

ВЛИЯНИЕ ДАВЛЕНИЯ ВОДОРОДА, ПРИРОДЫ РАСТВОРИТЕЛЯ И КАТАЛИЗАТОРА НА ЗАКОНОМЕРНОСТИ ГИДРОГЕНИЗАЦИИ 2-ХЛОР-4-НИТРОАНИЛИНА

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Впервые проведено исследование кинетики жидкофазной гидрогенизации 2-хлор-4-нитроанилина на нанесенных палладиевых и платиновых катализаторах, отличающихся по природе носителя и содержанию активного металла. Эксперимент проводился при повышенных давлениях водорода в интервале 9 - 12 атм и температуре 303 К в растворителях 2-пропанол-вода и этилацетат в автоклаве Вишневого. Определены основные кинетические параметры реакции, а также установлено влияние различных параметров на закономерности протекания процесса. Показано, что повышение содержания активного металла в катализаторе приводит к увеличению скорости реакции гидрогенизации 2-хлор-4-нитроанилина. При использовании нанесенных платиновых катализаторов скорости реакции гидрогенизации 2-хлор-4-нитроанилина существенно выше, чем при использовании нанесенных палладиевых катализаторов. Однако с течением реакции на платиновых катализаторах скорость падает достаточно резко, а затем стабилизируется. Для палладия характерно менее резкое падение начальных скоростей. При этом палладиевые катализаторы отличаются более высокими скоростями на "стабильном" участке кинетической кривой. Замена жидкой фазы каталитической системы с 2-пропанола на этилацетат негативно влияет на величины скорости реакции. Кроме того, использование растворителя с меньшей полярностью приводит к существенному снижению скорости реакции независимо от природы активного металла, что делает принципиально возможным управление параметрами активности и селективности процесса действием растворителя. Определен характер влияния природы и состава каталитической системы на степень дегалогенирования целевого продукта. Установлено, что при проведении реакции при повышенных давлениях водорода предпочтительнее использовать низкопроцентные платиновые катализаторы, а не палладиевые, поскольку первые обеспечивают меньшие показатели дегалогенирования целевого продукта.

Ключевые слова: 2-хлор-4-нитроанилин, водород, нанесенный палладиевый катализатор, нанесенный платиновый катализатор, скорость, гидрогенизация, 2-пропанол, этилацетат, автоклав Вишневого

HYDROGEN PRESSURE, SOLVENT AND CATALYST NATURE INFLUENCE ON 2-CHLORO-4-NITROANILINE HYDROGENATION REGULARITIES

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The 2-chloro-4-nitroaniline liquid-phase hydrogenation kinetics on supported palladium and platinum catalysts differing in the nature of the carrier and the active metal content was studied for the first time. The experiment was carried out at elevated hydrogen pressures in the range of 9 - 12 atm and 303 K in solvents 2-propanol-water and ethyl acetate in the reactor such as Vishnevsky autoclave. The main kinetic parameters of the reaction have been determined, and the influence of various parameters on the regularities of the process has been established. It is shown that an increase in the active metal content in the catalyst leads to an increase in the rate of the hydrogenation reaction of 2-chloro-4-nitroaniline. When using platinum supported catalysts, the rate of hydrogenation of 2-chloro-4-nitroaniline is significantly higher than when using supported palladium catalysts. The replacement of the liquid phase of the catalyst system with 2-propanol by ethyl acetate adversely affects the reaction rate. The influence of the catalytic system nature and composition on the target product dehalogenation degree was determined. It was found that when carrying out the reaction at elevated hydrogen pressures, it is preferable to use low-percentage platinum catalysts, rather than palladium catalysts, since the former provide less dehalogenation of the target product.

Key words: 2-chloro-4-nitroaniline, hydrogen, supported palladium catalyst, supported platinum catalyst, rate, hydrogenation, 2-propanol, ethyl acetate, Vishnevsky autoclave

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INTRODUCTION

The liquid-phase hydrogenation processes form the basis of many modern high technology of fine organic synthesis [1-8]. An important element of the scientific base of new technologies is information on the kinetics of reactions occurring at certain stages of the technological process. It is known that the liquid-phase hydrogenation reactions stoichiometric mechanisms and kinetic regularities for the various classes of organic compounds have been fairly well studied at atmospheric hydrogen pressures. At the same time, the causes of the solvent and catalyst nature influence on the rate and selectivity of hydrogenation processes remain unclear, and information on the kinetics of chemical transformations occurring at elevated hydrogen pressures remains extremely limited.

Halogenated amines find wide application in various organic synthesis technologies, such as the production of plastics, paint and varnish materials, pharmaceuticals, additives to polymers, synthetic fibers. Thus, for example, 2-chloro-1,4-phenylene-

diamine is used in the production of a new generation of aramid fibers used in the manufacture of products of various importance: starting from individual fire and armor protection and finishing with aviation and space technology components [2, 9].

The purpose of this study is to determine the effect of hydrogen pressure, the catalyst and the solvent nature on the 2-chloro-4-nitroaniline (2C4NA) liquid-phase hydrogenation kinetic parameters.

EXPERIMENTAL PART

To achieve the set aims, the 2C4NA hydrogenation kinetics study was made on low-percentage deposited platinum and palladium catalysts at elevated hydrogen pressures in the range of 9 - 12 atm at 303 K in 2-propanol and ethyl acetate.

Palladium (1.2% Pd/C and 0.8% Pd/C) and platinum catalysts (1% Pt/C, 0.5% Pt/C), produced by the scientific and technical center of the FKP Plant named Sverdlov were used in the work (Dzerzhinsk, Nizhny Novgorod region). The dispersed active carbon AR-B GOST 8703-74 with a specific surface of 600-800 m²/g and a particle size of not more than

85 nanometers was used as the carrier. The activation of the catalysts with hydrogen was carried out before the kinetic experiment directly in the liquid-phase hydrogenation reactor.

For the 2C4NA liquid-phase hydrogenation kinetics studying at elevated hydrogen pressures, the special equipment was used, the scheme of which is described in [2]. The plant is a Vishnevskiy autoclave helium-free reactor connected to a gas supply system and devices for measuring the amounts of absorbed hydrogen and maintaining the temperature of the reaction system. The design of the facility made it possible to measure the observed rates of hydrogen absorption in liquid-phase hydrogenation reactions at excess pressures of 1-12 atm, the intensity of mixing of the reaction media corresponding to the stirrer speed of 320-330 s⁻¹. The experimental errors in determining the absolute values of pressure and temperature in the reactor were ±0.0099 atm and ±0.5 K, respectively.

During the experiment the required amounts of the used catalyst together with the accurately known solvent volume were placed to the reactor. The autoclave was sealed, purged with hydrogen at a pressure of 0.99-1.97 atm, the working pressure was set, thermostated at the temperature of the experiment, and the catalyst was activated with stirring for 15 min. The amounts of hydrogen absorbed during the activation of palladium and platinum catalysts were close to the values measured at atmospheric pressure. Then, the mixing was turned off, the pressure was released, a precisely known amount of the hydrogenated compound was introduced through the input nozzle and hydrogenation was started after purging and a set of working hydrogen pressure. During the reaction, the hydrogen pressure drop in the reaction system was measured. If the pressure drop exceeded 0.3 atm, then a rapid set of the current pressure in the reactor was made before the working pressure. In this case, the total change in pressure was found by summing the changes in pressures in individual cycles. The measurements were terminated in the absence of the hydrogen pressure drop through the manometer in the gas phase. Each experiment was repeated 3-5 times, and in the calculation of the hydrogenation reaction kinetic parameters, the entire array of experimental data was used.

Fig. 1 presents the results of kinetic studies of 2C4NA hydrogenation on platinum catalysts supported on coal with different contents of the active metal in 2-propanol and ethyl acetate.

Fig. 2 presents the results of kinetic studies of 2C4NA hydrogenation on supported palladium catalysts with different active metal content in 2-propanol and ethyl acetate.

The kinetic curves shown in Fig. 3 illustrate the effect of the nature of the active metal on the 2C4NA hydrogenation in the ethyl acetate medium.

Fig. 4 shows the kinetic dependences of the 2C4NA hydrogenation in 2-propanol on platinum and palladium catalysts.

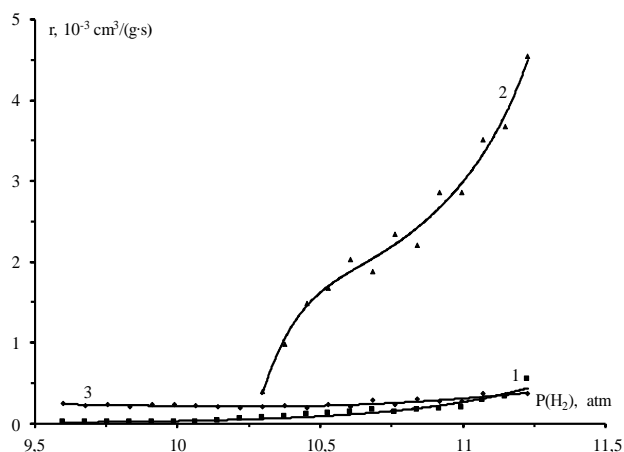


Fig. 1. Kinetic dependences of the 2C4NA hydrogenation on supported platinum catalysts in 2-propanol (2P) and ethyl acetate (EA) at T = 303 K and elevated hydrogen pressures: 1 – 1 % Pt/C in EA, 2 – 0.5 Pt/C in 2P, 3 – 1 % Pt/C in 2P

Рис. 1. Кинетические зависимости реакции гидрогенизации 2Х4НА на нанесенных платиновых катализаторах в среде 2-пропанола и этилацетата при T = 303 К и повышенных давлениях водорода 1 – 1 % Pt/C in EA, 2 – 0,5 Pt/C in 2P, 3 – 1 % Pt/C in 2P

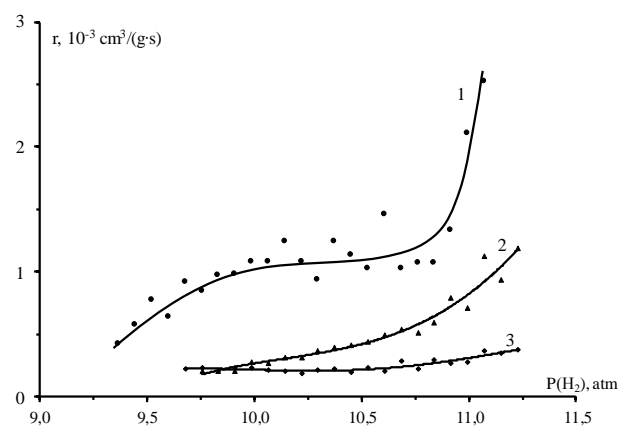


Fig. 2. Kinetic dependences of the 2C4NA hydrogenation on supported palladium catalysts in 2-propanol (2P) and ethyl acetate (EA) at T = 303 K and elevated hydrogen pressures: 1 – 1.2 % Pd/C in 2P, 2 – 0.8 Pd/C in 2P, 3 – 1.2 % Pd/C in EA

Рис. 2. Кинетические зависимости реакции гидрогенизации 2Х4НА на нанесенных палладиевых катализаторах в среде 2-пропанола и этилацетата при T=303 К и повышенных давлениях водорода 1 – 1,2 % Pd/C in 2P, 2 – 0,8 Pd/C in 2P, 3 – 1,2 % Pd/C in EA

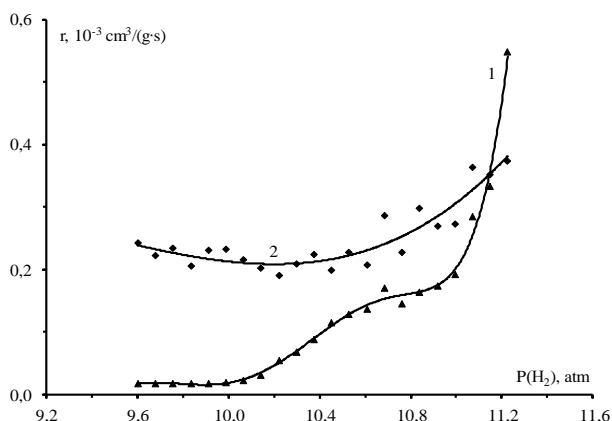


Fig. 3. Kinetic dependences of the 2C4NA hydrogenation on supported palladium and platinum catalysts in ethyl acetate at T = 303 K and elevated hydrogen pressures: 1 – 1.0 Pt/C, 2 – 1.2 % Pd/C

Рис. 3. Кинетические зависимости реакции гидрогенизации 2Х4НА на нанесенных палладиевых и платиновых катализаторах в среде этилацетата при T = 303 К и повышенных давлениях водорода 1 – 1,0 Pt/C, 2 – 1,2 % Pd/C

THE RESULTS AND THE DISCUSSION

From Fig. 1 it follows that for platinum catalysts deposited on coal, the rate increases with the content of the active metal in the 2-propanol medium. For ethyl acetate, the rate is lower by approximately 10 times.

The curves shown in Fig. 2 demonstrate that with an increase in the active metal content in the catalyst from 0.8 to 1.2%, an increase in the 2C4NA hydrogenation rate in the 2-propanol medium is observed to be approximately 2 - 2.5 times. The process speeds in ethyl acetate are lower than in alcohol, which can be explained by the solvent liquid phase stratification into the aqueous and organic parts when water forms in the surface layer during hydrogenation of the initial nitro compound and, as a result, by a decrease in the rate due to the absence of interfacial transfer between the layers formed.

From the data shown in Fig. 3, it follows that in the hydrogen pressure range 9.5 - 10.5 atm the hydrogenation rate on the palladium catalyst is higher than on the platinum catalyst by approximately 10 times. With an increase in the hydrogen pressure upon attainment of ~ 11.2 atm, the hydrogenation rates tend to a certain constant, the value of which for a deposited 1.2% palladium catalyst is greater than 1.0% of the platinum catalyst. This may indicate the preservation of the same process mechanism for the investigated catalysts.

In general, it can be noted that the supported palladium catalysts in the ethyl acetate environment are distinguished by significantly higher catalytic activity than platinum ones [10-13].

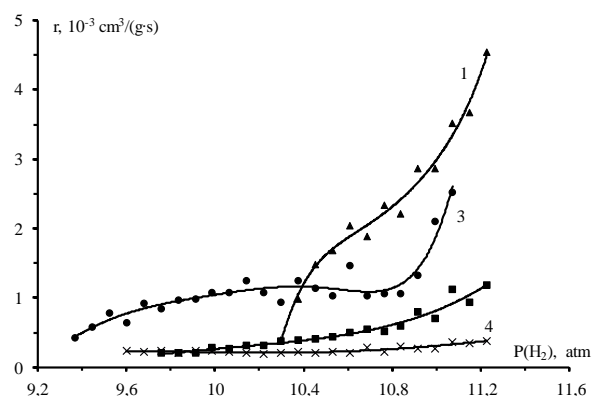


Fig. 4. Kinetic dependences of the 2C4NA hydrogenation on supported palladium and platinum catalysts in 2-propanol medium at T = 303 K and increased hydrogen pressures: 1 – 0.5 Pt/C, 2 – 0.8 % Pd/C, 3 – 1.2 % Pd/C, 4 – 1.5 Pd/C.

Рис. 4. Кинетические зависимости реакции гидрогенизации 2Х4НА на нанесенных палладиевых и платиновых катализаторах в среде 2-пропанола при T = 303 К и повышенных давлениях водорода 1 – 0,5 Pt/C, 2 – 0,8 % Pd/C, 3 – 1,2 % Pd/C, 4 – 1,5 Pd/C

A comparison of the kinetic dependences shown in Fig. 4, allows to locate the values of the observed reaction rate in the medium of 2-propanol for the catalysts used in the work in the following order:

1.0 % Pt/C > 0.5 % Pt/C > 1.2 % Pd > 0.8 % Pd/C

The results of formal processing of the kinetic curves of 2C4NA on supported catalysts in individual solvents are presented in Table 1. The rate constant values refer to the initial period of the reaction (the conversion rates do not exceed 0.2), and the rate of the hydrogenation reaction in all the systems considered is described by the first-order kinetic equation. It should be noted that increasing the pressure does not lead to a change in the reaction order for the hydrogenated compound, the first order is realized at atmospheric pressure [14-17].

Table 1

Kinetic characteristics of 2C4NA hydrogenation on supported catalysts at elevated hydrogen pressures in various solvents

Таблица 1. Кинетические характеристики гидрогенизации 2Х4НА на нанесённых катализаторах при повышенных давлениях водорода в различных растворителях

Catalyst	Solvent	The rate Constant reactions k, 10 ⁻³ s ⁻¹ .g ⁻¹
1.2 % Pd/C	2-propanol	1.8 ± 0.2
0.8 % Pd/C	2-propanol	0.8 ± 0.1
1.0 % Pt/C	2-propanol	5.1 ± 0.5
0.5 % Pt/C	2-propanol	4.7 ± 0.4
1.2 % Pd/C	ethyl acetate	0.2 ± 0.2
1.0 % Pt/C	ethyl acetate	1.8 ± 0.2

The data presented in Table 1 show that the solvent with a lower polarity using leads to a signifi-

cant decrease in the reaction rate regardless of the active metal nature. This makes it possible to control the parameters of activity and the selectivity of the process by the solvent action.

The initial 2C4NA hydrogenation rates for supported platinum catalysts are higher than for palladium catalysts. However, for the reaction proceeding on platinum catalysts, the rate falls quite sharply and stabilizes in the pressure region of 10.2 atm. Palladium is characterized by a less sharp drop in initial rates, and stabilization is observed at a pressure of about 10.5 atm. In this case, the palladium catalysts are characterized by higher rates at the "stable" section of the kinetic curve.

The results of a hydrogenate samples quantitative analysis during the 2C4NA reduction at elevated hydrogen pressures presents in Table 2. The yield of the 2C4NA reduction products: 2-chlorophenylenediamine (2CPhDA) – W_{2CPhDA} and phenylenediamine (PhDA) – W_{PhDA} , and the degree of conversion of 2C4NA (α_{2C4NA}) were determined spectrophotometrically using 2C4NA, 2CPhDA and PhDA standard solutions. It should be noted that the PhDA is an undesirable by-product, the amount of which in the hydrogenate is estimated the desired product dechlorination degree. In this regard, the quantities of other by-products were not established.

The data presented in Table 2 indicate that with increasing hydrogen pressure and using low-percentage palladium and platinum supported catalysts in 2-propanol, the yield of 2CPhDA remains fairly high. The transition from 2-propanol to ethyl acetate using 1% platinum supported catalyst does not lead to an increase in the dehalogenation degree.

Table 2

Yields of 2C4NA hydrogenation products for the different supported platinum and palladium catalysts at elevated hydrogen pressures

Таблица 2. Выходы продуктов гидрогенизации 2Х4НА на нанесенных платиновых и палладиевых катализаторах при повышенных давлениях водорода

Catalyst	Solvent	α_{2C4NA} , %	W_{2CPhDA} , %	W_{PhDA} , %
0.8 % Pd/C	2-propanol	100	71.0	0.0
1.0 % Pt/C	2-propanol	100	78.4	no more 7.0
0.5 % Pt/C	2-propanol	100	79.8	no more 7.0
1.2 % Pd/C	ethyl acetate	33	1.3	no more 14.7
1.0 % Pt/C	ethyl acetate	100	71.8	no more 6.0

When the 2C4NA hydrogenation is carried out on a 1.2% Pd/C in ethyl acetate, the conversion of the original nitrochlorobenzene remains sufficiently low. The results of the deposited platinum and palladium catalysts nature action on the degree of dehalogenation of 2C4NA hydrogenation reaction product obtained in this work are consistent with the data of the authors [15, 18-20].

Thus, for the 2C4NA liquid-phase hydrogenation at increased hydrogen pressure, it is preferable to use low-percentage platinum catalysts, rather than palladium catalysts, since the former provide higher process rates and lower de-halogenation rates of the target product. The use of a less polar organic solvent as the process flow medium is impractical due to a significant decrease in the reaction rate.

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