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## LIQUID-PHASE HYDROGENATION OF SODIUM 4-NITROPHENOLATE UNDER CONDITIONS OF NICKEL CATALYST PARTIAL DEACTIVATION

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**Abstract.** The paper investigates the activity of a skeletal nickel catalyst upon its partial controlled deactivation in the liquid-phase hydrogenation reaction of sodium 4-nitrophenolate. The reaction proceeds in aqueous solutions of sodium hydroxide at 303 K and atmospheric hydrogen pressure in a batch reactor. An aqueous solution of sodium sulphide with pH equal to the hydrogen value of the solvent in the reactor was a deactivating agent. We used the Bartholomew C.G. technique to assess the nature of the catalyst deactivation. Using this technique, we determined the number of active nickel atoms blocked by a single sulfide ion and proposed  $TON^{deact}$  as a parameter to show the resistance of the catalyst to deactivation. The authors proposed an original method for calculating  $TON^{deact}$  values for catalytic systems of liquid-phase hydrogenation under conditions of deactivation by catalytic poisons. Indeed, the initial decrease in activity in 0.01 M NaOH concerns with a decrease in the catalytic properties of the active centres. Subsequently, the activity of individual centres remains stable. However, the decrease in the overall activity of the catalyst occurs due to their proportional blocking. This explains the selective character of deactivation according to Bartholomew C.G. The poison proportionally removes active centres from the reaction zone in 0.1 M NaOH. This causes a non-selective character of poisoning. The kinetic relationships depend on the accumulation of different intermediates on the catalyst surface at different concentrations of the introduced sulfide ion. Therefore, the reaction rate and absolute activity can increase slightly at small amounts of catalytic poison. However, the activity of the catalyst is irretrievably lost with further increase in the concentration of sulfide ion.

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## Introduction

The activity and selectivity of heterogeneous catalysts used in liquid-phase hydrogenation reactions are determined by the presence on their surface of various forms of adsorbed hydrogen, which have different reactivity towards organic compounds [1-3]. However, the assessment of the reactivity effects of these hydrogen forms on selectivity and reaction rates is based on general assumptions and indirect data. The studies aimed at identifying the reactivity parameters of different forms of adsorbed hydrogen are poorly reported in the literature to date. A number of papers confirm the existence of equilibrium between different forms of hydrogen on the catalyst surface; they are suggested to be regulated by changing the solvent composition [1-2]. Apparently, a meaningful occurrence of these effects can be achieved by using catalytic poisons.

To estimate the total reaction rate in the regional velocity method, it is necessary to sum up the rates of processes on different types of active centres of the catalyst surface. Correct agreement between adsorption and reaction rate data requires consideration of the amount of hydrogen adsorbed on the various active centres. This approach has been used to determine the reactivity of adsorbed hydrogen, including in hydrogenation reactions on skeletal nickel [4]. Hydrogen can adsorb on the latter one, for example, in three forms: two atomic and one molecular [1-5].

In [5], a chemical dehydrogenation method was used to obtain catalysts with different amounts of adsorbed hydrogen. However, this method is problematic due to the impossibility of direct measurement of released hydrogen amount by conventional volumetric methods. Indeed, hydrogen contacting the surface of the prehydrogenated catalyst fills the porous space of the metal to the degree of filling characteristic of this reaction. We used adsorption-calorimetric titration to determine the process rate. It causes additional difficulties in the interpretation of the results.

A number of studies [2, 4] have proposed the use of catalysts controlled partial deactivation using catalytic poisons to change the equilibrium of the amount of adsorbed hydrogen and obtain catalytic systems with given parameters of activity and selectivity. However, several conditions should be met for the successful application of catalytic poisons (deactivating agents):

- the catalytic poison should interact irreversibly with the active centres of the catalyst;
- the chemical composition of the catalyst should not change under the influence of the poison, only the number of active centres;
- the influence of the solvent on the kinetic parameters of the hydrogenation reaction should not change with the addition of the catalytic poison.

We proposed to use the zero-order reaction rate of the hydrogenated compound and/or the observed rate constants at low degrees of conversion in external diffusion inhibition absence as parameters of catalyst activity at partial deactivation. Under such conditions, the reaction rate will initially depend only on the reactivity of the hydrogen adsorbed by the various active centres of the catalyst surface.

We chose sodium sulfide as a deactivating agent because sulfur compounds ( $S^{2-}$ ) are the most effective catalytic poisons significantly reducing the hydrogenation rate. According to [6, 7],



sulfur atoms can change the equilibrium between the forms of adsorbed hydrogen on the catalyst surface. Moreover, they differentially block the active centres and affect the activity of skeletal nickel in the hydrogenation reactions of nitro compounds.

The purpose of this study was to determine the effect of partial controlled deactivation by sulfide ion on the kinetic regularities of liquid-phase reduction of sodium 4-nitrophenolate and develop an approach to calculation of the  $TON^{\text{deact}}$  value characterising the catalyst in the deactivation process.

### Experimental part

We used a traditional skeletal nickel catalyst as a catalyst. It was obtained by treatment of nickel-aluminium alloy with aqueous sodium hydroxide solution according to the known method [8, 9]. The average radius of the catalyst particles was 4.8  $\mu\text{m}$ ; specific surface area was  $90 \pm 2 \text{ m}^2/\text{g}$ ; porosity was  $0.5 \pm 0.05 \text{ cm}^3/\text{cm}^3$ .

We investigated the kinetics of the hydrogenation reaction of the model compound by a static method in a sealed liquid-phase reactor. This method allowed us to measure the amount of absorbed hydrogen volumetrically. The stirrer rotation speed was 2500 rpm. This excluded the influence of external mass transfer on the kinetic parameters. According to some experiments, the effect of internal mass transfer on reaction kinetics is minimised at particle sizes are smaller than 5  $\mu\text{m}$ .

The reduction of aromatic nitro compounds with hydrogen proceeds according to complex stoichiometric schemes. Various reaction directions and formation of intermediate compounds are possible. Papers [10] and [11] describe the scheme for the reduction of substituted nitrobenzenes by catalytic process in details. The variability in the intermediates described in these studies is probably due to differences in experimental conditions. We used sodium 4-nitrophenolate as a model compound containing a nitro group, since its liquid-phase reduction produces negligible amount of intermediates and by-products in solution [12].

We verified the hydrogenisate using a Crystalux-4000M gas chromatograph with a flame ionisation detector. We used a TRB-PETROL capillary column (100 m  $\times$  0.25 mm  $\times$  0.5  $\mu\text{m}$ , 100% dimethylpolysiloxane). Analysis programme is as follows: analysis time is 120 min; initial column temperature is 35  $^\circ\text{C}$  (15 min); programmable heating is up to 150  $^\circ\text{C}$  at a rate of 5  $^\circ\text{C}/\text{min}$ , then to 250  $^\circ\text{C}$  for the remaining analysis time. Detector temperature is 270  $^\circ\text{C}$  and evaporator temperature is 270  $^\circ\text{C}$ . Sample volume for analysis is 0.4  $\mu\text{l}$ .

We conducted partial controlled deactivation of the catalyst by titration according to the previously developed method [4]. We used sodium sulfide as a catalytic poison and determined the concentration of  $\text{S}^{2-}$  ions by direct potentiometric method. We measured EMF using an ion-selective electrode with a saturated chlorosilver electrode EVL-1M3 as a reference electrode.

The applied studies on liquid-phase hydrogenation of organic compounds assessed catalyst activity by the reaction rate at the initial stage (at a degree of conversion less than 0.05) [1, 2, 4, 6, 7]. Assumedly, intermediate and final products affecting the reaction rate and the catalyst surface do not have time to accumulate in the reaction system at this stage. The calculation of absolute activity ( $TOF$ , Eqs. 4-6) for real multicomponent catalytic systems, especially under conditions of partial deactivation of the catalyst, has its own peculiarities.



For instance, the structure of the catalyst surface changes during the process of entering the operating regime, reaction, and deactivation [13].

The equations for assessment of reaction kinetics are as follows:

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

$$\alpha = \frac{V_{\tau}(\text{H}_2)}{\sum_{\tau=0}^{\infty} V(\text{H}_2)} = [\text{unit fractions}], \quad (2)$$

$$A = r_{\alpha \leq 0,05} = \left[ \frac{\text{cm}^3}{\text{s} \cdot \text{g}} \right], \quad (3)$$

$$TOF = \frac{N_{\text{mol}}}{N_{\text{ac}} \cdot \tau} = \left[ \frac{1}{\text{s}} \right], \quad (4)$$

$$TOF = \frac{1}{m_{\text{cat}}} \left( \frac{dV(\text{H}_2)}{d\tau} \right)_{\text{max}} \cdot \frac{N_A}{N_{\text{ac}}^{\text{norm}} \cdot 1000V_m} = \left[ \frac{1}{\text{s}} \right], \quad (5)$$

$$TOF \approx A \frac{N_A}{1000V_m S_{\text{spec}} \cdot N_{\text{Ni}}^{1\text{m}^2} \cdot \varepsilon} = \left[ \frac{1}{\text{s}} \right], \quad (6)$$

$$\varepsilon = 1 - \frac{N_A \cdot K_{\text{S-Ni}}}{S_{\text{spec}} \cdot N_{\text{Ni}}^{1\text{m}^2}} \cdot n(\text{Na}_2\text{S}) = 1 - \frac{n(\text{Na}_2\text{S})}{n_{\text{max}}(\text{Na}_2\text{S})} = [\text{unit fractions}], \quad (7)$$

$$TON = \frac{TOF \cdot t_{1/2}}{\text{Ln}2}, \quad (8)$$

$$TON^{\text{deact}} = \frac{TOF_{\text{cat}^0}}{k_B}, \quad (9)$$

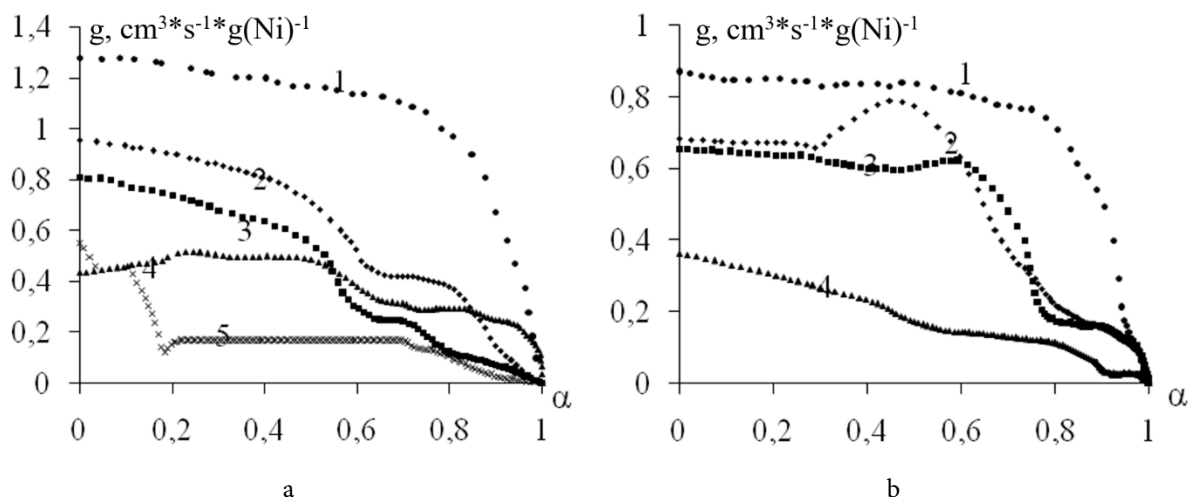
where:  $N_A$  is Avogadro number ( $6,022 \cdot 10^{23} \text{ mol}^{-1}$ );  $V_m$  is the molar volume of the gas (for hydrogen  $V_m = 22,43 \text{ dm}^3/\text{mol}$ );  $K_{\text{S-Ni}}$  shows how many active nickel atoms block one sulphur atom;  $\alpha$  is transformation rate;  $r$  is the reaction rate,  $m_{\text{cat}}$  is the catalyst mass,  $V(\text{H}_2)$  is the amount of absorbed hydrogen,  $\tau$  is the reaction time,  $\tau_{1/2}$  is the time for which  $\alpha = 0,5$  is reached;  $A$  is the catalyst activity;  $\varepsilon$  is the fraction of active centres unblocked by the catalytic poison;  $S_{\text{spec}}$  is a specific surface area;  $n(\text{Na}_2\text{S})$  is the number of moles of sodium sulphide per one gram of catalyst;  $n_{\text{max}}(\text{Na}_2\text{S})$  is the minimum amount of sodium sulphide (activity of the catalyst falls to zero);  $N_A$  is the number of active nickel atoms on 1 square metre of the catalyst surface;  $N_{\text{mol}}$  is the number of reactant molecules reacting per unit time ( $\tau$ ) on the active centres of the catalyst in the amount equal to  $N_{\text{ac}}$ ;  $N_{\text{ac}}$  is the number of active centres on one gram of the catalyst;  $TON$  is the stability of the catalyst operation (number of cycles of operation of one active centre of the catalyst);  $TON^{\text{deact}}$  is the stability of the catalyst to deactivation.

### Main body

We experimentally studied the kinetic regularities of the reduction of sodium 4-nitrophenolate on skeletal nickel catalyst in aqueous solutions of sodium hydroxide under partial deactivation. Fig. 1 shows the result of experimental data processing according to Equations 1 and 2. The study [14] presents the influence of the solvent on the kinetics of substituted nitrobenzenes hydrogenation. The effect of NaOH concentration on the hydrogenation kinetics is due to the change in the nature of the reaction. The process follows the hydrogenation path in neutral medium without accumulation of by-products. Moreover, condensation processes are activated in alkaline medium. It causes the accumulation of

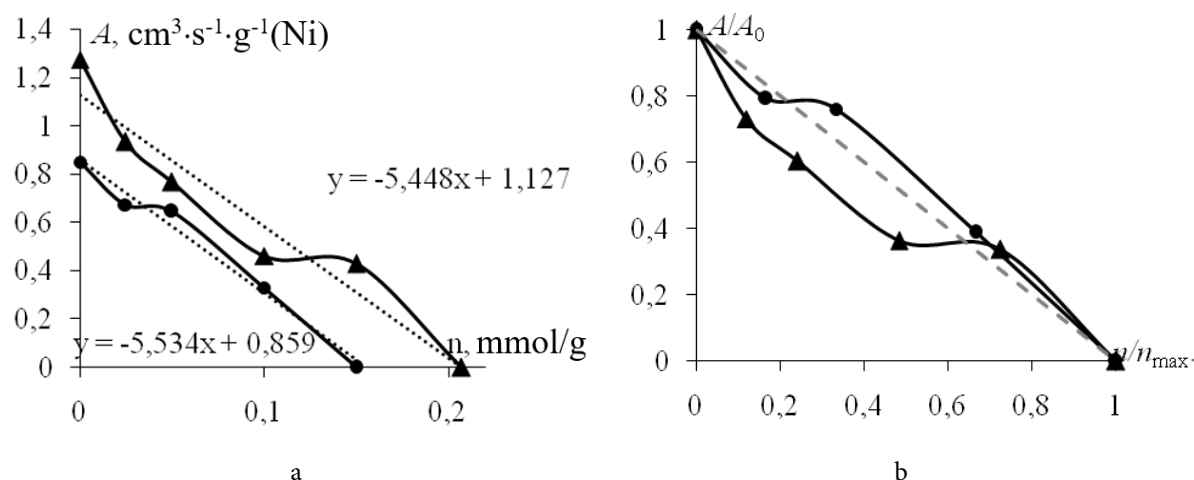


incomplete reduction products - azoxy- and azophenols; it explains the activity spikes (Fig. 1). Consequently, the kinetic regularities of hydrogenation of sodium 4-nitrophenolate are explained by changes in the rate of individual stages of nitro group reduction. Hence, excess intermediates, like sulfide ions, block the catalyst enhancing the action of the catalytic poison. As a result, the reaction stops at 0.21 mmol  $\text{Na}_2\text{S}$  per 1 g of catalyst in 0.01 M NaOH solvent, and at 0.15 mmol  $\text{Na}_2\text{S}$  per 1 g of catalyst in 0.1 M NaOH.



**Fig. 1.** Reaction rates of liquid-phase hydrogenation of sodium 4-nitrophenolate in aqueous sodium hydroxide solution: a) 0.01 M; b) 0.1 M with concentrations of sodium sulfide, mmol ( $\text{Na}_2\text{S}$ )/g kt: 1-0; 2-0.025; 3-0.050; 4-0.100; 5-0.15.

Fig. 2a shows the dependences characterising catalyst stability to deactivation in different solvents. The paper shows [2] the applicability of the catalyst deactivation evaluation technique proposed by Bartholomew C.G. for liquid-phase hydrogenation. Fig. 2b shows a graphical representation of this approach.



**Fig. 2.** Activity of the catalyst in the hydrogenation reaction of sodium 4-nitrophenolate in aqueous solution with NaOH: ▲ — 0,01 M; ● — 0,1 M; at different  $\text{Na}_2\text{S}$  content, a) in absolute, b) in relative units (where  $A_0$  is the activity of the undeviated catalyst;  $n_{\max}$  is the amount of sodium sulfide at which the catalyst activity is completely lost).

According to Fig. 2, we can determine tangent modulus of the trend line slope angle line required for the calculation of  $\text{TON}^{\text{deact}}$  (see equations on Fig. 2). According to the literature [3, 7],



the skeletal nickel surface can have from  $1.14 \cdot 10^{19}$  to  $1.86 \cdot 10^{19}$  atoms/m<sup>2</sup> depending on the crystallographic orientation. Therefore, one gram of the catalyst investigated in this research has  $1.35 \cdot 10^{22}$  active nickel atoms. They are completely blocked to a loss of activity of  $1.25 \cdot 10^{20}$  sulfide ions in 0.01 M NaOH or  $9.03 \cdot 10^{19}$  sulfide ions in 0.1 M NaOH. Hence, one sulfide ion blocks 10.8 active nickel atoms in 0.01 M NaOH and one sulfide ion blocks 15.0 active nickel atoms in 0.1 M NaOH.

The acidity of the medium also affects this process: the blocking character is selective at 0.01 M NaOH and non-selective at 0.1 M (see Fig. 2b).

Table 1 shows the kinetic data of the reduction of sodium 4-nitrophenolate on skeletal nickel catalyst in aqueous solutions of sodium hydroxide under partial deactivation.

**Table 1.** Kinetic parameters of skeletal nickel catalyst activity in the reduction reaction of sodium 4-nitrophenolate in aqueous NaOH solutions.

$n(\text{Na}_2\text{S})$ , mmol/g cat.	Concentration of sodium hydroxide solution							
	0,01M				0,1M			
	$A^*$	$TOF$ , 100s <sup>-1</sup>	$K_{S-Ni}$	$TON^{deact}$	$A^*$	$TOF$ , 100s <sup>-1</sup>	$K_{S-Ni}$	$TON^{deact}$
0	1.27±0.06	1.1	10.8	0.043	0.85±0.04	0.4	15.0	0.016
0.025	0.93±0.05	0.4			0.67±0.03	0.2		
0.05	0.77±0.04	0.4			0.65±0.03	0.2		
0.1	0.46±0.02	0.5			0.33±0.02	0.4		
0.15	0.43±0.02	0.5			0	-		
0.2	0	-			0	-		

\* [cm<sup>3</sup>·s<sup>-1</sup>·g<sup>-1</sup>(Ni)]

The data obtained numerically confirm higher catalyst resistance to deactivation at 0.01M NaOH than at 0.1 M.

## Conclusions and recommendations

This paper investigates the activity of a skeletal nickel catalyst in the liquid-phase hydrogenation reaction of sodium 4-nitrophenolate under conditions of partial controlled deactivation. Indeed, a single sulfide ion removes 10.8 nickel atoms from the reaction zone at a concentration of 0.01 M NaOH and 15.0 at a concentration of 0.1 M NaOH. The absolute activity of the catalyst decreases by 2-2.5 times upon introduction of sodium sulfide. However, further increasing of catalytic poison concentration does not causes a significant change in the  $TOF$  value.

The authors proposed a method for calculating the index  $TON^{deact}$ . It characterizes the resistance of the catalyst to deactivation by its poison. The value of  $TON^{deact}$ , when combined with the approach proposed by Bartholomew, allows a more complete description of catalyst deactivation. Hence, the acidity of the medium has a significant influence on the character of deactivation: at the NaOH content of 0.01 M the process proceeds selectively, and at the concentration of 0.1 M NaOH it is non-selective.

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