

CHEMICAL KINETICS  
AND CATALYSIS

**Kinetics of the Hydrogenation of 2-Chloro-4-nitroaniline  
over Skeletal Nickel and Supported Palladium Catalysts  
in an Aqueous Solution of 2-Propanol**

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**Abstract**—The kinetics of the liquid-phase hydrogenation of 2-chloro-4-nitroaniline in an aqueous solution of 2-propanol over skeletal nickel and supported palladium catalysts is studied. The selectivity of the reaction with respect to 2-chloro-1,4-phenylenediamine is determined. It is found that samples of supported palladium catalysts differ with respect to the amount of the active component and the nature of the support. Some of their structural characteristics are provided.

**Keywords:** 2-chloro-4-nitroaniline, skeletal nickel, supported palladium catalyst, adsorption, rate of hydrogenation, specific surface area, dispersity of a catalyst

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INTRODUCTION

Kinetic studies of the hydrogenation reactions of organic compounds containing various unsaturated groups over transition metal catalysts are of scientific and practical interest. The wide use of halogen-substituted aromatic amines in the production of pesticides, herbicides, synthetic dyes and fibers, pharmaceutical products, and other substances ensures great interest in their synthesis. Liquid-phase processes of hydrogenation of substituted nitrobenzenes are considered the most efficient and economical technologies for preparing aromatic amines with various structures [1–3].

The aims of this work were to study the effect the nature of the active metal and its concentration on the support have on the rate and selectivity of the hydrogenation of 2-chloro-4-nitroaniline using kinetic approach, and to identify the reasons for the effect the active metal content and nature of the support have on the above factors.

EXPERIMENTAL

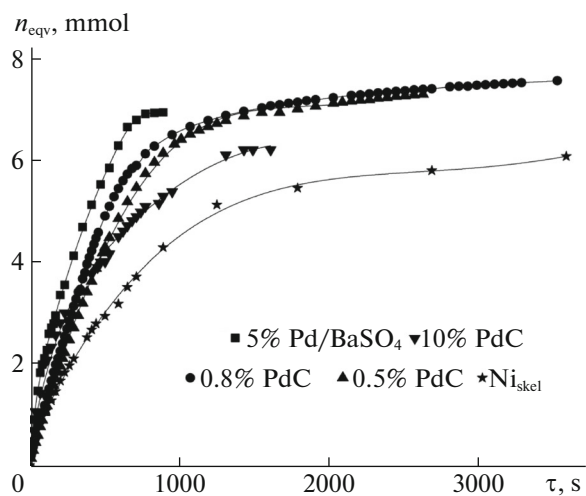
A static method for conducting the hydrogenation reaction in a closed system under a constant pressure of hydrogen with the vigorous stirring of the liquid phase was used to study the kinetics of the hydrogenation of 2-chloro-4-nitroaniline (CNA) over skeletal nickel and supported palladium catalysts. The experimental setup ensured exclusion of the effect of internal mass transfer on the observed rates of the

reactions and allowed us to determine them with a high level of reliability. The procedure for the kinetic experiment and a description of the experimental unit were given in [4].

The skeletal nickel catalyst was obtained by treating a nickel–aluminum alloy with a 25% aqueous solution of sodium hydroxide for 1 h at 273–278 K, and for 4 h at 373 K according to the procedure in [4]. The treated catalyst was washed with distilled water up to a negative reaction by phenolphthalein and stored under a layer of water for no longer than one day. The active catalyst had a specific surface area and a porosity of  $90 \pm 2 \text{ m}^2/\text{g}$  and  $0.5 \pm 0.06 \text{ cm}^3/\text{cm}^3 \text{ Ni}$ , respectively [4]. The required amount of the catalyst was weighed using a hydrostatic method with an accuracy of no less than  $\pm 0.001 \text{ g}$ . Prior to loading the catalyst into the reactor, active skeletal nickel was carefully rinsed with a solvent with the corresponding composition.

Supported palladium catalysts were prepared by impregnating the support with a solution of palladium chloride according to the procedure in [3]. ARD activated carbon and barium sulfate were used as the support. Samples with concentrations of the active component of 10, 0.8, and 0.5 on carbon and 5% on  $\text{BaSO}_4$ %, respectively, were obtained.

An aqueous solution of 2-propanol with an azeotropic composition ( $x_2 = 0.68$  molar parts,  $100 \text{ cm}^3$ ) was used as the solvent. The amount of skeletal nickel was  $0.5 \pm 0.001 \text{ g}$ ; the amount of 10% Pd/C,  $\sim 0.3 \pm 0.001 \text{ g}$ ; and the amount of the initial CNA,  $5.70 \pm$



**Fig. 1.** Curves of the absorption of hydrogen in the hydrogenation of CNA in an aqueous solution of 2-propanol over different samples of catalysts;  $T = 298$  K,  $1 \pm 0.03$  g of CNA, and  $1 \pm 0.03$  g of the catalyst.

0.03 mmol. During the experiment, the volumes of absorbed hydrogen were determined by means of volumetry, while the concentrations of the initial compounds and reaction products, 2-chloro-1,4-phenylenediamine (CPDA) and 1,4-phenylenediamine (PDA), were calculated using spectrophotometric data. A LEKISS 2110 UV scanning spectrophotometer was used to analyze the initial compound and reaction products. The sensitivity of our method was no lower than  $10^{-2}$  mmol.

The values of the initial rates and rate constants of the absorption of hydrogen  $r_{H_2}^0$ , the formation of CPDA and PDA, and the transformation of CPDA at high degrees of conversion of the initial CNA were used as the main kinetic characteristics of the reaction under study. Statistical analysis of the experimental results showed that the errors in determining the rates did not exceed 10%. In determining the current concentrations of CNA, CPDA, and PDA, the accuracy was 5%, and in determining the rate constants, it was 15% of the measured quantity. Each experiment was repeated at least three times in order to obtain convergent results.

The kinetic features of the hydrogenation of CNA over skeletal nickel and supported palladium catalysts in an aqueous solution of 2-propanol with the azeotropic composition ( $x_2 = 0.68$  molar parts) were studied. Figure 1 shows the curves of the absorption of hydrogen over time, which were subsequently used in calculating the rates of the absorption of hydrogen and the observed rate constants of the reaction. The kinetic curves with respect to hydrogen are provided with allowance for the stoichiometry of the reaction: 3 mol  $H_2$ /mol CNA, based on the transformation of

the nitro group into the amine group. Processing the obtained dependences within linear coordinates confirmed the retention of the zero order of the reaction with respect to hydrogen in all cases.

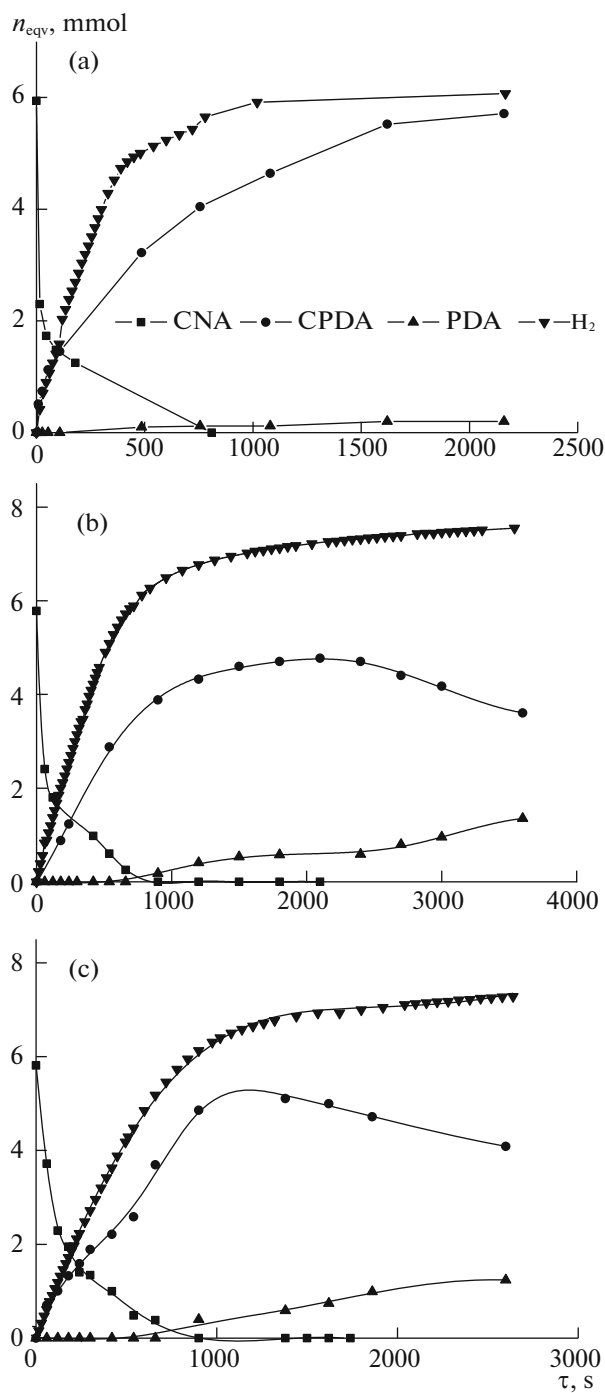
Concentration curves that illustrate the change in the amounts of all participants during the hydrogenation of CNA over time are presented in Figs. 2 and 3. The shape of the obtained dependences shows that the transformation of CNA can proceed in a sequential network of transformations, in agreement with the data of [5]. In the case of supported palladium catalysts with low active metal contents compared to skeletal nickel, a sharp decrease in the concentration of CPDA accompanied by a growth in PDA is observed at high degrees of the conversion of initial CNA. In contrast, a rise in the concentration of PDA is observed right from the onset of the reaction in the case of the 10% Pd/C and especially the 5% Pd/BaSO<sub>4</sub> catalysts.

## RESULTS AND DISCUSSION

According to the dependences presented in Fig. 1 and the calculated values of the rate constants of the hydrogenation of CNA, the catalysts used in this work can be ranged as follows with respect to their catalytic activity: 5% Pd/BaSO<sub>4</sub> > 10% Pd/C > Ni<sub>skel</sub> > 0.8% Pd/C > 0.5% Pd/C. The first two points were not used in calculating the rate of the transformation of CNA, since the loss of CNA from the solution at the onset of the reaction was determined not only by the interaction with hydrogen but also to a great extent by the adsorption of the initial compound. The increase in the observed rate constants of the transformation of the nitro group for the series of supported palladium catalysts could be due to the rise in the number of active centers on the surface of the catalysts in the case of increasing dispersion of metal particles ( $D_{Pd}$ ) and specific surface area of the catalyst  $S_{sp}$  (table).

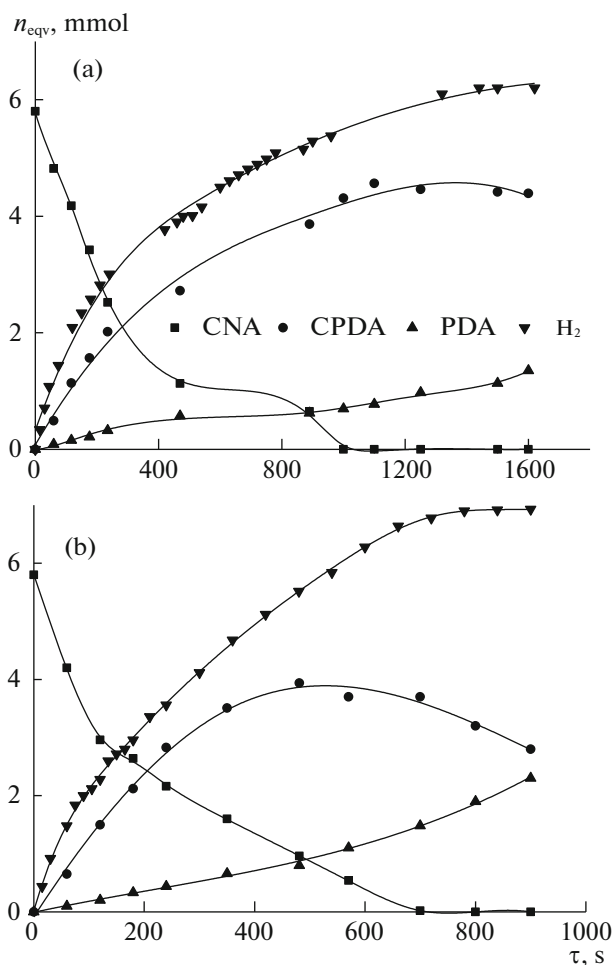
Skeletal nickel has a fundamentally different structure, so the amount of the active phase in skeletal nickel is substantially higher at a relatively lower surface area, compared to supported palladium catalysts. We should also remember that the presence of weakly bound molecular and strongly bound atomic forms of adsorbed hydrogen is characteristic of skeletal nickel, while the surface of supported palladium catalysts is more energetically uniform as a result of the high concentration of dissolved hydrogen [6].

The ratio of the amounts of initial CNA and the catalyst was selected so as to exclude the nonreversible oxidation of the surface and minimize the contribution from the diffusion resistance with respect to hydrogen to the total rate of the reaction [7]. With skeletal nickel and low-percentage palladium catalysts (Fig. 2), the amounts of absorbed hydrogen and



**Fig. 2.** Concentration curves of the hydrogenation of 2-CNA over (a) skeletal nickel, (b) 0.8% Pd/C, and (c) 0.5% Pd/C in an aqueous solution of 2-propanol (0.68 molar parts);  $T = 298$  K.

formed CPDA are the same or differ within the limits of the error in the time range of 0 to 250 s. This is because CNA is selectively reduced to CPDA at the onset of the reaction, since no PDA or other intermediate products are registered in the reaction mixture.



**Fig. 3.** Concentration curves of the hydrogenation of 2-CNA over (a) 10% Pd/C and (b) 5% Pd/BaSO<sub>4</sub> in an aqueous solution of 2-propanol (0.68 molar parts);  $T = 298$  K.

The maximum discrepancy between the initial amount of CNA and registered products corresponds to 125 s from the onset of the reaction for Pd/BaSO<sub>4</sub> and skeletal nickel, 175 s for 10% Pd/C, and 250 s for 0.8 and 0.5% Pd/C. Analysis of the material balances showed that under our reaction conditions, the amount of adsorbed substance was 2.8–3 mmol for low-percentage palladium catalysts and skeletal nickel. For the samples of 10% Pd/C and 5% Pd/BaSO<sub>4</sub> catalysts, this value was around three times lower (1.0–1.3 mmol). It is characteristic that for these catalysts, the shapes of kinetic curves reflecting the change in the amounts of CNA and PDA during the reaction also change substantially. The CNA content thus remains quite high for a long period of time (Fig. 3), while the amounts of formed PDA are consistently registered right from the onset of the reaction.

Kinetic characteristics of the reaction and values of some physicochemical properties of the catalysts

Characteristic	10% Pd/C	5% Pd/BaSO <sub>4</sub>	0.8% Pd/C	0.5% Pd/C	Ni <sub>skel</sub>
$k_{\text{CNA}} \times 10^6$ , 1/(s g)	0.11	0.15	0.22	0.20	0.31
$k_{\text{CPDA}} \times 10^6$ , mol/(s g)	29.7	40.6	17.8	18.0	41.6
$K_{\text{PDA}} \times 10^6$ , mol/(s g) (initial section of the curve)	4.6	6.1	<0.5	<0.6	<0.02
$K_{\text{PDA}} \times 10^6$ , mol/(s g) (final section of the curve)	3.7	13.7	2.1	2.8	0.2
$k_{\text{H}_2} \times 10^6$ , mol/(s g)	64.0	102.2	33.5	28.8	41.6
$S_{\text{sp}}$ , m <sup>2</sup> /g	462	616	1108	924	90 ± 2
$D_{\text{Pd}}$	0.09	0.12	0.21	0.18	—
$S_{\text{CPDA}}$ , %	73 ± 2	62 ± 2	76 ± 2	89 ± 2	93 ± 2

A sharper rise in the amounts of PDA is observed after reaching the maximum amount of CPDA for all samples of the catalysts we used. However, while the degree of conversion of CNA is 1 by this time for low-percentage catalysts and skeletal nickel (Fig. 1), the reaction is still far from complete for, e.g., 10% Pd/C (the degree of conversion is 0.83). Changes in the shape of kinetic curves (see Figs. 2 and 3) could indicate an increase in the rate constant of the hydrogenation of CNA and a rise in the rate constant of the dehalogenation of CPDA upon moving to high-percentage palladium catalysts and/or replacing the support during their preparation.

Processing the sections of kinetic curves that correspond to the decrease in CPDA amounts, and corresponding sections where PDA amounts increase (the final section of the curve,  $K_{\text{PDA}}$  table) for all our catalysts showed that in the case of low-percentage catalysts with the palladium contents of 0.8 and 0.5%, the rates of the dehalogenation of CPDA and formation of PDA were close. In the case of high-percentage catalysts (10% and especially 5% Pd/BaSO<sub>4</sub>), the rates of the formation of PDA exceeded those of the dehalogenation of CPDA (table). We may assume that in the case of 10% Pd/C and 5% Pd/BaSO<sub>4</sub>, dechlorination is already possible at the stage of the adsorption of the initial CNA or the formation of chloro-substituted intermediate products. The rate of the transformation of CNA thus slows even at high contents of the active metal in the catalyst (Fig. 3). Using barium sulfate as the support instead of carbon could also promote dichlorination, due possibly to an increase in the active hydrogen content as a result of the nature of the support.

The obtained values of rate constants ( $k_{\text{abs.H}_2}$ ,  $k_{\text{transf.CNA}}$ ,  $k_{\text{form.CPDA}}$ ,  $k_{\text{form.PDA}}$ ) and the value of the maximum selectivity of the reaction with respect to

CPDA ( $S_{\text{CPDA}}$ ) allow us to arrange the catalysts used in this work as follows:

$$\begin{aligned}
 K_{\text{transf.CNA}}: & \quad \text{Ni}_{\text{skel}} > 0.5\% \text{ Pd/C} \approx 0.8\% \text{ Pd/C} > 10\% \\
 & \quad \text{Pd/C} \approx 5\% \text{ Pd/BaSO}_4 \\
 K_{\text{form.CPDA}}: & \quad \text{Ni}_{\text{skel}} > 5\% \text{ Pd/BaSO}_4 > 10\% \text{ Pd/C} > 0.8\% \\
 & \quad \text{Pd/C} \approx 0.5\% \text{ Pd/C} \\
 K_{\text{form.PDA}}: & \quad 5\% \text{ Pd/BaSO}_4 > 10\% \text{ Pd/C} > 0.8\% \\
 & \quad \text{Pd/C} \approx 0.5\% \text{ Pd/C} > \text{Ni}_{\text{skel}} \\
 K_{\text{abs.H}_2}: & \quad 5\% \text{ Pd/BaSO}_4 > 10\% \text{ Pd/C} > \text{Ni}_{\text{skel}} > 0.8\% \\
 & \quad \text{Pd/C} \approx 0.5\% \text{ Pd/C} \\
 S_{\text{CPDA}}, \%: & \quad \text{Ni}_{\text{skel}} > 0.5\% \text{ Pd/C} \approx 0.8\% \text{ Pd/C} > 10\% \\
 & \quad \text{Pd/C} > 5\% \text{ Pd/BaSO}_4
 \end{aligned}$$

Based on an analysis of the obtained data, we can say that the ratio of the rates of individual stages in the sequential network of transformations of CNA is determined not only by the nature of the active component but also by the structural characteristics of the catalyst. To achieve high indices of selectivity with respect to CPDA, it is better to use catalysts with low activity; with supported catalysts, this can be solved by reducing the content of active metal while increasing the dispersity and selecting a suitable support.

## CONCLUSIONS

There is a logical association between the structural and physicochemical characteristics of our catalysts and the kinetic features of the hydrogenation of CNA, demonstrating the need for and importance of conducting systematic studies to gain a reliable idea of the causes and nature of such interrelations. There are grounds for assuming that the indices of selectivity of nickel and supported palladium catalysts could be

close when successfully selecting their structural and physicochemical characteristics.

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