (6) is equivalent to Formula (1) is given below (chapter 10).

9. The need to revise the status of TOF in catalysis

Formula (6) shows that the TOF value depends on a set of parameters. As the characteristics of a substance, it includes the oxidation states of the substances participating in the reaction. The new formula for calculating includes TOF and catalyst characteristics ($k_1 - k_2$), and the characteristics of reagents ($z_1 - z_2$), and the parameters of donor-acceptor interaction, τ_D , τ_A . In other words, correlation (6) shows that TOF incorporates not only the characteristics of catalyst substance, but

also the characteristics of the reactants, and also takes into account the mechanism of interaction between the catalyst and reactants. Equation (6) shows that TOF is not a complete and unambiguous characteristic of the catalyst, as was commonly believed. This does not mean that TOF is not suitable for assessing the effectiveness of catalysts, but it should be borne in mind that the TOF value only partially depends on the characteristics of the catalyst substance. TOF is more than a catalyst characteristic. Formula (6) indicates the need to revise the TOF status in catalysis. TOF more claims to be an integral characteristic of the catalysis process, taking into account the donor-acceptor interaction of the catalyst with the reagents. TOF refers not so much to the catalyst, but more to the “catalyst+reagents” system and its content is directly related to the mechanism of catalysis. In this regard, it becomes urgent to search for another measure instead of TOF for comparing the activity of catalysts, which should depend only on the characteristics of the catalyst substance.

In formula (6), the inverse ratio $(z_1 - z_2)/(k_1 - k_2)$ is the number of elementary acts of electron transfer required to form one molecule of the target product. Note that this inverse ratio of oxidation states shows a connection and commonality with the stoichiometric Horiuti numbers, which are characteristic of electrode processes kinetics [50 - 52].

Formula (6) provides another way to calculate TOF in addition to Formula (1). Formula (6) reveals the meaningful essence of TOF and shows that this characteristic is directly related to the donor-acceptor mechanism of catalysis. As we can see, the application of electronic concepts to heterogeneous catalysis and the choice of the donor-acceptor mechanism of catalysis led to quantitative results showing that TOF is a function not only of the electronic state of the catalyzing surface, but also a function of the catalysis mechanism and a function of the oxidation state of the reactants.

10. Two ways to calculate TOF and TON

Let us give a proof that formula (6) is equivalent to formula (1). We will use the equation for calculating the yield n of the catalytic reaction [53]. The amount (mol) of the obtained target product n (reaction yield) directly follows from the ratio (3):

$$n = \frac{e \cdot n_a \cdot t \cdot |k_1 - k_2|}{F \cdot (\tau_D + \tau_A) \cdot |z_1 - z_2|}; \quad (7)$$

where: t - is the time of catalysis.

The ratio for the rate of the catalysis reaction (v), depending on TOF, has the form:

$$v = \frac{e \cdot n_a \cdot TOF}{F}; \quad (8)$$

The amount (mol) of the obtained target product (n), depending on TON, is determined from the following ratio:

$$n = \frac{e \cdot n_a \cdot TON}{F}; \quad (9)$$

In formula (9), TON is represented by the following ratio:

$$TON = \frac{|k_1 - k_2| \cdot t}{(\tau_D + \tau_A) \cdot |z_1 - z_2|}; \quad (10)$$

Formulas (8) and (9) show that the key parameters for calculating such characteristics of catalysis as the reaction rate (v) and the reaction yield (n) are TOF and TON. These formulas (8) and (9) are structurally very similar and exhibit striking symmetry. From equations (3), (6) - (10), taking into account the fact that $F = eN_A$, important equivalent relations for TOF and TON follow :

$$TOF = \frac{n \cdot N_A}{t \cdot n_a} = \frac{|k_1 - k_2|}{(\tau_D + \tau_A) \cdot |z_1 - z_2|}; \quad (11)$$

$$TON = \frac{n \cdot N_A}{n_a} = \frac{|k_1 - k_2| \cdot t}{(\tau_D + \tau_A) \cdot |z_1 - z_2|}; \quad (12)$$

where: N_A - Avogadro's number.

Equations (11) and (12) are the proof of equivalence of formulas (1) and (6) and formulas (2) and (10). The equivalence of these formulas equalizes two approaches for calculating TOF and TON - one using the characteristics of the catalysis process, the other using the characteristics of the catalyst substance and reagents. Therefore, there is no reason to question the validity of using the characteristics of the catalysis process for calculating TOF and TON. The only

unexpected thing was that TOF and TON are not complete and unambiguous characteristics of the catalyst, therefore, for the correct application of these characteristics, a revision of their status in catalysis is required.

Equations (11) and (12) imply that the TOF and TON values can be calculated in two equivalent ways. The first way is using the characteristics of the catalysis process. The second method is using the characteristics of the catalyst substance and reagents. These are two equivalent calculation methods that lead to the same result. The first method allows you to get the TOF value without revealing its nature. The second method allows one to calculate TOF using the following characteristics: catalyst oxidation states, reactant oxidation states, and the duration of the donor-acceptor stage of catalysis ($\tau_D + \tau_A$). Time ($\tau_D + \tau_A$) is a cycle of change in the oxidation state of the catalyst. The time is determined by the rate of electron transfer from the catalyst to the reagents and back during the donor-acceptor interaction.

As you can see, the second method for calculating TOF and TON is more informative than the well-known first method. Formulas (6) and (10) show the donor-acceptor mechanism of catalysis based on the cyclic transfer of electrons from the catalyst to the reactants and vice versa. In particular, the second calculation method shows that the TOF and TON values depend on the oxidation state of the substance. It turns out that oxidation states are such important characteristics of a catalyst substance that they directly affect the mechanism of catalysis; moreover, the oxidation states of a catalyst initiate the mechanism of catalysis itself. This important and defining moment has not received enough attention in studies of the phenomenon of catalysis.

When obtaining new analytical ratios for calculating TOF and TON, we set out to reveal which catalyst parameters these characteristics depend on and to determine how the revealed parameters affect their numerical values. The task was to obtain compact records of new formulas for calculating TOF and TON. In this article we do not consider methods for calculating the parameters included in formulas (11) and (12) or methods for their experimental obtaining. We also did not touch on such important issues as the influence of reagent concentration, pressure and temperature

on TOF and TON values. This is beyond the scope of this article and is the task of a separate study. Some information about them can be found in research in the field of quantum chemistry. For example, the kinetics of electron transfer during donor-acceptor interaction and redox transformation of electron carriers are considered in detail in [31, 54 - 58]. Methods for determining the number of active sites of catalysts are described in [11, 59, 60]. Note that such parameters of the catalysis process as the concentration of reagents, pressure and temperature affect the TOF and TON values through their influence on the time of electron transfer ($\tau_D + \tau_A$) and on the depth of change in the oxidation state of the active sites of catalyst ($k_1 - k_2$).

In practice, to calculate TOF and TON, it is convenient to use the first method of calculating them and apply the following ratios:

$$TOF = \frac{n \cdot N_A}{t \cdot n_a} ; \quad (13)$$

$$TON = \frac{n \cdot N_A}{n_a} ; \quad (14)$$

where: n - is the number of moles of the resulting product; n_a/N_A - is the number of moles of active catalyst atoms; t - reaction time, N_A - Avogadro's number.

Here you can see the complete coincidence of formulas (13) and (1) and formulas (14) and (2). The values of n and t included in these formulas are easily determined in the practice of catalysis. The n_a value is easily determined only for homogeneous catalysts. In heterogeneous catalysis, obtaining n_a is more laborious process, but also available for determination [11]. More details on the methods for calculating and measuring the active sites of catalysts can be found in [9 - 11, 59, 60].

Instead of the time interval ($\tau_D + \tau_A$) in the formulas for calculating TOF and TON (6), (10), (11), (12), you can use its inverse value - the frequency of the change in the oxidation state of active sites of the catalyst f_{D-A} . Then the ratio for TOF will take the form:

$$TOF = \frac{f_{D-A}}{\sigma} ; \quad (15)$$

Here σ - is the stoichiometric Horiuti number:

$$\sigma = \frac{|z_1 - z_2|}{|k_1 - k_2|}; \quad (16)$$

A deeper study of the ratio between TOF and Horiuti numbers requires special research. Here we note that the frequency f_{D-A} is the main driving frequency for the catalytic reaction. Frequency f_{D-A} may be more readily measurable in catalysis practice than calculating a value $(\tau_D + \tau_A)$. The f_{D-A} value can be obtained by measuring the frequency of the change in electrical potential of the catalyst, the value of which changes synchronously with the change in the oxidation state of active sites.

The evidence that the TOF and TON values can be calculated in two ways and the equivalence of the two calculation methods gives more confidence to the traditional method of deriving them from the characteristics of the catalysis process according to formulas (1) and (2). The first method (1), (2) makes it easy to obtain their values from the characteristics of the catalysis process. The second way (6), (10) is more informative. It reveals the essence of TOF and TON. The second method for calculating TOF and TON shows how the oxidation states of the catalyst and reagents affect their values and indicates the ways and possibilities of controlling the TOF and TON values, both through the correct choice of catalyst and through the external influence on the catalyst, which will be shown below (chapters 13,14).

11. The oxidation states of catalyst and reagents are the main factors affecting the rate of catalysis

Equations (6), (7), (10), (11), (12) show that the oxidation states of the catalyst and reagents are the main parameters for determining the three most important numerical characteristics of catalysis process - the reaction yield n , TOF and TON. The role and place of the oxidation states of the participants in the catalytic process has been underestimated in catalysis. It can now be seen that the role of oxidation states is decisive. The oxidation states of its active sites are the characteristics of the catalyst that directly affect catalysis mechanism itself and even initiate the donor-acceptor mechanism of the process. The characteristics of reagents that affect the catalytic mechanism and determine the rate of the catalytic reaction

are also their oxidation states. Three most important characteristics of the catalysis process (TOF, TON, reaction yield n) turned out to be dependent on the oxidation state of the catalyst and reagents. The revealed interrelation of the oxidation states of catalyst and reagents with the Horiuti numbers and the influence of the Horiuti numbers on the TOF value can be useful for finding reaction routes and for creating a theory of selectivity. Thus, the redox status and redox transformations of the catalyst and reagents are the determining factors of catalysis, which directly affect such characteristics of catalysis process as the rate of catalysis, the yield of catalysis reaction, TOF and TON values. Without taking into account the redox status and redox transformations of catalyst and reagents, an adequate description of catalysis process is impossible.

In our opinion, concepts such as the oxidation state, oxidation rate, the range of changes in the oxidation state not only acquire the status of the most important characteristics for the participants in the catalytic reaction, but should also become the central concepts of catalysis. Such shift in emphasis to the important role of oxidation states in catalytic reaction participants may require adjustments to the modern philosophy of catalysis and even touch upon the terminology of catalysis. Electrons claim to be the main acting factor in the donor-acceptor mechanism of heterogeneous catalysis. The exchange of electrons between the catalyst and the reactants leads to changes in their oxidation states. The time of electron transfer from the donor to the acceptor and back sets the main and defining parameter of catalysis - the frequency of the oscillation of the oxidation state of active sites of the catalyst f_{D-A} .

Since, as shown above (chapter 9), TOF is not a complete and unambiguous characteristic of a catalyst, then instead of TOF, the frequency f_{D-A} can be used as a measure for comparing the activity of catalysts. The oscillations frequency of redox state of the active sites of catalyst was called the redox frequency (ROF) of the catalyst. The formula for calculating the ROF value is:

$$ROF = f_{D-A} = \frac{n \cdot N_A \cdot \sigma}{t \cdot n_a} ; \quad (17)$$

where: σ - is the stoichiometric number of Horiuti.

Unlike TOF, which is a characteristic of the “catalyst+reagents” system, ROF, more than TOF, depends on the characteristics of the catalyst substance. In this regard, ROF is more suitable for evaluating and comparing the activity of catalysts and, in the future, can replace TOF in catalysis. In turn, the status of TOF in catalysis should be reviewed and replaced with a more fundamental one.

12. TOF and the Sabatier principle

There is a limitation on the activity of catalyst and on the rate of the catalytic reaction, which sets an upper limit on the efficiency of catalyst and an upper limit on the rate of reaction. Catalysts that satisfy the Sabatier principle [61] are effective. Sabatier discovered that the best catalysts must bind atoms and molecules with an intermediate strength - not too weak to be able to activate the reactants, and not too strong to be able to desorb products. The fastest achievable reaction rate is called the Sabatier maximum. The Sabatier principle is considered one of the most important in catalysis. Thanks to the catalyst, the reaction is accelerated, but it cannot proceed faster than allowed by the Sabatier principle [59].

The use of the oxidation state of the active sites of catalyst as the main parameter of the catalysis process allows one to give a new broader interpretation of the Sabatier principle and turn this principle into a quantitative measure of limiting catalyst activity. The extended status of the Sabatier principle directly follows from the new relation (6) for calculating TOF, which shows the influence of this principle on the TOF value, as the main measure of catalyst activity today.

From equation (6) for TOF and equation (10) for TON it follows that the most effective catalyst will be the one that is capable of changing the oxidation state over a wide range during the catalysis cycle. In this case, the catalyst must be an active electron donor during a certain time of catalysis cycle, and during the other part of the catalysis cycle must be an active electron acceptor. For a particular catalyst, these requirements are conflicting. For this reason, for each catalyst there is a limit of its effectiveness, which follows from the Sabatier principle, in which the catalyst should be both - not strongly active donor and not a strongly active acceptor. In relation to equations (6) and (10), this means that the Sabatier principle imposes a constraint on the value $(k_1 - k_2)$, thereby limiting the values of TOF and TON. In

other words, the Sabatier principle imposes a restriction on multielectron transitions upon a change in the oxidation state of the active sites of catalyst, which sets the upper bound for the TOF value. Our conclusion that the application of the Sabatier principle imposes a limitation on the TOF value is in good agreement with recent studies [62], where for the selection of potential catalysts instead of volcanic charts of Balandin A.A. [63, 64], volcanic charts TOF (“TOF volcanoes”) were used.

Equations (6) and (10) for calculating TOF and TON allow using the Sabatier principle in a different aspect of its application. Since it directly limits the TOF and TON values, the Sabatier principle becomes a quantitative measure from a recommendation rule for evaluating a catalyst. Equations (6) and (10) show that the application of the Sabatier principle to specific parameters - to the oxidation states of the catalyst, leads to a limitation of the TOF and TON values, i.e., the Sabatier principle turns from a qualitative assessment of a catalyst into a quantitative assessment. This is a convenient addition to the volcanic charts of A.A. Balandin [63, 64]. New knowledge is the fact that the principle of Sabatier is able to provide not only quality, but, in a sense, a quantitative estimate of the catalyst, resulting in a limitation of numerical values of TOF and TON.

13. Overcoming of Sabatier maximum

Quite recently, a condition has been found under which heterogeneous catalysis can occur at a rate significantly exceeding the Sabatier maximum [30, 65-71]. This became possible due to the frequency of external influence on the catalyst, in which the catalyst passes from a static state to a dynamic state. When the frequency of the external action coincides with the natural frequency of the catalytic reaction, catalytic resonance occurs. In this case, a significant increase in the TOF value is observed [30].

Let us consider the possibility of controlling the TOF value and the possibility of exceeding the Sabatier maximum using the example of equations (6) and (15). An increase in catalyst activity is realized when the frequency of external action coincides with the cyclic frequency of changes in the redox state of the catalyst or exceeds it:

$$f_e \geq f_{D-A}; \quad (18)$$

where: f_e - frequency of external influence on the catalyst.

Increasing the TOF value can be achieved by changing the two values in formula (6). This is an increase in the value $(k_1 - k_2)$ and a decrease in the value $(\tau_D + \tau_A)$. Both quantities can be controlled by external influences. Let us demonstrate this by the example of the coincidence of the frequency of external action f_e with the cyclic frequency of change in the redox state of catalyst f_{D-A} , i.e. let us consider the case when catalytic resonance is realized.

Under the influence of a variable external influence on the catalyst, there is a periodic change in the electronic state of its surface. For example, if the external influence is an electrical potential, then the catalyst will acquire additional electrical potential. This provides an easier transfer of electrons from the catalyst to the reagent in that part of the cycle where the external negative potential acts. In that part of the cycle, where the external positive potential will act, the catalyst will effectively capture electrons from the reactant and will act as an effective electron acceptor. As a result, two mutually exclusive catalyst states - a state with a high electron-donor activity and a state with a high electron-acceptor activity will be separated in time. This allows two processes - the process of transferring electrons from the catalyst to the reagent and the process of reducing the catalyst to its initial state - to proceed independently at the maximum speed, i.e., the Sabatier principle does not apply to this situation.

The amplitude of the external action on the catalyst affects the change in electrical potential of the active centers. With an increase in the amplitude, the range of changes in the oxidation state of active centers increases, which leads to an increase in the difference $(k_1 - k_2)$ in formula (6). This, in turn, leads to a decrease in the value $(\tau_D + \tau_A)$ due to more efficient electron transfer. As a result, the TOF value increases significantly. For example, instead of one-electron transitions ($(k_1 - k_2) = 1$), which follows from the Sabatier principle in the absence of an external action, under an external action, many-electron transitions are realized, at which $(k_1 - k_2) \gg 1$. Expansion of the range in the oxidation state change of catalyst active sites

(increase in the difference $(k_1 - k_2)$) is proportional to the amplitude of external influence on the catalyst.

14. TOF external synchronization effect

It follows from equations (6) and (15) that an even greater effect of increasing TOF will be achieved if the frequency of the external action exceeds the cyclic frequency of the change in the redox state of catalyst:

$$f_e \gg f_{D-A}; \quad (19)$$

In this case, the frequency of changes in the redox state of the catalyst will be determined not by natural frequency f_{D-A} , but by the frequency of the external action f_e . Accordingly, the TOF value becomes dependent on the frequency of the external stimulus:

$$TOF = \frac{f_e \cdot |k_1 - k_2|}{|z_1 - z_2|}; \quad (20)$$

This effect, when the frequency of the change in the redox state of the catalyst is imposed and determined by the external frequency, we call the “TOF external synchronization effect”. With this effect, the greatest increase in the TOF value is realized. Note that with a gradual increase in the frequency and amplitude of external action, an abrupt increase in TOF will occur, since many-electron transitions will occur. The discrete TOF spectrum has an upper limit and is determined by the maximum variation range $(k_1 - k_2)$.

Thus, by changing the amplitude of the external influence on the catalyst, it is possible to control the range of changes in its oxidation state $(k_1 - k_2)$, achieving the condition: $(k_1 - k_2) \gg 1$. By increasing the frequency of external action, the “TOF external synchronization effect” is achieved, which significantly reduces the time of changing the redox state of the catalyst. A simultaneous increase in the amplitude and frequency of external stimulus leads to the greatest increase in the TOF value, which allows one to exceed the Sabatier maximum.

15. The list of oxidation degrees of the chemical elements - a new tool for catalysts selection

When studying catalysts, their effect on four parameters of catalysis process is usually considered: the yield of the catalysis reaction, TOF, TON, and

selectivity. The obtained relations (7), (6), (10) show that three of the four important parameters of catalysis depend on the oxidation state of the catalyst and reagents. The oxidation state as a parameter is included in formulas for calculating the reaction yield n (7), TOF value (6) and TON value (10). To achieve high values of these characteristics of catalysis, catalysts are needed that can easily change the oxidation state of cations over a wide range. Therefore, the correct choice of catalyst directly depends on the knowledge of all its possible oxidation states. The oxidation states of elements are actively studied in chemistry. They are important characteristics of chemical elements and are summarized in the table [72]. This means that the list of oxidation states of chemical elements becomes the main tool for the selection of catalysts [72]. This list is constantly updated and supplemented by newly discovered values of oxidation states. For example, it is already known that iron has a maximum oxidation state of plus eight (+8), and a minimum – minus four (-4) [72, 73]. It can be seen from table [72] that ridium, ruthenium, osmium and iron have the widest ranges of oxidation states. It follows from relations (6), (7), (10) that wide ranges of changes in the oxidation states of these chemical elements indicate that they should have high catalytic activity. It is known that both ridium, ruthenium and osmium exhibit high activity, but the belonging of iron to the group of active catalysts is not so obvious. This unexpected conclusion about the high catalytic activity of iron, which follows from the table [72] and equations (6), (7), (10), is in good agreement with the results of recent studies given in [74], where the unique catalytic properties of high-dispersed iron are revealed and the key role of the oxidation state of iron in the activity of the iron catalyst is shown.

The list of oxidation states gives extremely important information for catalysis on the most stable oxidation states, it shows the ranges of changes in the oxidation states of elements and the distribution of the spectrum of oxidation states within the range. The full predictive power of the list of oxidation states of chemical elements for catalysis remains to be find out. But even at this stage, preliminary conclusions can be drawn about the usefulness of this list. In particular, using the table [72], one can predict that:

- the most versatile catalysts will be those chemical elements that have the widest range of oxidation states and are able to easily change the oxidation state of cations over a wide range;
- among cheap catalysts, iron must have high catalytic activity;
- the value of the most stable oxidation state of a chemical element is a hint when choosing a catalyst for the oxidation or reduction reaction;
- suitable for oxidative catalysis are catalysts that have a continuous spectrum of oxidation states in the field of high oxidation states and the most stable oxidation state in the same field;
- suitable for reductive catalysis are catalysts having a continuous spectrum of oxidation states in the field of low oxidation states and the most stable oxidation state in the same field.

The requirement for a continuous spectrum of oxidation states (oxidation states should be a continuous sequence of natural numbers) is due to the fact that the probability of one-electron transitions with a change in the oxidation state of a catalyst is much higher than multielectronic ones. This requirement also follows from the Sabatier principle for a catalyst.

16. Conclusion

Found a new way to calculate TOF using the characteristics of the substance instead of the characteristics of the catalysis process. TOF is considered a characteristic of the catalyst, but it turned out that its value depends not only on the characteristics of the catalyst, but also on the parameters of the donor-acceptor interaction of the catalyst with the reagents and on the characteristics of reagents. In fact, TOF turned out to be not a characteristic of a catalyst, but a characteristic of the “catalyst + reagents” system, which indicates that the current notions about TOF are erroneous. The results obtained indicate the need to revise the TOF status in catalysis. The status of an auxiliary characteristic suitable for evaluating catalysts is not suitable for TOF. It should be replaced by a more significant (possibly fundamental) status affecting the mechanism of catalysis.

For the three most important quantitative characteristics of catalysis (the reaction yield n , TOF, and TON), the dependence of their values on the oxidation state of the

reactants and the oxidation state of active sites of catalyst was established. It remains to find out how the fourth important characteristic of catalysis, selectivity, depends on the characteristics of the catalyst substance. In particular, it is necessary to clarify the dependence of selectivity on the oxidation state of surface atoms of the catalyst. These are the tasks of advanced research. Researchers have faced the problem of selectivity for many years, but no satisfactory theory of selectivity has yet been created [75 - 77]. Selectivity can also be dependent on the oxidation state of the reactants and the oxidation state of the catalyst surface. There is indirect evidence of this. For example, in [75, 78], the selectivity is directly related to the electronic state of the active sites of catalyst, and in [79, 80] it is noted that an increase in selectivity may be associated with an increase in the electron density of the catalyst.

In our opinion, the most important consequence of the results obtained is the possibility of using the table of chemical elements oxidation states for the selection of effective catalysts.

In this regard, I would like to note the forecast of the authors of [8]: “*The debate is far from finished, but it may come the day when the catalyst will be neatly tabulated according to their kinetic behavior, much like the standard thermodynamic tables*”. Even taking into account the fact that TOF includes the characteristics of not only the catalyst, but also the reagents, it turned out that the characteristics of the catalyst and the characteristics of the reagents included in TOF are indeed tabular. These characteristics are found in the table of oxidation states of chemical elements [72]. In our opinion, this bold forecast comes true even in a more advantageous version. There is no need to create a special table of catalysts - it already exists in chemistry and can be used when selecting catalysts.

In this article, we have made an attempt to make our humble contribution to solving one of the central problems of catalysis, identified by G.K. Boreskov and M. Boudart . We deliberately did not avoid sharp wording and, perhaps, made too categorical statements. This was dictated by the desire to stimulate discussion on this topic.

17. Conclusions

1. There are two formulas (1) and (6), which allow two ways to obtain the TOF

value. The equivalence of these formulas is proved. The first method allows one to obtain the TOF value using the characteristics of catalysis process without disclosing its essence. The second method allows the TOF value to be obtained using the characteristics of the catalyst material and reagents. The second method is more informative, it reveals the essence of TOF and indicates the ways and possibilities of controlling its value, both through the correct choice of the catalyst and through external influence on the catalyst.

2. TOF is not a complete and unambiguous characteristic of catalyst activity. The TOF value is only partially dependent on the characteristics of the catalyst material. This is a characteristic of the “catalyst + reagents” system. TOF is more than a catalyst characteristic, its status remains to be studied. The role and place of TOF in catalysis goes far beyond the characterization of catalysts. Its status is more significant - it is an integral characteristic of the catalysis process, which shows how and what parameters of the catalyst substance and reagents affect the mechanism of catalysis.

3. The TOF and TON values directly depend on the oxidation state of the reactants and the active sites of catalyst. The oxidation states are such important characteristics of the catalyst substance and reagents that they directly affect the catalysis mechanism itself; moreover, the oxidation states of the catalyst initiate the catalysis mechanism [81,82]. The key operating factors in the mechanism of heterogeneous catalysis are the redox state of the catalyst and the change in the oxidation state of active sites of the catalyst. These important features of catalysts have received insufficient attention in studies of the phenomenon of catalysis.

4. Instead of turnover frequency (TOF), it was proposed to use redox frequency (ROF) as a characteristic for comparing the activity of catalysts. The formula for calculating ROF is given [83].

5. The Sabatier principle imposes a restriction on multielectron transitions upon a change in the oxidation state of the active centers of catalyst. The Sabatier principle directly limits the TOF and TON values, limiting the range of changes in the oxidation states of the active sites of the catalyst [84-86]. As a result, the Sabatier principle becomes, in a sense, a quantitative measure for limiting the activity of a catalyst.

6. The external synchronization effect of TOF allows you to overcome the Sabatier maximum [82, 84-86].

7. It is proposed to use the list of oxidation states of chemical elements for the selection of effective catalysts. The list of oxidation states of chemical elements can be the main tool for the selection of catalysts.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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