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RESEARCH ARTICLE

Effect of adsorption-catalytic deformation and partial deactivation on the determination of the absolute activity of a liquid phase hydrogenation catalyst

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Abstract

Objectives. *To take into account the change in the number of active sites during the adsorption-catalytic deformation and deactivation of a catalyst surface by means of a catalytic poison when calculating the turnover frequency (TOF) of a hydrogenation catalyst.*
Methods. *The activity was determined by a static method, using a titanium reactor having a volume of 400 mL, an experimental temperature controlled using a liquid thermostat with an accuracy of 0.5 K, with a paddle stirrer rotation speed of 3600 rpm and system hydrogen pressure equal to atmospheric. The consumption of hydrogen used to reduce the model compound was taken into account via the volumetric method. The heats of hydrogen adsorption were determined using a reaction calorimeter with an operating mode close to that of a chemical reactor. After measuring the specific surface area using low temperature nitrogen adsorption, the results were processed using Brunauer–Emmett–Teller theory approximations. Deactivation was carried out by introducing dosed amounts of catalytic poison into the system in titration mode.*

Results. *A kinetic experiment for the reduction of a multiple carbon bond in a sodium maleate molecule using aqueous solutions of sodium hydroxide with additions of monohydric aliphatic alcohols as solvents under conditions of partial deactivation of the catalyst was carried out. The obtained values of heats of hydrogen adsorption on skeletal nickel in the course of the experiment are given. The described approach is used to calculate TOF values taking into account changes in the number of active surface sites during the course of a catalytic reaction and upon the introduction of a deactivating agent. A refined equation for the correct calculation of TOF is proposed along with its mathematical justification. The results of TOF calculations under various assumptions for a number of catalytic systems are shown.*

Conclusions. *When calculating absolute activity values, a change in the number of active sites has a significant effect on the obtained values. The physical meaning of a number of constants in the proposed equation relates the activity of the catalyst to the distribution of hydrogen on its surface in terms of heats of adsorption.*

Keywords: *liquid-phase hydrogenation, active sites, catalyst deactivation, nickel catalyst, bulk catalysts, adsorption-catalytic deformation, TOF*

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НАУЧНАЯ СТАТЬЯ

Влияние адсорбционно-каталитической деформации и частичной дезактивации на определение абсолютной активности катализатора жидкофазного гидрирования

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Аннотация

Цели. *Учесть изменение количества активных центров при адсорбционно-каталитической деформации и дезактивации поверхности каталитическим ядом при расчете величин абсолютных активностей (turnover frequency, TOF) катализатора гидрирования.*

Методы. *Определение активности проводили статическим методом, использовали титановый реактор объемом 400 мл, заданную температуру опыта контролировали с помощью жидкостного термостата с точностью до 0.5 К, скорость вращения лопастной мешалки составляла 3600 об/мин, давление водорода в системе равно атмосферному. Расход водорода на восстановление модельного соединения учитывался волюмометрическим методом. Теплоты адсорбции водорода определяли с помощью реакционного калориметра, режим работы которого был близок к режиму работы химического реактора. Удельная площадь поверхности измерялась с помощью низкотемпературной адсорбции* *азота, результаты обрабатывали, используя приближения теории Брунауэра–Эммета–Теллера (БЭТ). Дезактивация проводилась введением в систему дозированных количеств каталитического яда в режиме титрования.*

Результаты. *Получены результаты кинетического эксперимента восстановления кратной углеродной связи в молекуле малеата натрия в растворителях различной природы и состава в условиях частичной дезактивации катализатора. В качестве растворителей использовали водные растворы гидроксида натрия с добавками одноатомных алифатических спиртов. Приведены значения теплот адсорбции водорода на скелетном никеле, полученные в ходе адсорбционно-калориметрического эксперимента. Показан подход, позволяющий учесть изменение количества активных центров поверхности в процессе протекания каталитической реакции и при введении дезактивирующего агента, при расчете значений TOF. Предложено уточненное уравнение для корректного расчета TOF, а также представлено математическое его обоснование. Показаны результаты расчета TOF при различных допущениях для ряда каталитических систем.*

Выводы. *Продемонстрировано, что учет изменения количества активных центров при расчете величин абсолютной активности оказывает значительное влияние на полученные значения. Показан физический смысл ряда констант в предложенном уравнении, связывающем активность катализатора и распределение на его поверхности водорода по теплотам адсорбции.*

Ключевые слова: *жидкофазное гидрирование, активные центры, дезактивация катализатора, никелевый катализатор, массивные катализаторы, адсорбционно-каталитическая деформация, TOF*

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INTRODUCTION

The hypothesis of cyclically activated complexes with alternate rupture and formation of bonds was generalized for the first time in relation to particular cases of individual reactions on the example of a very wide range of chemical processes in the works of Ya.K. Syrkin [1–4]. In heterogeneous catalysis, the adsorption, surface diffusion, chemical rearrangement, reaction, and desorption of the product must occur in such a way that the surface of the catalyst can be replenished with new substrate molecules. The faster such a cycle is carried out, the faster the process progresses. Thus, the turnover rate or turnover frequency (TOF), normalized by the number of active sites and consequently representing the rate at which a full catalytic cycle is performed once, should be considered as one of the best measures of catalytic activity [5–8]. This value, which is also referred to as absolute activity [9], is defined as the maximum number of molecules (N_{mol}) that reacted on one active site (N_{as}) per unit of time τ [9]:

$$\mathrm{TOF} = \frac{N_{\mathrm{mol}}}{N_{\mathrm{as}} \cdot \tau} = [\mathrm{s}^{-1}] \cdot \qquad (1)$$

In order to compare the indicators reported by different research groups, it is necessary to carefully describe the methodology used to determine the number of active sites. The main unsolved problem is that the densities of active sites measured prior to the catalytic reaction are not necessarily identical to those present under reaction conditions. In the case of non-porous catalysts, the values of the working surface and the total surface are almost equal, whereas, in the case of porous catalysts, it is only the surface accessible to the reagents that works. Nevertheless, even on an accessible surface, the number of active sites (in the selected specific reaction) is typically unknown.

Therefore, a different approach is also often used. According to [9], the activity (*A*) of a catalyst is defined as the difference in reaction rates in the presence of a catalyst (r_{cat}). This is related to the unit of the amount of catalyst (*g*): mass (m_{cat}), volume, moles, or surface area). In the absence of a catalyst (r_{-cat}), $A = r_{cat}/g - r_{-cat}$. However, since usually $r_{cat} >> r_{-cat}$, the last term in this equation can be disregarded. Thus, the catalytic activity for liquid-phase processes is expressed in terms of the reaction rate, which Syrkin *et al*. proposed to normalize to the amount of catalyst (*g*) [10]. Thus, in the case of liquid-phase hydrogenation, the activity can be determined as follows (2)–(4) [11]:

$$r = \frac{1}{m_{\text{cat}}} \frac{dV(\text{H}_2)}{d\tau} = \left[\frac{\text{cm}^3}{\text{s} \cdot \text{g}}\right], \tag{2}$$

$$\alpha = \frac{(\nu_0 - \nu)}{\nu_0} = \frac{(c_0 - c)}{c_0} = \frac{V_0(\text{H}_2)}{V_\infty(\text{H}_2)}, \tag{3}$$

$$A = r_{\alpha=0\div0.05} = \left[\frac{\text{cm}^3}{\text{s} \cdot \text{g}}\right], \tag{4}$$

where α is the degree of transformation (conversion); *c* is the concentration of the substrate to the current time (τ), c_0 is the initial concentration (α = 0); *r* is the conversion rate of the substrate, *v* is the number of moles of the substrate to the current moment (τ), v_0 is the initial number of moles (α = 0); $V_0(H_2)$ is the initial volume of hydrogen (α = 0), $V(H_2)$ is the volume of hydrogen absorbed to the current moment, $V_\infty(H_2)$ is the total volume of hydrogen that went into the reaction, at its complete completion (α = 1).

The use of Eq. (4) is justified by the fact that the initial rates of the hydrogenation reaction can be considered as objective parameters of the activity of catalysts [12, 13]. For conversions below 0.05, since the hydrogenation rate is directly related to the reactivity of the catalytically active site, the course of side processes has not yet had time to have a significant effect. However, this approach requires that the initial conditions (temperature, hydrogen pressure, reactant concentrations, etc.) are accurately set to be identical each time.

Previously [12–20] it was found that an adsorption-catalytic deformation can in some cases occur during reactions in which the number of active catalyst sites changes. It is therefore necessary to find an approach that allows such changes to be taken into account. It is also known that the action of a catalytic poison is based on its removal of the active site from the reaction zone in some way (blocking, destruction, etc.). That is, the number of active sites should increase during adsorption-catalytic deformation, but when blocked, the number should decrease. The aim of the present work, then, was to find a way to take into account the change in the active sites of the surface during the course of the reaction when calculating the TOF value.

One of the ways to account for the number of active sites removed from the reaction zone can be the analysis of the equation relating the distribution of adsorbed hydrogen by binding energies to the active sites of the catalyst (5)–(7) [21]:

$$A_{\text{calc}} = K_{H\to A} \cdot \Delta_\alpha H^{\text{peak}}_{\text{meas}}(\text{H}_2) - K_{\text{pois}} \cdot n(CDA) + A_{\max}, \tag{5}$$

$$\begin{aligned} \Delta_\alpha H^{\text{peak}}_{\text{calc}}(\text{H}_2) &= K^{-1}_{H\to A} \cdot A_{\text{meas}} + \\ &+ K_{\text{pois}} \cdot K^{-1}_{H\to A} \cdot n(\text{CDA}) + \Delta_\alpha H^{\text{peak}}_{\max}(\text{H}_2), \end{aligned} \tag{6}$$

$$\Delta_\alpha H^{\text{peak}}_{\max}(\text{H}_2) = -A_{\max} \cdot K^{-1}_{H\to A}, \tag{7}$$

where A_{meas} and A_{calc} are the activities of the catalyst measured in kinetic experiment (see Eq. (4)) and calculated from thermochemical data, respectively, [$\text{cm}^3 \cdot \text{s}^{-1} \cdot \text{g}^{-1}$]; $\Delta_\alpha H^{\text{peak}}_{\text{calc}}(\text{H}_2)$ is the peak position calculated from kinetic data, [$\text{kJ}\cdot\text{mol}^{-1}$]; $\Delta_\alpha H^{\text{peak}}_{\text{meas}}(\text{H}_2)$ is the peak position according to the distribution functions (determined in a thermochemical experiment using calorimetric data), [$\text{kJ}\cdot\text{mol}^{-1}$]; CDA (cross dehydrogenative arylation) is catalytic poison (deactivating agent for the catalyst); *n*(CDA) is the amount of catalytic poison introduced into the system per gram of catalyst, [$\text{mol}\cdot\text{g}^{-1}$]; $A_{\max}$ is the calculated maximum activity for the recovery of the selected compound on a given catalyst, [$\text{cm}^3 \cdot \text{s}^{-1} \cdot \text{g}^{-1}$]; $\Delta_\alpha H^{\text{peak}}_{\max}(\text{H}_2)$ is the limiting heat of hydrogen adsorption (weakly bound hydrogen can participate in hydrogenation, while strongly bound hydrogen cannot); K_{pois}, $K^{-1}_{H\to A}$, $K_{H\to A}$ are constants, the physical meaning of which must be established.

Thus, by using the above equations to determine the physical meaning of a number of constants, it may be possible to determine the number of active sites removed from the reaction zone by the catalytic poison. By taking into account the changes in surface area during the adsorption deformation, as well as the active sites removed from the reaction zone, it will be possible to accurately determine the number of active sites involved in the reaction, which should in turn allow the absolute activity of the catalyst to be accurately calculated.

EXPERIMENTAL

Sodium maleate with a purity of >98% (*Merck*, Germany) was chosen as a hydrogen acceptor: since the mechanism and kinetics of its reduction by hydrogen in the presence of a catalyst are well known and the formation of a minimum number of intermediates and by-products has been recorded, it is often used as a model compound [12, 13, 22, 23].

Skeletal nickel obtained by leaching the Raney alloy (*Merck*, Germany) according to the described method [12, 13] was used as a catalyst. Previously, it was shown that the deactivation of skeletal nickel by the dosed introduction of sulfide ions into the catalytic system, depending on the nature of the solvent, is able to selectively block the active sites of the surface with a given metal-hydrogen bond energy [12].

Hydrogenation was carried out using a static method in a closed system with intensive mixing of the liquid phase to exclude the influence of external mass transfer on the experimental results [12, 13]. The reactor was designed in such a way that the rate of the hydrogenation reaction could be measured by the volume of hydrogen absorbed during the reaction per unit of time. The obtained values were reduced to the standard temperature and pressure (273.15 K, 1 bar). The experimental conditions were as follows: mixing speed is 3600 rpm^{-1}; hydrogen pressure is atmospheric; temperature of the liquid phase is 303 K; mass of the catalyst is $m_{cat} = 0.5 \pm 0.01$ g; volume of the liquid phase is 100 cm^3; reactor volume is 400 cm^3. The experimental procedure and the reactor diagram are presented in more detail in [12, 13]. The rate of hydrogen uptake, the degree of conversion, and the catalytic activity were calculated according to Eqs. (2)–(4).

Hydrogenate analysis was performed on a Crystallux-4000M gas chromatograph (*META-CHROME*, Russia) with a flame ionization detector. A TRB-PETROL 100 m × 0.25 mm × 0.5 µm capillary column (*Teknokroma Analytica S.A.*, Spain) was used to separate the extractant. The parameters of the analysis program were as follows: analysis time is 60 min; initial temperature of the columns is 35°C; programmed heating to 150°C at a rate of 5°C/min, then to 250°C for the remaining analysis time; detector temperature is 270°C; evaporator temperature is 270°C; volume of sample taken for analysis is 0.4 µL.

RESULTS AND DISCUSSION

In order to obtain a set of data on the activity of the catalyst, nine solvents were considered in the work, including water, sodium hydroxide, and aliphatic monatomic alcohol. The effect of the solvent on the observed kinetic patterns is well documented in the organic synthesis literature [24]. Although similar effects have been described in the literature on heterogeneous catalysis, the chemical basis of the observed effects remains unclear. Solvent effects in heterogeneous catalysis have been rationalized by comparing reaction rates and product distribution with solvent polarity or permittivity [25–28]. Although there is no doubt that such properties of the solvent can affect the kinetics of the reaction, further research is needed in this area to better understand and quantify these effects, which become even more difficult when switching to metal catalysts on a support due to possible solvent/support interactions [29, 30]. The authors associate the solvent effects with the adsorption equilibrium constant and the volume concentration of H_2 [31].

An example of primary data is shown in Fig. 1a. These data were differentiated and then normalized per 1 g of catalyst according to Eqs. (2) and (3) (see example in Fig. 1b).

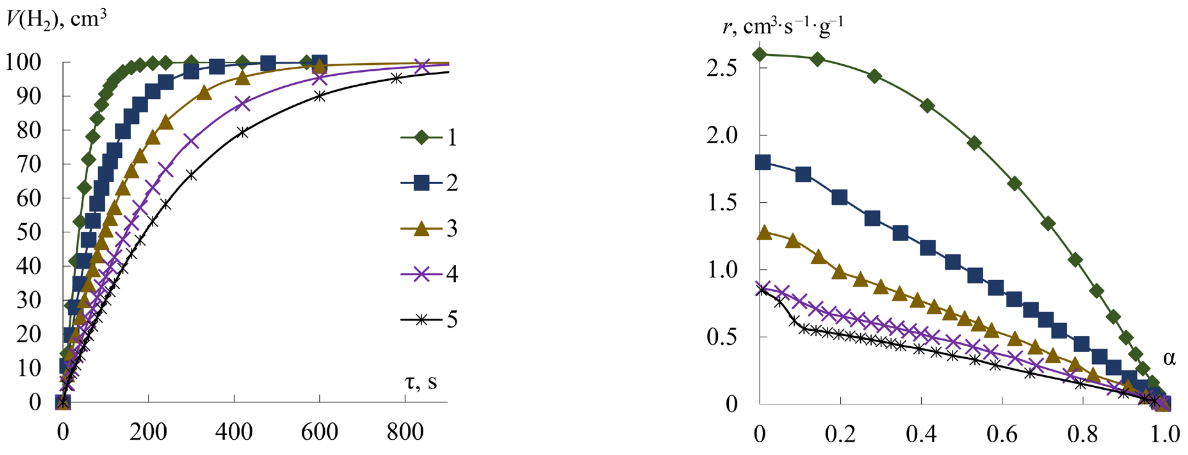
The activity of the catalyst is calculated from Eqs. (2) and (4) and summarized in Table 1.

To calculate the TOF, Eq. (8), obtained from Eqs. (1) and (2), can be used:

$$\mathrm{TOF} = \frac{1}{m_{\mathrm{cat}}} \cdot \frac{dV(\mathrm{H}_2)}{d\tau} \cdot \frac{N_{\mathrm{A}}}{N_{\mathrm{as}}^{\mathrm{norm}} \cdot 1000 \cdot V_{\mathrm{m}}} = \left[\frac{1}{\mathrm{s}}\right], \tag{8}$$

where N_A is the Avogadro number (6.02×10^{23} mol^{-1}); N_{as}^{norm} is the number of active sites normalized per 1 g of catalyst (g^{-1}); V_m is the molar volume of gas (for hydrogen $V_m = 22.43$ dm^3/mol [32]).

According to the definition given in [6–8], the TOF of a catalyst is the maximum number of molecules that reacted on one active site per unit of time. Therefore, this value is determined at the moment when the catalytic reaction reaches its maximum speed. When a reaction is carried out in a batch reactor, the maximum reaction rate is typically observed at the beginning of the



(a) (b)

Fig. 1. Primary data on the absorption of hydrogen during the hydrogenation of sodium maleate in a solution of water–0.01 M NaOH–ethanol 0.11 mole fraction at different amounts of introduced sodium sulfide, mmol (Na_2S)/g (Ni): 1(♦) 0; 2(■) 0.025; 3(▲) 0.075; 4(×) 0.125; 5(∗) 0.175; (a) absorbed hydrogen volume, (b) hydrogen absorption rate.

Table 1. Activity (A) of a porous nickel catalyst in aqueous solutions with additions of sodium hydroxide, aliphatic alcohol, and catalyst poison, [cm^3(H_2)/(s·g(Ni))]

Additives to water	**$n(Na_2S)$, [mmol (Na_2S) · g^{-1} (Ni)]**				
	–	**0.025**	**0.075**	**0.125**	**0.175**
0.01 M NaOH	2.97 ± 0.45	2.23 ± 0.33	1.78 ± 0.27	1.18 ± 0.18	0.90 ± 0.13
0.1 M NaOH	2.82 ± 0.42	2.60 ± 0.38	2.20 ± 0.33	1.48 ± 0.22	1.03 ± 0.15
1 M NaOH	2.32 ± 0.35	2.08 ± 0.32	1.63 ± 0.25	1.18 ± 0.18	0.75 ± 0.12
0.01 M NaOH–MeOH	2.43 ± 0.37	1.68 ± 0.25	1.32 ± 0.20	0.93 ± 0.13	0.38 ± 0.05
0.1 M NaOH–MeOH	2.73 ± 0.42	2.40 ± 0.37	2.22 ± 0.33	1.77 ± 0.27	0.92 ± 0.13
1 M NaOH–MeOH	2.05 ± 0.30	1.73 ± 0.27	1.53 ± 0.23	1.45 ± 0.22	1.15 ± 0.17
0.01 M NaOH–EtOH	2.62 ± 0.38	1.80 ± 0.27	1.28 ± 0.20	0.87 ± 0.13	0.85 ± 0.13
0.1 M NaOH–EtOH	2.88 ± 0.43	3.13 ± 0.47	2.48 ± 0.37	1.77 ± 0.27	1.43 ± 0.22
1 M NaOH–EtOH	1.63 ± 0.25	1.83 ± 0.28	1.57 ± 0.23	1.50 ± 0.23	1.28 ± 0.20

Note: MeOH is methanol; EtOH is ethanol.

reaction. In the present work, the maximum speed occurred at the beginning of the process in all cases (see Fig. 1b). The TOF is thus determined at the same time as the catalyst activity. Thus, with some assumptions about the hydrogenation reactions of the model compounds considered, the absolute activity can be expressed by Eq. (9):

$$\mathrm{TOF} \approx \frac{A\cdot N_{\mathrm{A}}}{N_{\mathrm{as}}^{\mathrm{norm}}\cdot 60\cdot 1000\cdot V_{\mathrm{m}}} = \left[\frac{1}{\mathrm{s}}\right]. \quad (9)$$

G.D. Zakumbaeva *et al.* [33] found that $1.5\cdot 10^{19}$ nickel atoms are located on 1 m^2 of the surface of skeletal nickel, that is, $N_{\mathrm{as}}^{1\,\mathrm{m}^2} = 1.5\cdot 10^{19}$.

Consequently, the normalized number of active sites per 1 g of catalyst can be expressed by Eq. (10):

$$N_{\text{as}}^{\text{norm}} = S_{\text{sp}} \cdot N_{\text{as}}^{1\ \text{m}^2}, \tag{10}$$

where S_{sp} is the specific surface area of the catalyst.

Combining Eqs. (9) and (10) gives Eq. (11):

$$\text{TOF} \approx A \cdot \frac{N_{\text{A}}}{S_{\text{sp}} \cdot N_{\text{as}}^{1\ \text{m}^2} \cdot 1000 \cdot V_{\text{m}}} = \frac{A \cdot \psi}{S_{\text{sp}} \cdot 1000} = \left[\frac{1}{\text{s}}\right], \tag{11}$$

where, for skeletal nickel, $\psi = 1789$.

Using Eq. (11), absolute activities (TOF) were calculated and summarized in Table 2.

Analyzing the data presented in Table 2, it can be seen that the TOF values decrease monotonically. However, this should not be the case. It is logical to assume that there should be changes upon initial introduction of the catalytic poison, since the energy profile of the surface changes and the binding energies of hydrogen with the surface begin to increase [12]. However, further values should change slightly, since additional introduction of the catalytic poison should only change the number of active sites available to the reactants, not their nature.

When calculating TOF according to the above Eq. (11), S_{sp} was considered as a constant. However, as mentioned above, the specific surface area will change due to the adsorption deformation that occurs when the catalyst is poisoned. It was therefore decided to measure the specific surface area (low temperature nitrogen adsorption by the Brunauer–Emmett–Teller (BET) method) in order to take its changes into account for a more accurate calculation of the TOF.

The data shown in Fig. 2 are in good agreement with the data published in [20]. There, an initial increase in specific surface area is also followed by

Table 2. Absolute activity (TOF) of a porous nickel catalyst in aqueous solutions with various additives of sodium hydroxide, aliphatic alcohol, and catalytic poison, without taking into account adsorption deformation or blocking of active sites by catalytic poison, 100/s

Additives to water	**$n(Na_2S)$, [mmol (Na_2S) · g^{-1} (Ni)]**				
	–	**0.025**	**0.075**	**0.125**	**0.175**
0.01 M NaOH*	5.90	4.44	3.55	2.35	1.79
0.1 M NaOH*	5.60	5.17	4.37	2.95	2.05
1 M NaOH*	4.61	4.14	3.25	2.35	1.49
0.01 M NaOH–MeOH**	7.14	4.94	3.86	2.74	1.12
0.1 M NaOH–MeOH**	8.02	7.04	6.50	5.18	2.69
1 M NaOH–MeOH**	6.01	5.08	4.50	4.25	3.37
0.01 M NaOH–EtOH**	7.67	5.28	3.76	2.54	2.49
0.1 M NaOH–EtOH**	8.46	9.19	7.28	5.18	4.20
1 M NaOH–EtOH**	4.79	5.38	4.60	4.40	3.76

* Specific surface area of the catalyst (S_{sp}) = 90 m^2/g;

** Specific surface area of the catalyst (S_{sp}) = 61 m^2/g.

a decrease as the level of poisoning increases. In [20], such a change in specific surface area is explained by the initial adsorption deformation, where the catalyst particles fall apart into smaller particles, leading to an increase in specific surface area. This is also reflected in the increased activity of the catalyst, which occurs despite the poisoning of its catalytic poison in a number of solvents. Taking into account the obtained data, a new calculation of TOF was made, where S_{sp} is no longer a constant, but is measured for all cases. The data are presented in Table 3.

In Table 3, the TOF for poisoned catalysts is less dependent on the solvent and the values are close, whereas, without taking into account the adsorption deformation, there is practically no correlation of similar values. It is therefore advisable to use the proposed approximation to calculate the TOF. However, this approximation does not take into account the reduction in the number of active sites due to blocking by a catalytic poison. Consequently, with this approach to calculating TOF, the resulting value also decreases as the level of poisoning increases. However, in some cases (solutions of H_2O–EtOH–0.1 M NaOH and H_2O–EtOH–1 M NaOH), a promotional effect was observed: in order to correctly calculate TOF, it is necessary to somehow take into account changes in the number of active sites during partial poisoning. This requires further research.

To account for the number of active sites removed from the reaction zone, it is necessary to reveal the physical meaning of K_{pois} in Eq. (5). According to [21] for skeletal nickel, A_{max} = 196 cm^3·s^{-1}·g^{-1}, = −247.76·10^3 kJ·mol^{-1}, and K_{pois} = 509887 s^{-1}; Eqs. (5) and (6) take the form (12) and (13), respectively:

$$A_{calc} = 8.11\cdot10^{-4}\cdot\Delta_\alpha H^{peak}_{meas}(H_2) - \\ -5.09887\cdot10^{5}\cdot n(Na_2S) + 196, \tag{12}$$

$$\Delta_\alpha H^{peak}_{calc}(H_2) = 1.2335\cdot10^{3}\cdot A_{meas} + \\ +6.2894\cdot10^{8}\cdot n(Na_2S) - 241.76\cdot10^{3}. \tag{13}$$

If expressed $K_{H\to A}$ from Eq. (7) and substituted into Eq. (5), we get the following Eq. (14):

$$A_{calc} = \frac{-A_{max}}{\Delta_\alpha H^{peak}_{max}(H_2)}\cdot\Delta_\alpha H^{peak}_{meas}(H_2) - \\ -K_{pois}\cdot n(Na_2S) + A_{max}. \tag{14}$$

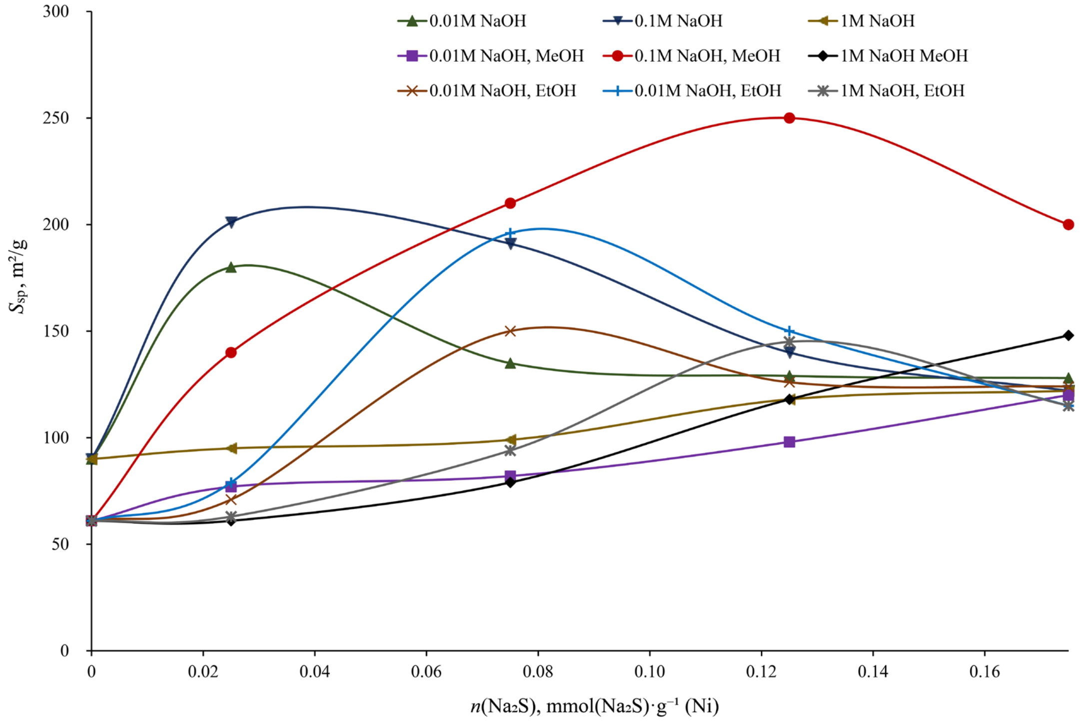


Fig. 2. Influence of the amount of introduced catalytic poison on the specific surface area of the catalyst.

Table 3. Absolute activity (TOF) of a porous nickel catalyst in aqueous solutions with various additions of sodium hydroxide, aliphatic alcohol, and catalytic poison, taking into account adsorption deformation, but without blocking of active sites by catalytic poison, 100/s

Additives to water	$n(\text{Na}_2\text{S})$, [mmol $(\text{Na}_2\text{S}) \cdot \text{g}^{-1}$ (Ni)]				
	–	0.025	0.075	0.125	0.175
0.01 M NaOH	5.90	2.22	2.36	1.64	1.26
0.1 M NaOH	5.60	2.31	2.06	1.90	1.52
1 M NaOH	4.61	3.92	2.95	1.79	1.10
0.01 M NaOH–MeOH	7.14	4.24	1.57	1.33	0.55
0.1 M NaOH–MeOH	8.02	5.44	2.02	2.11	1.43
1 M NaOH–MeOH	6.01	4.92	2.92	1.79	1.79
0.01 M NaOH–EtOH	7.67	4.18	2.80	1.58	1.27
0.1 M NaOH–EtOH	8.46	4.00	2.12	1.26	1.28
1 M NaOH–EtOH	4.79	5.38	3.55	2.27	1.55

Now let us try to group this equation into a different form (15):

$$A_{\text{calc}} = A_{\max}\left(1-\frac{\Delta_\alpha H^{\text{peak}}_{\text{meas}}(\text{H}_2)}{\Delta_\alpha H^{\text{peak}}_{\max}(\text{H}_2)} - \frac{K_{\text{pois}}}{A_{\max}}\cdot n(\text{Na}_2\text{S})\right). \qquad (15)$$

Based on Eq. (15) and the information that the dimension K_{pois} = [$\text{cm}^3(\text{H}_2)\cdot\text{s}^{-1}\cdot\text{mol}^{-1}(\text{S}^{2-})$], Eq. (16) is:

$$K_{\text{pois}} = \frac{A_{\max}\cdot N_A \cdot K_{\text{S–Ni}}}{N^{\text{norm}}_{\text{as}}}. \qquad (16)$$

Substituting the figures obtained for skeletal nickel into this equation, we get $K_{\text{S–Ni}} = 8$. Thus, $K_{\text{S–Ni}}$ can be assumed to be the coordination number for sulfide with respect to nickel, which is in good agreement with the previously obtained data [12, 13]. As a result, Eq. (15) can be expressed in a finite general form (17):

$$A_{\text{calc}} = A_{\max}\left(1-\frac{\Delta_\alpha H^{\text{peak}}_{\text{meas}}(\text{H}_2)}{\Delta_\alpha H^{\text{peak}}_{\max}(\text{H}_2)} - \frac{N_{\text{A}}\cdot K_{\text{S–Ni}}}{N^{\text{norm}}_{\text{as}}}\cdot n(\text{Na}_2\text{S})\right). \qquad (17)$$

It is clear that one sulfur atom blocks eight nickel atoms. Thus, it is possible to set a limit at which all nickel atoms will be blocked, as well as taking into account the number of unblocked atoms $N^{\text{norm}}_{\text{as}_{\text{unblock}}}$ (18):

$$N^{\text{norm}}_{\text{as}_{\text{unblock}}} = N^{\text{norm}}_{\text{as}} - N_{\text{A}}\cdot K_{\text{S–Ni}}\cdot n(\text{Na}_2\text{S}). \qquad (18)$$

Based on the equations given above, it becomes clear that K_{pois} represents the degree of blocking of active sites multiplied by the maximum possible activity for the selected catalyst. Based on this, the following Eq. (19) was obtained for calculating TOF:

$$\begin{aligned}\mathrm{TOF} &\approx A\cdot\frac{N_\mathrm{A}}{\left(S_\mathrm{sp}\cdot N_\mathrm{as}^{1\,\mathrm{m}^2}-N_\mathrm{A}\cdot K_{\mathrm{S-Ni}}\cdot n(\mathrm{Na_2S})\right)\cdot 1000\cdot V_\mathrm{m}}=\\ &=A\cdot\left(\frac{N_\mathrm{A}}{S_\mathrm{sp}\cdot N_\mathrm{as}^{1\,\mathrm{m}^2}\cdot 1000\cdot V_\mathrm{m}}-\frac{1}{K_{\mathrm{S-Ni}}\cdot n(\mathrm{Na_2S})\cdot 1000\cdot V_\mathrm{m}}\right)= \\ &=A\cdot\left(\frac{\psi}{S_\mathrm{sp}\cdot 1000}-\frac{1}{K_{\mathrm{S-Ni}}\cdot n(\mathrm{Na_2S})\cdot 1000\cdot V_\mathrm{m}}\right).\end{aligned} \quad (19)$$

The results of calculating the absolute error taking into account the adsorption deformation and deactivation of the catalyst are shown in Table 4.

As shown in Table 4, the data show close values of absolute activity in all the considered systems, having already introduced the catalytic poison. Thus, taking into account the adsorption deformation and the physical blocking of the active sites by the catalytic poison, the TOF values begin to depend less on the amount of catalytic poison to instead primarily depend on the fact of its introduction. Thus, with the exception of a few cases related to severe selective poisoning (e.g., with a solution of MeOH–0.01 M NaOH) [12,13], a further decrease in TOF after blocking 16% of the active atoms is already insignificant, which was expected since TOF shows the activity of an active site. The obtained deviations can be explained by an increase in the heat of adsorption with an increase in the amount of catalytic poison injected.

CONCLUSIONS

The studies carried out allow us to take into account the number of atoms currently available for the reaction (Eq. (18)).

Table 4. Absolute activity (TOF) of a porous nickel catalyst in aqueous solutions with various additives of sodium hydroxide, aliphatic alcohol, and catalytic poison, taking into account adsorption deformation and blocking of active sites by catalytic poison, 100/s

Additives to water	**Degree of blocking nickel atoms**				
	0%	**11%**	**16%**	**32%**	**45%**
0.01 M NaOH	5.9	2.3	2.9	2.4	2.2
0.1 M NaOH	5.6	2.4	2.4	2.7	2.8
1 M NaOH	4.6	4.3	3.9	2.7	2.0
0.01 M NaOH–MeOH	7.1	4.8	1.9	1.9	1.0
0.1 M NaOH–MeOH	8.0	6.1	2.3	2.9	2.8
1 M NaOH–MeOH	6.0	5.6	3.9	2.5	3.5
0.01 M NaOH–EtOH	7.7	4.7	4.0	2.7	2.4
0.1 M NaOH–EtOH	8.5	4.2	2.4	1.5	1.8
1 M NaOH–EtOH	4.8	6.2	5.1	3.4	2.5

The physical meaning of K_{pois} is established to represent the product of the maximum possible activity for the selected catalyst by the degree of blocking of active sites (Eq. (16)). It is shown that the lack of consideration of adsorption-catalytic deformation and blocking of active sites leads to an incorrect calculation of the TOF. With this calculation, the absolute activity decreases evenly. Moreover, when these two processes are taken into account, it can be seen that the absolute activity initially drops sharply with the initial introduction of the catalytic poison, since the energy profile of the surface changes along with an increase in the binding energies of hydrogen with the surface. However, with an increased amount of catalytic poison in the system, the values further change insignificantly, since additional poisoning of the catalyst only changes the number of active sites available to the reactants, but not their nature.

Equation (19) allows the absolute activity of a liquid phase hydrogenation catalyst to be calculated taking into account the adsorption catalytic deformation.

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Authors' contribution

All authors equally contributed to the research work.

The authors declare no conflicts of interest.

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