

# Liquid Phase Hydrogenation of Maleic Acid Diethyl Ester and Its Mixture with 4-Nitrotoluene over Modified Skeletal Nickel

Andrei Vladimirovich Afineevskii<sup>\*</sup>, Tatiana Yurievna Osadchaia, Dmitrii Alekseevich Prozorov, Mikhail Viktorovich Lukin, Yaroslav Pavlovich Suhachev, Marina Dmitrievna Chelysheva, Vladislav Olegovich Gundorov

Department of Physical and Colloidal Chemistry, Ivanovo State University of Chemistry and Technology, Ivanovo Region, Ivanovo, Russia

## Email address:

afineevskiy@mail.ru (A. V. Afineevskii), osadchayaty@gmail.com (T. Y. Osadchaia), prozorovda@mail.ru (D. A. Prozorov), luckmv@mail.ru (M. V. Lukin), hi.chok.3@gmail.com (Y. P. Suhachev), marina.chelysheva.95@mail.ru (M. D. Chelysheva), gundorovvlad@mail.ru (V. O. Gundorov)

<sup>\*</sup>Corresponding author

## To cite this article:

Andrei Vladimirovich Afineevskii, Tatiana Yurievna Osadchaia, Dmitrii Alekseevich Prozorov, Mikhail Viktorovich Lukin, Yaroslav Pavlovich Suhachev, Marina Dmitrievna Chelysheva, Vladislav Olegovich Gundorov. Liquid Phase Hydrogenation of Maleic Acid Diethyl Ester and Its Mixture with 4-Nitrotoluene over Modified Skeletal Nickel. *International Journal of Oil, Gas and Coal Engineering*. Vol. 5, No. 6, 2017, pp. 153-157. doi: 10.11648/j.ogce.20170506.15

**Received:** February 17, 2017; **Accepted:** March 10, 2017; **Published:** November 28, 2017

---

**Abstract:** 4-aminotoluene is known as a good octane additive, the mixture of maleic acid diethyl ester and Succinate acid diethyl ester has good lubricating characteristics. The process of hydrogenation of maleic acid diethyl ester at atmospheric pressure in aqueous solution of 2-propanol over skeletal nickel and modified skeletal one was investigated. It is established that the nickel surface modification by sulfur does not lead to the increase of the catalyst activity in the hydrogenation of maleic acid diethyl ester as opposed to 4-nitrotoluene. The principal possibility of selective hydrogenation of mixture of maleic acid diethyl ester with 4-nitrotoluene was demonstrated.

**Keywords:** Liquid-Phase Hydrogenation, 4-Nitrotoluene, Maleic Acid Diethyl Ester, Skeletal Nickel

---

## 1. Introduction

The main problem of the reduction of organic compounds with different hydrogenation able functional groups is to select the process conditions of hydrogen attachment, that provide the selective reduction only of one of the functional groups [1-3]. Targeted regulation of the hydrogenation process parameters is possible only under the control of the concentration of the catalyst surface active sites. The most effective way to regulate adsorption and catalytic properties of the heterogeneous catalyst surface obviously is the introduction of modifying additives. For such a change the selectivity and stability of heterogeneous catalysts it is necessary to create the summarizing of kinetic models of liquid-phase reactions, that allow to describe the kinetic curves, to explain variations in the reaction speed, selectivity

and stability of the catalytic system under the influence of various factors [4, 5]. It is obvious the development of such models is impossible without a detailed study of kinetic regularities of the hydrogenation processes of compounds containing certain functional groups having a different reactivity and deactivating effect on the active sites of the catalyst surface [6]. The study of hydrogenation kinetics of a model compound mixture with different functional groups in the chosen conditions allows experimentally to split up processes of heterogeneous reduction and homogeneous regrouping [7], which increase the number of possible routes of the occurrence of the reduction processes and the number of components of the catalytic system, due to the formation of intermediates partial reduction and condensation. In addition, the formation of intermediates of partial reduction, for example, nitroso compounds, can significantly reduce the activity of a heterogeneous catalyst due to irreversible

interaction of these substances with surface active sites [6].

The purposes of this paper are the determination of the effect from injected modifier on the hydrogenation kinetics of maleic acid diethyl ester (MADE), the investigation of the catalyst stability with different quantity of the introduced modifier and the evaluation of the hydrogenation selectivity of the model mixture of organic compounds containing  $-\text{NO}_2$  and  $>\text{C}=\text{C}<$  group.

## 2. Methods

### 2.1. Catalyst

The skeletal nickel was prepared by treatment a nickel aluminum alloy (average particle radius of  $4.8\ \mu\text{m}$ ) by sodium hydroxide in a known manner [8]. Such catalyst had a specific surface area:  $170 \pm 2\ \text{m}^2/\text{g}$ , a porosity:  $0.50 \pm 0.05\ \text{cm}^3/\text{cm}^3$ , it had a high activity in the liquid phase hydrogenation reactions [9]. The hydrogenation process was carried out by a static method in a closed system under vigorous stirring of a liquid phase, which excludes the effect of the external mass transfer to the experimental results. The reactor was designed to be capable of measuring the rate of hydrogenation reaction by volume of hydrogen, absorbed during the reaction. Under the experimental conditions stirring rate was  $3600\ \text{rev}\cdot\text{min}^{-1}$ , the hydrogen pressure was atmospheric, the temperature of the liquid phase was  $303\ \text{K}$ ,  $m_{\text{kat}} = 0.5 \pm 0.01\ \text{g}$ , the liquid phase volume:  $V = 102\ \text{cm}^3$ .

### 2.2. Hydrogenated Substances

MADE was chosen as a first model compound because regularities of which heterogeneous catalytic reduction over skeletal nickel are well studied and indicate that the kind of kinetic curves is the same type as the kinetic curves of the liquid-phase hydrogenation of other molecules with carbon-carbon double bond: sodium maleate [10], maleic anhydride [11, 12] and styrene [13, 14].

As the second model compound containing a nitro group was chosen 4-nitrotoluene, kinetics of the hydrogenation of which was also well-studied [15, 16]. Chromatographic analysis of the reaction products indicated that the selectivity of the obtaining of p-toluidine in chosen experimental conditions exceeds 95%, and nitroso compounds not detected. Previously [16] it has been shown that in systems with an alcohol content of less than 0.075 mole fraction the intermediate product (4-gidroksilaminotoluol) can be observed, the reduction rate of the one is nevertheless high, and its concentration in the reaction medium does not exceed 3%, which is well-confirmed by methods of liquid chromatography.

The process of reduction of 4-nitrotoluene has an order for the nitro compound close to zero, over the whole reaction time, that indicates the constancy of the hydrogen concentration in the reaction zone and the constancy of the hydrogen filling degree on the catalyst surface [15, 17].

Hydrogenation of 4-nitrotoluene was carried out in a quantity  $4.8 \times 10^{-3}\ \text{mole/g}(\text{Ni})$ , which was chosen in order to avoid occurrence of side reactions. The reaction was carried

out in aqueous solutions of 2-propanol with alcohol mole fraction  $x_2 = 0.073$ . Selection of such a solvent for liquid phase catalytic hydrogenation reaction was caused by the frequent use of aqueous-alcoholic medium, with various additives [18] for carrying out hydrogenation reactions in the industry. Selection of concentrations of these hydrogenated compounds in the mixture was performed to be absorbed  $160\ \text{cm}^3$  of hydrogen at one experiment, so for each of the components of the mixture the same amount of hydrogen was been absorbed.

### 2.3. Modification of the Catalyst Surface

Selecting of sodium sulfide as a modifier was caused by its ability to not only block the active sites of skeletal nickel catalyst [15, 19], but also by the possibility of promoting the processes of liquid-phase hydrogenation [15], which may be associated with several factors: the redistribution of adsorbed hydrogen on metal-hydrogen binding energy [20], the adsorptive deformation of the adsorbent, increasing the specific catalyst surface [9, 21] and the change of the solubility of the organic substrate.

According to the study [15], pretreatment of skeletal nickel by  $\text{Na}_2\text{S}$  increased as the stability of the catalyst during multiple inputs of 4-nitrotoluene as the part of the adsorptive complexes of hydrogen-metal with high binding energies, that are the most active in the process of hydrogenation of the nitro group [22].

The modification of catalyst by sodium sulfide was carried out by the method described in [15]. The concentration of sulfide ions at a partial deactivation was controlled by potentiometry using ion-selective electrode and by elemental analysis (CHNS-O Analyzer ThermoQuest). To test the effect of the hydrogenation product of 4-nitrotoluene to kinetics of MADE reduction the series of MADE reduction in the presence of p-toluidine were carried out. The quantity of p-toluidine was  $4.8 \times 10^{-3}\ \text{mol/g}(\text{Ni})$ , which corresponds to the stoichiometric quantity of 4-nitrotoluene hydrogenated in the same experiment (see section 2.2.).

### 2.4. Methods for Calculating of the Kinetic Characteristics of the Hydrogenation Reactions

The main kinetic parameter for characterizing of the nickel catalyst activity (A) was the reaction rate of hydrogenation at less than 0.05 from conversion level. The rate of hydrogenation reaction at such conversion ratio of the substrate is directly related to the reactivity of the catalytically active sites [10, 17]. In this case, by-products was not yet gave of its influence to the overall rate of the process, and the pressure and the concentration of hydrogen in the solution remained constant. Thus, the initial reaction rate will not depend on the initial concentration of the compound for hydrogenation, which was selected in all the experiments the same.

The reaction rate at the initial moment was calculated by the following equation:

$$r_R = -\frac{dc}{d\tau} \frac{1}{m_{kt}} = \frac{c_0}{m_{kt}} \frac{d\alpha}{d\tau}$$

Where  $c_0$  is the initial concentration of the reactant;  $c$  is the reactant concentration at the moment of time  $\tau$ ;  $\alpha = V_i / V_{\text{tot}}$  is the conversion ratio;  $V_i$  is volume of hydrogen absorbed to the time  $\tau$ ;  $V_{\text{tot}}$  is the total amount of absorbed hydrogen, the values was adjusted to standard temperature and pressure (273.15K, 1 bar).

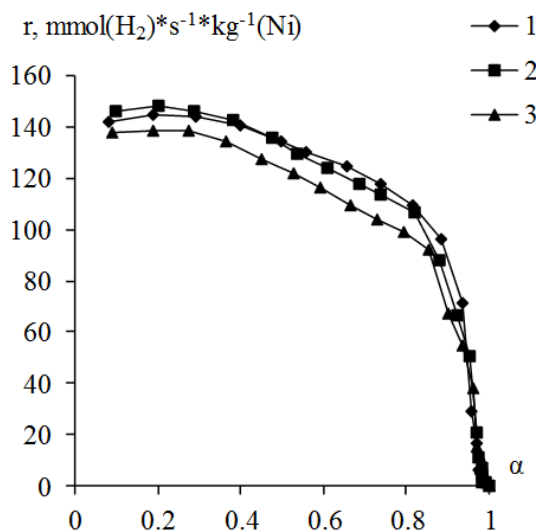
The observed rate constant was calculated from the equation:  $k_R = r_R \cdot \rho \cdot 760 \cdot \alpha^{-1} \cdot P_{H_2}^{-1}$ ; where  $\rho$  is the apparent density of the catalyst (for the used catalyst it was 4.5 g/cm<sup>3</sup>);  $r_R$  is the observed reaction rate (cm<sup>3</sup>(H<sub>2</sub>) s<sup>-1</sup>·g<sup>-1</sup>(Ni)) at less than 5% from conversion level;  $\alpha$  is Bunsen coefficient for hydrogen at 303 K in cm<sup>3</sup>(H<sub>2</sub>)/cm<sup>3</sup> (liquid phase);  $P_{H_2}$  is partial pressure of H<sub>2</sub>.

### 3. Results and Discussion

The dependencies of the observed rate of MADE hydrogenation at its successively injected samples in one portion of the catalyst are shown in Figure 1.

14.4·10<sup>-3</sup> mol/g(Ni) was injected for one time, this quantity corresponds to the same quantity of hydrogen, which goes to the hydrogenation of the 4-nitrotoluene in section 2.2. (4.8·10<sup>-3</sup> mol/g(Ni)).

The analysis of dependencies from Figure 1 showed that the activity of the catalyst in successive injections of MADE (unlike to the successive injections of 4-nitrotoluene [15]) decreased slightly, that is likely indicates the small surface oxidation of nickel atoms by the reagent, the product of the hydrogenation and the components of the catalyst system.



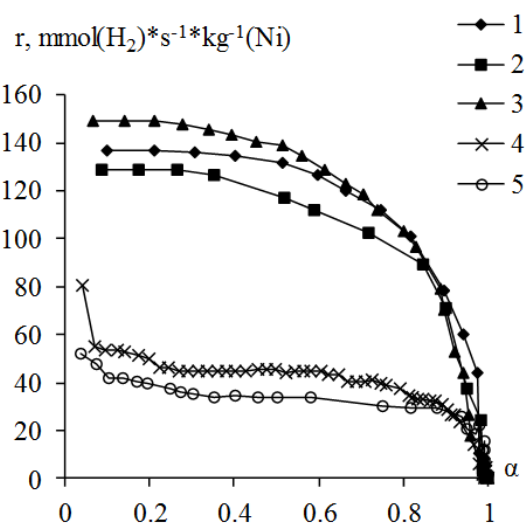
**Figure 1.** The hydrogenation kinetic curves of successive injections of MADE over one portion of the catalyst:  $T = 303K$ ,  $n_{MADE} = 14.4 \cdot 10^{-3}$  mol/g(Ni),  $m_{kat} = 0.50 \pm 0.01g$ : 1-1st injection; 2-2nd injection; 3-3d injection.

On the other hand, the surface modification of skeletal nickel by sodium sulfide up to 0.025 mmol (Na<sub>2</sub>S)/g(Ni) concentration (which leads to a marked promotion of the 4-nitrotoluene hydrogenation reaction [15]) showed an opposite effect on the catalyst activity in the MADE reduction reaction. An illustration of this fact is the data in Figure 2,

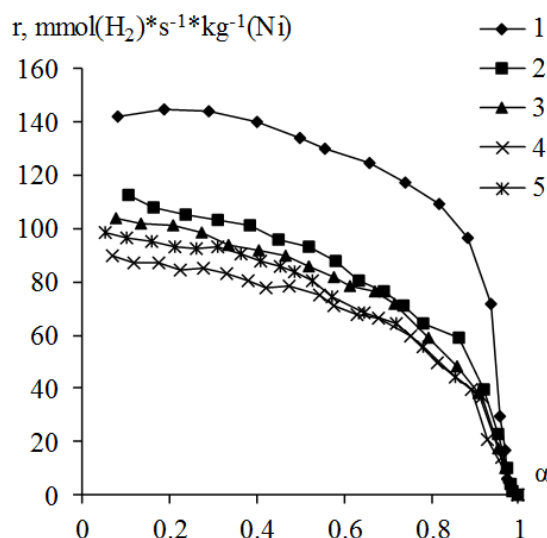
which shows the dependences of the reaction rate versus the conversion ratio of the MADE hydrogenation process over skeletal nickel modified by different quantity of sodium sulfide.

The data in Figure 2 correspond to [19], according to which any additives of sodium sulfide in aqueous solutions of sodium hydroxide always decreased skeletal nickel activity in the hydrogenation reaction of sodium maleate.

Figure 3 shows the dependences of the reaction rate versus the conversion ratio of the MADE hydrogenation process over unmodified catalyst and successive injections of MADE over one portion of the catalyst modified with sodium sulfide in the chosen conditions.



**Figure 2.** Dependences of the MADE hydrogenation rate ( $n_{MADE} = 14.4 \cdot 10^{-3}$  mol/g(Ni)) versus the conversion ratio ( $\alpha$ ) of the reaction over the modified skeletal nickel ( $m_{kat} = 0.50 \pm 0.01g$ ) in 2-propanol-water solvent ( $x_2 = 0.073$ ):  $T = 303K$ ,  $C_{Na_2S}$ , mmol S<sup>2-</sup>/g(Ni): 1-0; 2-0.025; 3-0.05; 4-0.6; 5-1.



**Figure 3.** Hydrogenation kinetic curves of: MADE over the unmodified catalyst - (1) and successive injections of MADE over one portion of the modified catalyst by sodium sulfide (0.05 mmol (Na<sub>2</sub>S)/g(Ni)) in 2-propanol-water solvent ( $x_2 = 0.073$ ,  $T = 303K$ ,  $n_{MADE} = 14.4 \cdot 10^{-3}$  mol/g(Ni),  $m_{kat} = 0.50 \pm 0.01g$ , 2-1st injection; 3-2nd injection; 4-3d injection; 5-4th injection.

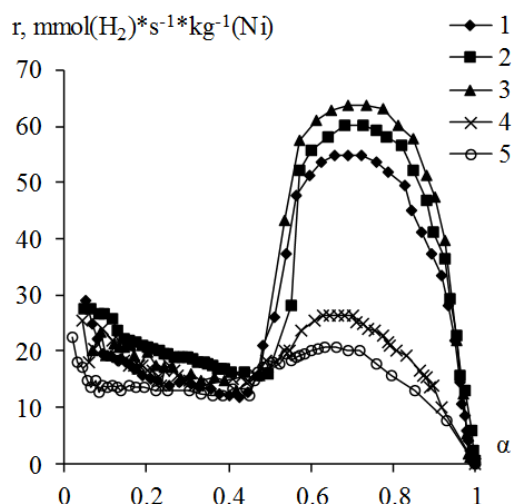
The data in Figure 3 indicate that the treatment of skeletal nickel by sodium sulfide does not increase the stability of the catalyst and also increases the effect of deactivating while there are successive injections of MADE. At the same time the kind of the kinetic curves for successive injections of MADE remains similar to the data in Figure 1. Moreover, in a series of pilot experiments it is shown that any treatment by p-toluidine also leads to a definite activity decrease of skeletal nickel for MADE hydrogenation.

The table shows the value of skeletal nickel activity in selected model processes. The table and [15] show that the character of the catalyst surface modification by sodium sulfide is antibate in hydrogenation reactions of MADE and of 4-nitrotoluene. The totality of these facts allows to predict not only the possibility of separate hydrogenation of various functional groups in the model mixture but the possibility of purposeful change in the properties of the catalyst system by the sulfidation of catalysts, which leads to a change in the selectivity in the hydrogenation process.

**Table 1.** The parameters of the catalytic activity of the modified skeletal nickel catalyst in model hydrogenation reactions of 4-nitrotoluene and of MADE,  $T = 303K$ ,  $n_{4-nt} = 4.8 \cdot 10^{-3} \text{ mol/g(Ni)}$ ,  $n_{MADE} = 14.4 \cdot 10^{-3} \text{ mol/g(Ni)}$ ,  $m_{kat} = 0.50 \pm 0.01g$ ,  $x_2 = 0.073$ .

$n_{Na_2S} \cdot 10^5, \text{ mol} \cdot g^{-1}(\text{Ni})$	$r_R^0 \cdot 10^2, *$	$k_R^0, s^{-1}$	$r_R^0 \cdot 10^2, *$	$k_R^0, s^{-1}$
	4-nitrotoluene [15]		MADE	
0	3.8±0.2	400±16	13.6±0.2	815±19
2.5	4.5±0.2	467±12	12.9±0.2	777±18
5	5.2±0.2	541±13	10.8±0.2	626±16
60	3.4±0.2	381±11	9.9±0.2	585±13
100	2.5±0.2	149±10	4.4±0.2	217±11

\*  $\text{mol}(\text{H}_2) \cdot s^{-1} \cdot \text{kg}^{-1}(\text{Ni})$



**Figure 4.** Kinetic curves of a mixture hydrogenation of 4-nitrotoluene and MADE in the 2-propanol-water solvent with  $x_2 = 0.073$ ,  $T=303K$ ,  $n_{4-nt} = 4.8 \cdot 10^{-3} \text{ mol/g(Ni)}$ ,  $n_{MADE}=14.4 \cdot 10^{-3} \text{ mol/g(Ni)}$  over skeletal nickel ( $m_{kat} = 0.5 \pm 0.01g$ ) and over the catalyst modified by sodium sulfide,  $1-n_{Na_2S} = 0$ ;  $2-0.025 \text{ mmol}(\text{Na}_2\text{S})/\text{g}(\text{Ni})$ ;  $3-0.05 \text{ mmol}(\text{Na}_2\text{S})/\text{g}(\text{Ni})$ ;  $4-0.6 \text{ mmol}(\text{Na}_2\text{S})/\text{g}(\text{Ni})$ ;  $5-1 \text{ mmol}(\text{Na}_2\text{S})/\text{g}(\text{Ni})$ .

Figure 4 shows an example of the hydrogenation kinetic curve of mixture of MADE and of 4-nitrotoluene. The mixture

contains 0.75 mole fraction of MADE and 0.25 mole fraction of 4-nitrotoluene, this ratio provides the same quantity of absorbed hydrogen in relation to each reagent. Comparison of the initial rates of hydrogenation of MADE and of 4-nitrotoluene (given in the table) allows to assume that the linear area of the dependence should be responsible for the hydrogenation of nitro compounds, and the subsequent maximum is for MADE. However catalyzates chromatographic analysis shows that the interaction of both organic substrates with hydrogen is concurrently but at different speeds. According to Figure 4 sulphidation of surface has a significant influence on the hydrogenation only of MADE, while the hydrogenation of 4-nitrotoluene occurs without any significant changes. Furthermore, additional mutual influence of reagents effected in the decrease the observed effect of addition promoting from sodium sulfide at a hydrogenation reaction of 4-nitrotoluene to experimental error and in the fall of MADE hydrogenation rate from  $\approx 140$  to  $\approx 70 \text{ mmol}/(s \cdot \text{kg}(\text{Ni}))$ .

## 4. Conclusions

The results of these studies have shown that the effect of the sulfidation of the catalyst to the hydrogenation of 4-nitrotoluene and of MADE has a different character. It has been found that the addition of sodium sulphide can promote the hydrogenation process of 4-nitrotoluene and how to increase the stability of the catalyst systems in the case of the hydrogenation of 4-nitrotoluene, and decrease it when in the case of the hydrogenation of MADE. It was established experimentally that the hydrogenation of the two compounds occurs parallel but can be with different rates, it depends on the solvent composition and the amount of adsorbed sodium sulfide.

## Acknowledgements

The work is supported by the Russian Ministry of Education and Science as part of the State task (№3.1371.2017/project part).

Work is executed at the Institute of Thermodynamics and kinetics of chemical laboratories processes "Ivanovo State University of Chemistry and Technology".

## References

- [1] Stakheev A. Y., Isaeva V. I., Kustov L. M. et al. Novel catalysts for selective hydrogenation of  $C \equiv C$  bond based on Pd nanoparticles immobilized in phenylencarboxylate frameworks (NH<sub>2</sub>)-MIL-53 (Al). Russian Chemical Bulletin, 2015, 64 (2), 284-290.
- [2] Cárdenas-Lizana F., Gómez-Quero S., Keane M. A. Clean production of chloroanilines by selective gas phase hydrogenation over supported Ni catalysts. Applied Catalysis A: General, 2008, 334 (1), 199-206.
- [3] Cárdenas-Lizana F., Gómez-Quero S., Keane M. A. et al. Pd-promoted selective gas phase hydrogenation of p-chloronitrobenzene over alumina supported Au. Journal of Catalysis, 2009, 262 (2), 235-243.

- [4] Ostrovski N. M. Catalyst deactivation: mechanisms, kinetics, testing. *Hemijska Industrija*, 2009, 63 (5), 545-555.
- [5] Rumyantsev R. N., Il'in A. A., Il'in A. P., Pazukhin I. V. Influence of mechanical activation of molybdenum oxide on its catalytic activity in the reaction of the partial oxidation of methanol. *Theoretical and Experimental Chemistry*, 2011, 47 (1), 41-44.
- [6] Mäki-Arvela P., Kuusisto J., Sevilla E. M., et al. Catalytic hydrogenation of linoleic acid to stearic acid over different Pd- and Ru-supported catalysts. *Applied Catalysis A: General*, 2008, 345 (2), 201-212.
- [7] Gelder E. A., Jackson S. D., Lok C. M. The hydrogenation of nitrobenzene to aniline: a new mechanism. *Chemical communications*, 2005, 4, 522-524.
- [8] Barbov A. V., Nabilkov V. E., Ulitin M. V. Effect of Residual Aluminum in Raney Nickel on the Results of Thermochemical Studies on Hydrogenation. *Russian journal of physical chemistry*, 1997, 71 (3), 367-370.
- [9] Afineevskii A. V., Osadchaia T. Y., Prozorov D. A., et al. Selective blockage of the catalyst active sites for the hydrogenation of various functional groups over Raney nickel and nickel supported on silica. *Trends Green Chem.* 2016, 2: 1.
- [10] Lukin M. V., Afineevskii A. V. The concentration effect of adsorption nanocomplexes on the catalytic activity of skeletal nickel in liquid-phase hydrogenation of sodium maleate in aqueous organic environments. *Protection of Metals and Physical Chemistry of Surfaces*, 2013, 49 (4), 451-454.
- [11] Gao C. G., Zhao Y. X., Liu D. S. Liquid phase hydrogenation of maleic anhydride over nickel catalyst supported on  $ZrO_2$ - $SiO_2$  composite aerogels. *Catalysis Letters*, 2007, 118 (1-2), 50-54.
- [12] Feng Y., Yin H., Wang A., Xie T., Jiang T. Selective hydrogenation of maleic anhydride to succinic anhydride catalyzed by metallic nickel catalysts. *Applied Catalysis A: General*, 2012, 425, 205-212.
- [13] Dowden D. A., Reynolds P. W. Some reactions over alloy catalysts. *Discussions of the Faraday Society*, 1950, 8, 184-190.
- [14] Nijhuis T. A., Dautzenberg F. M., Moulijn J. A. Modeling of monolithic and trickle-bed reactors for the hydrogenation of styrene. *Chemical Engineering Science*, 2003, 58 (7), 1113-1124.
- [15] Osadchaia T. Y., Afineevskii A. V., Prozorov D. A., Lukin M. V. Catalytic properties of the modified skeletal nickel in the reaction of liquid phase hydrogenation of 4-nitrotoluene. *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 2015, 58 (3), 26-31, (in Russian).
- [16] Neri G., Musolino M. G., Rotondo E., Galvagno S. Catalytic hydrogenation of 2, 4-dinitrotoluene over a Pd/C catalyst: identification of 2-(hydroxyamino)-4-nitrotoluene (2HA4NT) as reaction intermediate. *Journal of Molecular Catalysis A: Chemical*, 1996, 111 (3), 257-260.
- [17] Sokolsky D. V. Hydrogenation in solutions. [Gidrirovanie v rastvorakh]. Almaty: Nauka, 1979.
- [18] Min K. I., Choi J. S., Chung Y. M., et al. p-Aminophenol synthesis in an organic/aqueous system using Pt supported on mesoporous carbons. *Applied Catalysis A: General*, 2008, 337 (1), 97-104.
- [19] Lukin M. V., Prozorov D. A., Ulitin M. V., et al. Controlled deactivation of a skeletal nickel catalyst with sodium silfide in liquid-phase hydrogenation reactions. *Kinetics and Catalysis*, 2013, 54 (4), 412-419.
- [20] Prozorov D. A., Lukin M. V., Ulitin M. V. Effect of controlled deactivation on the thermochemical characteristics of hydrogen adsorption on skeletal nickel from sodium hydroxide-water solutions. *Russian Journal of Physical Chemistry A*, 2013, 87 (4), 576-579.
- [21] Ma X., Liu Y., Li X., et al. Water: the most effective solvent for liquid-phase hydrodechlorination of chlorophenols over Raney Ni catalyst. *Applied Catalysis B: Environmental*, 2015, 165, 351-359.
- [22] Lukin M. V., Prozorov D. A., Ulitin M. V., et al. Dependence of the thermodynamic characteristics of forms of hydrogen adsorbed on a porous nickel surface on the degree of deactivation. *Russian Journal of Physical Chemistry A*, 2013, 87 (7), 1092-1096.