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ВОССТАНОВЛЕНИЕ СОЕДИНЕНИЙ, СОДЕРЖАЩИХ СВЯЗЬ «АЗОТ-КИСЛОРОД», НА СКЕЛЕТНОМ НИКЕЛЕ В ВОДНЫХ РАСТВОРАХ 2-ПРОПАНОЛА

Экспериментально установлено, что количество водорода, поглощенного при восстановлении нитробензола и нитрозобензола на скелетном никеле в водных растворах 2-пропанола, в отличие от азоксибензола, не отвечает стехиометрии реакции. При введении в водный раствор 2-пропанола добавок кислоты или основания скорости восстановления нитро-, нитрозо- и азоксибензола изменяются в различной степени. В ходе реакции возможно обратимое или необратимое окисление поверхности катализатора. Адсорбция анилина на окисленной поверхности катализатора не протекает. Как следует из приведенных данных, во всех случаях количество образующегося анилина превышает количество водорода, поглощенного из газовой фазы. Расхождение в количествах образовавшегося анилина и поглощенного водорода (α=0,5) для нитро- и нитрозобензола больше, чем при гидрогенизации азоксибензола. Это свидетельствует о росте диффузионного торможения по восстановителю при переходе от нитрозобензола к нитро- и азоксибензолу. Адсорбционная и реакционная способность водорода, нитробензола и промежуточных соединений может изменяться под влиянием растворителя. Реакции гидрогенизации нитро- и нитрозобензола на скелетном никеле в водных растворах 2-пропанола сопровождаются протеканием параллельного процесса окисления поверхности катализатора, что приводит к нарушению стехиометрии реакции во всех изученных растворителях. В присутствии гидроксида натрия следует ожидать более высоких степеней окисления активных центров, чем в растворителе с добавкой уксусной кислоты. Необратимое окисление скелетного никеля отсутствует при гидрогенизации азоксибензола. При проведении данной реакции не исключено обратимое окисление активной поверхности катализатора с сохранением стехиометрии для всех составов растворителей, при отсутствии необратимого окисления поверхности катализатора значения $k^0_н$ ***можно считать объективной характеристикой для проведения сравнительного анализа реакционной способности различных групп. Уменьшение количества анилина при полной конверсии гидрируемого соединения свидетельствует о конкурирующем характере адсорбции.***

Ключевые слова: нитробензол, нитрозобензол, азоксибензол, анилин, водород, скелетный никель, восстановление, адсорбция, скорость гидрогенизации, водные растворы 2-пропанола, уксусная кислота, гидроксид натрия

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A STUDY ON THE REDUCTION OF COMPOUNDS CONTAINING NITROGEN-OXYGEN BOND ON SKELETAL NICKEL IN AQUEOUS SOLUTIONS OF 2-PROPANOL

It was experimentally established that the amounts of hydrogen absorbed from gaseous phase at the hydrogenation of nitrobenzene and nitrosobenzene on skeletal nickel in aqueous 2-propanol do not correspond to the stoichiometry of the reaction. Acetic acid or sodium hydroxide additions into the aqueous solutions of 2-propanol act differently on the rate of the nitro-, nitroso- and azoxybenzene hydrogenation. During the reaction the reversible or irreversible oxidation of the catalyst surface can take place. The adsorption of aniline does not take place on oxidized catalyst surface.

Key words: nitrobenzene, nitrosobenzene, azoxybenzene, aniline, skeletal nickel, adsorption, hydrogenation rate, 2-propanol aqueous solutions, acetic acid, sodium hydroxide

INTRODUCTION

The catalytic hydrogenation of nitrobenzene has been of both theoretical and practical interest for many years. Changing the reaction conditions may lead to the formation of various compounds. It is known that the reduction of nitro group may proceed by steps [1, 2]. Sequential addition of hydrogen to nitro group leads to the formation of nitrosobenzene, aniline and phenylhydroxylamine. The associative interactions on the catalyst surface between nitrobenzene and hydrogen, resulting in the formation of semi-hydrogenated form R-NOH are not excluded. Under hydrogen deficient conditions R-NOH particles may combine to form azoxybenzene [3]. It is noted that particles such as R-NOH have high reactivity and actively interact among themselves at pH > 9 [4, 5].

The adsorption and reactivity properties of hydrogen, nitrobenzene, nitrosobenzene and intermediate compounds may be changed under the influence of solvents. Therefore, studying of the reaction kinetics of the reduction of nitrobenzene and its hydrogenated intermediates is of interest for the informed choices of solvents.

The purpose of the present work is to study the reaction kinetics of hydrogenations of nitrobenzene (NB), nitrosobenzene (NZ) and azoxybenzene (AZOB) on skeletal nickel in aqueous solutions of propanol, including solutions with acetic acid or sodium hydroxide additions.

MATERIALS AND METHODS

Skeletal nickel, which was used in this work, had been prepared from nickel – aluminum alloy with composition Ni:Al:Fe = 47.5:50.2:0.3 wt%. The mother alloy was firstly pulverized into a disperser and followed by fractionated in the Gonell air separator. The particle-size distribution of the obtained powders was determined by conductometric method on «Coultronics» counter. The particle radius of used alloy is 4.5 – 4.8 μm.

The active catalyst was prepared by treating the initial alloy with 7.5 M aqueous solution of sodium hydroxide, followed by washing with distilled water until pH = 7 [6]. The specific surface area and porosity of the obtained catalyst were 90±2 m^2 /g и 0.5±0.06 cm^3/cm^3 Ni, respectively [6].

The hydrogenations of nitrobenzene, nitrosobenzene and azoxybenzene were carried out in a closed vessel with vigorous agitation of the liquid phase at atmospheric pressure of hydrogen [6]. The azeotropic aqueous solutions of 2-propanol (x_2 = 0.68 mole fraction) with the addition of acetic acid or sodium hydroxide (0.01 M) were used.

During the experiment, the amount of absorbed hydrogen was measured by volumetric method. The concentrations of reactants and products were controlled by HPLC and spectrophotometric methods.

Sample analysis was performed on liquid chromatograph «Shimadzu» under the following conditions: Column filler – «Lichrosorb RP-18", eluent – acetonitrile – water (30 vol % acetonitrile.), eluent flow-rate – 0.9 cm^3/min, the column thermostat temperature 30.8 °C. The wavelengths of detector were 250 nm (for nitrobenzene and aniline) and 280 nm (for nitrosobenzene). The retention times were 690±10s; 800±20s; 310±10s for nitrobenzene, nitrosobenzene, and aniline, respectively.

Concentrations of azoxybenzene were determined using spectrophotometer «CARY 50 scan UV-Visible Spectrophotometers». The thickness of the absorbing layer was 1 cm, the wavelength – 323 nm.

RESULTS AND DISCUSSIONS

The obtained kinetics curves during the hydrogenations of nitrobenzene, azoxybenzene and nitrosobenzene on skeletal nickel in aqueous solutions of 2-propanol (x_2 = 0.68) are presented in Fig. 1-3. Similar relationships were also obtained for solutions with acetic acid (0.01 M) or sodium hydroxide (0.01 M).

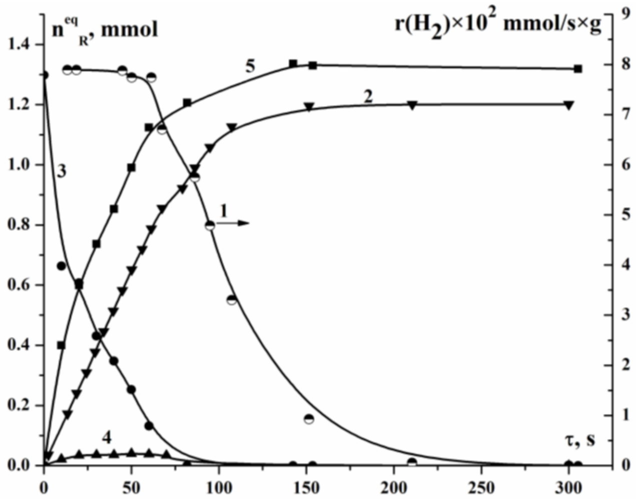

Fig. 1. The kinetic curves of hydrogenation reaction of nitrobenzene on skeletal nickel in aqueous solutions of 2-propanol: x_2 = 0.68; m_{kat} = 0.500 ± 0.001 g, $R_{кат}$ = 4.5 μ, T = 303 K; n^0_{RNO2} = (1.6 ± 0.1) mmol, $V_{reactor}$ = 100 cm^3: 1 – reaction rate, 2 – hydrogen, 3 - nitrobenzene, 4 – phenylhydroxylamine, 5 – aniline

Рис. 1. Кинетические кривые реакции гидронеизации нитробензола на скелетном никеле в водном растворе 2-пропанола: x_2 = 0,68; $m_{кат}$ = 0,500 ± 0,001 г, $R_{кат}$ = 4,5 мкм, T = 303 К; n^0_{RNO2} = (1.6 ± 0.1) ммоль, $V_{реактор}$ =100 cm^3: 1 – наблюдаемая скорость, 2 – водород, 3 - нитробензол, 4 – фенилгидроксиламин, 5 – анилин

As can be seen from the data, for all cases, the amount of formed aniline exceeds the amount of hydrogen absorbed from the gas phase.

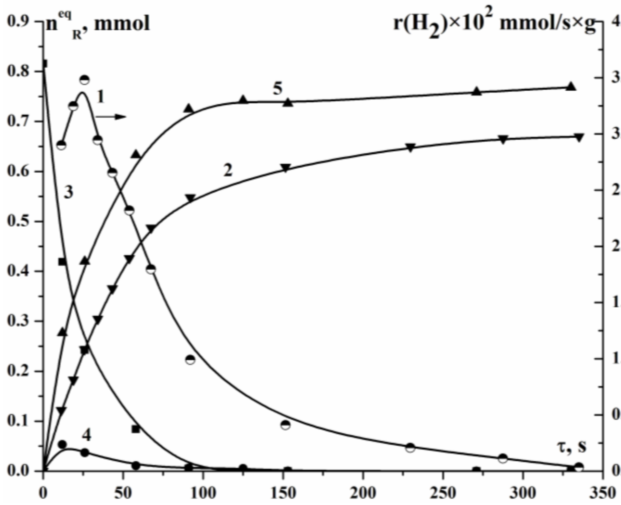

Fig. 2. The kinetic curves of hydrogenation reaction of nitrosobenzene on skeletal nickel in aqueous solutions of 2-propanol: x_2=0.68; m_{kat}=0.500±0.001 g, $R_{кат}$=4.5 μ, T=303 K; C^0_{RNO} = 0.85±0.01 mmol, $V_{reactor}$=100 cm^3: 1– reaction rate, 2–hydrogen, 3-nitrosobenzene, 4–azoxybenzene, 5–aniline

Рис. 2. Кинетические кривые реакции гидронеизации нитрозобензола на скелетном никеле в водном растворе 2-пропанола: x_2 = 0,68; $m_{кат}$ = 0,500 ± 0,001 г, $R_{кат}$ = 4,5 мкм, T = 303K; n^0_{RNO} = (0,85 ± 0,01) ммоль, $V_{реактор}$ =100 cm^3: 1 – наблюдаемая скорость, 2 – водород, 3 - нитрозобензол, 4 – азоксибензол, 5 – анилин

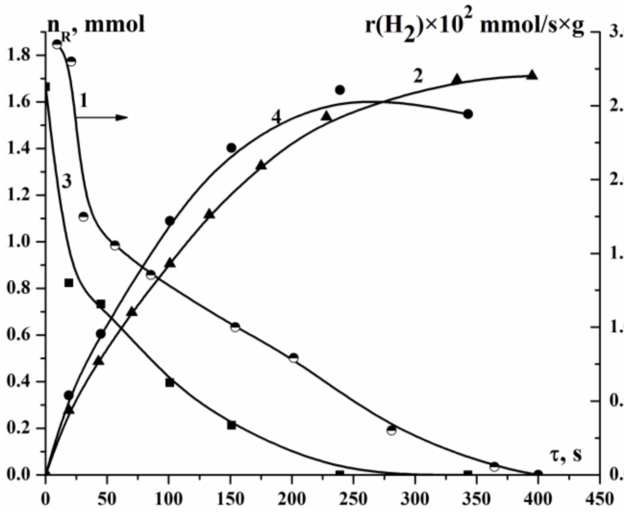

Fig. 3. The kinetic curves of hydrogenation reaction of azoxybenzene on skeletal nickel in aqueous solvents of 2-propanol: x_2 = 0.68; m_{kat} = 0.500 ± 0.001 g, $R_{кат}$ = 4.5 μ, T = 303 K; C^0_{RNHOH} = (1.6 ± 0.1) mmol, $V_{reactor}$ = 100 cm^3: 1 – reaction rate, 2 – hydrogen, 3 - azoxybenzene, 4 – aniline

Рис. 3. Кинетические кривые реакции гидронеизации азоксибензола на скелетном никеле в водном растворе 2-пропанола: x_2 = 0,68; $m_{кат}$ = 0,500 ± 0,001 г, $R_{кат}$ = 4,5 мкм, T = 303K; $n^0_{азоксибензола}$ = (1,6 ± 0,1) ммоль, $V_{реактор}$ = 100 cm^3: 1 – наблюдаемая скорость, 2 – водород, 3 - азоксибензол, 4 –анилин

In Table 1, we present the values of the observed reaction rate constant – $k_{obs.}$ calculated after treatment with C_R = f(τ) in the linear coordinates of the first-order reaction. The values of Δn were calculated at the moment that the initial reactant converted 50%, by the formula: $\Delta n = n_R - n_{H2}$, where n_R – the equivalent amount of the hydrogenated compound (mol), n_{H2} – the equivalent amount of the hydrogen absorbed from the gas phase (mol). The adsorptions of nitro-, nitroso- and azoxybenzene – g_R were calculated from the material balance conditions. The stoichiometry coefficient of the reaction – γ (H_2 mmol/mmol of reactant) was calculated from the total quantity of hydrogen absorbed during the reaction.

Table 1

Characteristics of hydrogenation reactions of nitro-, nitroso- and azoxybenzene on skeletal nickel in aqueous solutions of 2-propanol with different composition

Таблица 1. **Характеристики реакций гидрогенизации нитро-, нитрозо- и азоксибензолов на скелетном никеле в водных растворах 2-пропанола различного состава**

Solutions	k_H, s^{-1}	Δn, mmol	g_R, mmol/kg	γ, mmol/mmol
nitrobenzene				
2-propanol-water	110 ± 5	0.30 ± 0.03	400 ± 30	2.75 ± 0.05
2-propanol-water-H^+	20 ± 2	0.10 ± 0.02	300 ± 20	2.85 ± 0.05
2-propanol-water-OH^-	57 ± 3	0.30 ± 0.03	200 ± 30	2.60 ± 0.03
nitrosobenzene				
2-propanol-water	45 ± 2	0.32 ± 0.04	300 ± 20	1.65 ± 0.02
2-propanol-water-H^+	58 ± 3	0.16 ± 0.02	200 ± 30	1.70 ± 0.02
2-propanol-water-OH^-	41 ± 2	0.40 ± 0.05	1400 ± 50	1.60 ± 0.02
azoxybenzene				
2-propanol-water	41 ± 2	0.10 ± 0.02	500 ± 30	3.00 ± 0.02
2-propanol-water-H^+	6 ± 1	≈ 0.01	100 ±10	3.00 ± 0.03
2-propanol-water-OH^-	61 ± 3	0.13 ± 0.01	1200 ± 30	2.95 ± 0.03

The difference between the amounts of absorbed hydrogen and aniline in the cases of nitro- and nitrosobenzene hydrogenation is higher than that in azoxybenzene hydrogenation. It shows the growth of inhibited diffusion from the nitrosobenzene to the nitro- and azoxybenzene.

Δn characterizes the active participation of adsorbed hydrogen in the initial reaction phase and demonstrates the high reactivity of the hydrogenated compounds. In all the solutions the values of Δn are in the order:

Nitrobenzene ≈ nitrosobenzene > azoxybenzene

The observed initial rates of hydrogenation reactions ($\mathbf{r_{H2}}$) and the effective charge on the reaction sites of studied compounds ($\mathbf{q_{eff}}$) vary in the same order.

$\mathbf{r_{H_2}}$: NB > NS > AZOB; $\mathbf{q_{eff}}$: NB > NS > AZOB

The values of $\mathbf{q_{eff}}$ and the LUMO energy of NB, NS and AZOB are showed in the Table 2.

Table 2

The atom charge on nitrogen (q_{eff}) and energy of LUMO (E_{LUMO}) calculated at PM3 level for the adducts of nitro-, nitroso- and azoxybenzene with one 2-propanol molecule [7]

Таблица 2. **Эффективные заряды на атомах азота (q_{eff}) и значения энергии низших свободных молекулярных орбиталей (E_{LUMO}), рассчитанные методом PM3 для аддуктов нитро-, нитрозо- или азоксибензола с одной молекулой 2-пропанола [7]**

Compound	nitrobenzene	nitrosobenzene	azoxybenzene
$\mathbf{q_{eff}}$	0.105	0.037	-0.029
$\mathbf{E_{LUMO}}$**, eV**	-1.24	-0.98	-1.09

The LUMO energies of nitro, nitroso and azoxybenzene correspond to the followed sequence: NS > AZOB > NB. Thus, we can conclude that the hydrogenation reactions of the studied compounds were affected by the atomic charges more than by the orbital energy [8].

It is known that nitroso- and nitrobenzenes have higher oxidation potentials compared to these of the azoxy compounds [9]. This can lead to the reaction stoichiometry violation due to the surface oxidation of skeletal nickel. Indeed, according to Table 1, reaction stoichiometry and the amount of absorbed hydrogen only coincide in the case of azoxybenzene hydrogenation. By hydrogenation of nitrosobenzene and nitrobenzene on Raney nickel in aqueous solution of 2-propanol added sodium hydroxide, the amounts of absorbed hydrogen from gaseous phase are 45% and 13% less than stoichiometry, respectively. For all compounds, the stoichiometric coefficient of hydrogen decreases in transition from an aqueous solution of 2-propanol consisting of acetic acid to neutral solution and solution consisting sodium hydroxide.

The adsorption capacities of hydrogenated compound increase in the order: neutral solution < solution consisting acid < solution consisting base. Increasing the concentration of reactive oxygen-containing compounds in the surface layer promotes the catalyst oxidation.

The data shown in Fig. 3 indicate that the concentration of aniline initially increases, reaches a maximum and then decreases. For the nitro- and nitrosobenzene hydrogenation in the aqueous solution of 2-propanol or solution added sodium hydroxide, the noticeable decreasing of aniline concentration after complete conversion of the hydrogenated compound was not observed. It is known that the oxidation of active site of skeletal nickel leads to the sharp decreasing or complete elimination of aniline adsorption on the catalyst surface [10].

Probably, the absence of the maximum on the kinetic curves, that characterizes the accumulation of aniline, associates with the irreversible oxidation of the catalyst active surface. The presence of maximum was mathematically justified in the work [11]. According to the obtained results [11], the maximum on the kinetic curves associates with the different absorption capacity of the initial compound and the reaction product. As specified by Belonogov and co-authors [10], the adsorption coefficients of nitrophenolate and sodium aminophenolate differ by more than an order of magnitude.

Based on the data, presented in the Fig. 1 and Fig. 2, the hydrogenations of nitrobenzene and nitrosobenzene on skeletal nickel lead to the formation of different intermediates: phenylhydroxylamine and azoxybenzene, respectively. This fact may indicate the various type of interactions between the hydrogenated compounds and the catalyst active site.

In Fig. 4 and Fig. 5 we present the probable mechanisms of active adsorption and transformation of nitrobenzene and nitrosobenzene on skeletal nickel catalyst surface, saturated by hydrogen.

The nitro group has three reactive sites, including two oxygen atoms, and nitrogen atom. The attacks of hydrogen on adsorbed oxygen and nitrogen atoms result in the formation of associative complexes (I) и (II). Followed by the cleavage of water molecule from complexes may form nitrosobenzene. Nitrosobenzene is chemically adsorbed on the active sites (III) and oriented parallel to the catalyst surface.

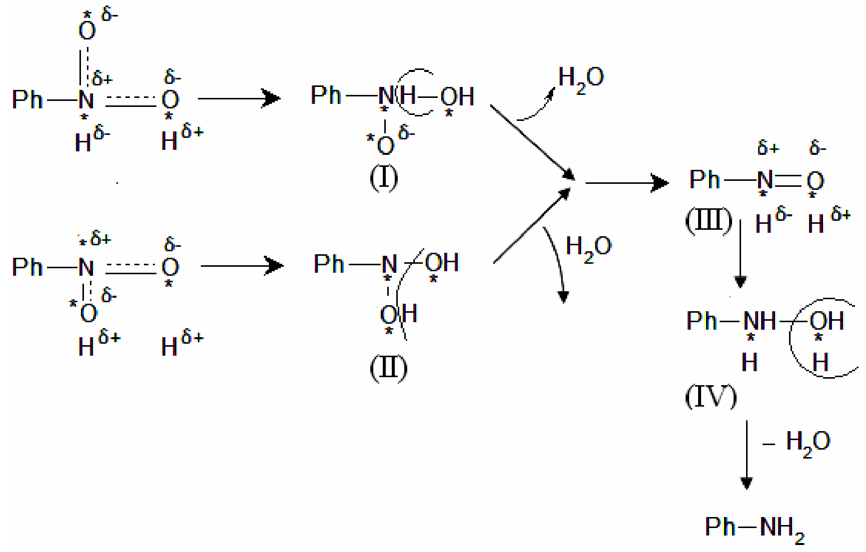

Fig. 4. The mechanism of nitrobenzene activated adsorption process and the steps of transformation of nitro group on the catalyst surface
Рис. 4. Механизм активированной адсорбции нитробензола и стадийность превращений нитрогруппы на поверхности катализатора

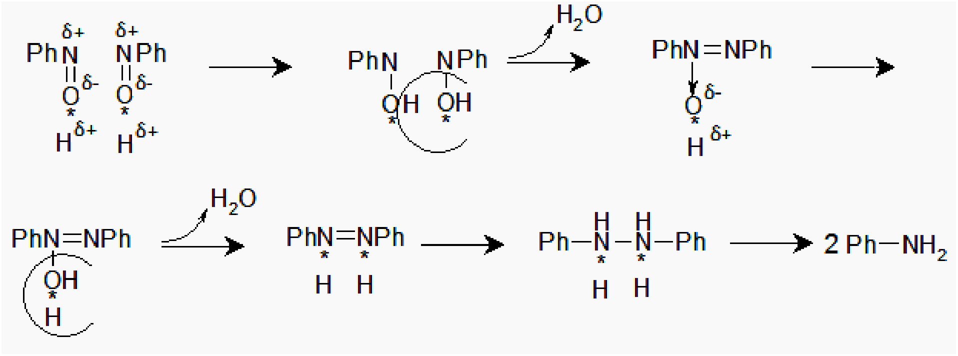

Fig. 5. The mechanism of nitrobenzene activated adsorption process and the steps of transformation of nitroso group on the catalyst surface
Рис. 5. Механизм активированной адсорбции нитрозобензола и стадийность превращений нитрозогруппы на поверхности катализатора

The subsequent attachment of hydrogen atoms on nitrogen and oxygen may be accompanied by the formation of phenylhydroxylamine (IV). In the presence of adsorbed hydrogen on the surface, phenylhydroxylamine is exclusively reduced to the aniline. Simultaneous hydrogen attack on all reaction centers of the nitro group is less probably, so the formation of intermediate products may be preceded by the stepwise addition of hydrogen to form associative semi-hydrogenated forms.

Characteristically, during the hydrogenation of nitrobenzene, the presence of nitrosobenzene in the liquid phase has not been recorded. This may be due to the higher adsorption capacity of nitrosobenzene compared to nitrobenzene [12, 13].

Chemisorption of nitrosobenzene molecules will be determined by the distribution of π-electron density along the N=O bond. This bond is strongly polarized, resulting in a high electron density on the oxygen atom, in contrast to the oxygen atoms of the nitro group. In this regard, nitrosobenzene is expected to orient vertically rather than parallel to the catalyst surface, saturated with hydrogen. It is known that oxygen atom in the N=O bond is out of the plane, which greatly reduces the probability of interaction between π-electrons of the benzene ring with the vacant orbitals of the catalyst. In this case, the attack on the nitrogen atom becomes unlikely (Fig. 5). In Fig. 5 the PhNOH particle is a semi-hydrogenated form of nitrosobenzene. The interaction of two neighboring PhNOH particles, as mentioned above, is accompanied by the formation of azoxybenzene. Thus, it is believed that the main reasons of the formation of phenylhydroxylamine and azoxybenzene from nitrobenzene and nitrosobenzene hydrogenation, respectively, are different orientations and different mechanisms of activation of reactive groups on the catalyst surface.

CONCLUSION

It can be noted that:

– the hydrogenation reactions of nitro- and nitrosobenzene on skeletal nickel in aqueous solutions of 2-propanol are accompanied by the occurrence of the parallel oxidation processes on the catalyst surface, resulting in the violation of reaction stoichiometry. The presence of sodium hydroxide may lead to the sharper oxidation of active sites compared to the solutions consisting acetic acid. The irreversible oxidation of skeletal nickel during the azoxybenzene hydrogenation is not observed;

- during the azoxybenzene hydrogenation the reversible oxidation of the catalyst active surface is not excluded while maintaining the reaction stoichiometry in all studied solutions;

- in the absence of irreversible catalyst surface oxidation the values of $k^{0}_{\text{н}}$ can be regarded as an objective characteristic for the comparative analysis of the reactivity of the different groups.

– on the oxidized catalyst surface the adsorption of aniline does not occur, due to the absence of the maximum on the kinetic curves;

– the decreasing of aniline concentration after complete conversion of hydrogenated compounds indicates the competitive adsorption of the reactant and the reaction product.

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