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Қ. И. Сәтпаев атындағы Қазақ ұлттық техникалық зерттеу университеті

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ГЕОЛОГИЯ ЖӘНЕ ТЕХНИКАЛЫҚ ҒЫЛЫМДАР СЕРИЯСЫ

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СЕРИЯ ГЕОЛОГИИ И ТЕХНИЧЕСКИХ НАУК

♦

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THEORETICAL AND EXPERIMENTAL RESEARCHES OF CATALYTIC REDUCTION OF AROMATIC NITRO COMPOUNDS BY MOLECULAR HYDROGEN IN LIQUID PHASE

Abstract. Aromatic mono-, di- and polyamines are used in the production of various compounds. Synthesis of amines by catalytic hydrogenation (in the vapor or liquid phase) of the corresponding nitro compounds is the most promising and ecologically pure method. In this article issues of reduction of aromatic nitro compounds for producing amines, valuable intermediate and final products are considered. Comparative data from literary and patent sources for the last decades are given. Various variants of the mechanism of hydrogenation of the nitro group in aromatic nitro compounds are considered. Analysis of the literature shows that, most likely, regardless of the composition and methods of preparation of the catalyst, the solvent used and the presence of substituents in the nitro compound molecule, hydrogenation proceeds in accordance with the Haber-Lukashevich scheme. Nevertheless, a change in the composition of catalyst and solvent can significantly change the ratio of the rates of individual process steps.

Keywords: catalysis, aromatic nitro compounds, amines, hydrogenation, supported catalysts.

Nitro compounds: brief information. Nitro compounds are derivatives of hydrocarbons of the general formula R-NO_2 having in their composition a nitro group directly linked to an aliphatic or aromatic radical [1]. Depending on the nature of the hydrocarbon radical "R", nitro compounds are divided into aliphatic and aromatic. Aromatic nitro compounds (figure 1) are a group of organic substances, headed by nitrobenzene and formed from benzene and its homologues (toluene and xylene), naphthalene and anthracene by replacing one or more atoms with a nitro group. In aromatic nitro compounds the nitro group is bound to the aromatic ring. The nitro group can be replaced, along with halogen and some alkyl radicals, in almost any place of the ring [2].

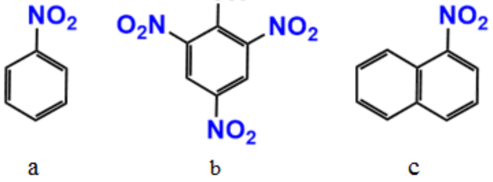

Figure 1 – Aromatic nitro compounds of different structure:
a – nitrobenzene, b – 2,4,6-trinitrophenol (picric acid), c – 1-nitronaphthalene

In the nitro group there is a π-conjugation (p-π-conjugation), as a result of which both bonds become equivalent. The structure of the nitro group can be represented by two equivalent mesomeric structures (or resonant structures). The nitro group is flat, some of its geometric parameters are given in the figure using the example of nitromethane (figure 2).

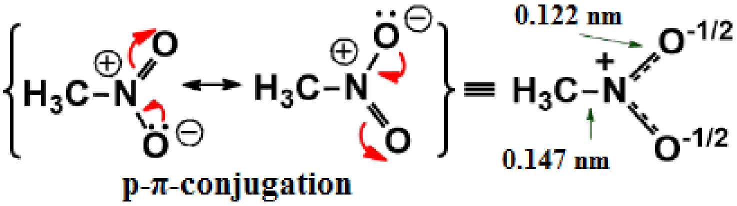

Figure 2 – Nitromethane

Nitro compounds that have the most important industrial significance include nitrobenzene, mono- and dinitrotoluenes, trinitrotoluene, tetryl, mononitrochlorobenzenes, nitroanilines, nitrochlorotoluenes, nitronaphthalene, dinitrophenol, picric acid (trinitrophenol), and dinitrocresol.

The most important property of the nitro group is its ability to be reduced to an amino group.

In the last 30-40 years, the processes of catalytic reduction of aromatic nitrocompounds by hydrogen to amines have practically superseded all other methods for the production of aromatic amines in large-tonnage plants. Aromatic mono-, di- and polyamines, due to their high reactivity, are widely used in the production of various compounds: synthetic dyes of various shades (for photography, in the paint and varnish industry, for painting natural and synthetic fibers), photochemicals, fuel stabilizers and additives lubricating oils, chemical plant protection products, synthetic fibers, sorbents, medicines, etc. [3-9]. Taking into account the extremely high volumes of commercial production of aniline and toluene diamines, the total production of which in the world is more than 3-4 million tons/year, the problem of improving the technology of obtaining these compounds can be considered actual [10].

Amines production from nitro compounds. The vapor phase and liquid-phase hydrogenation of nitro compounds hydrogenation of nitro compounds. The catalytic reduction of organic compounds, including aromatic mono- and polynitro compounds, to the corresponding amines is carried out in many variants, differing in the composition of the reaction masses, the aggregate state of the phases, the nature and type of the hydrogenation catalyst, the apparatus design of the process, the conditions of its conduct, etc. [11-40].

The reaction of reducing aromatic nitro compounds to amines by the action of ammonium sulphide on heating was discovered by N.N. Zinin in 1842 (“Zinin reaction”) [12]. Zinin’s reaction is a method of obtaining aromatic amines by reduction of nitro compounds (1):

$$R\text{-}NO_2 + 6H = R\text{-}NH_2 + 2H_2O. \tag{1}$$

Zinin acting on nitrobenzene with ammonium sulfide, obtained aniline (2):

$$C_6H_5NO_2 + 3(NH_4)_2S \rightarrow C_6H_5NH_2 + 6NH_3 + 3S + 2H_2O. \tag{2}$$

Later, Zinin showed that the reaction he discovered was of a general nature. The principles of the Zinin reaction form the basis for the synthesis of various aromatic amines, many of which serve as starting materials in the production of synthetic dyes, pharmaceuticals, explosives, fragrances, medicines, and other substances. The wide application of Zinin’s reaction has largely determined the development of organic synthesis. With the help of Zinin’s reaction, aniline and other aromatic amines were synthesized for the first time [13, 14], the foundations for the development of industrial organic synthesis of dyes, explosives and fragrances, and drugs were laid. During the time that elapsed since the discovery of the reaction of obtaining aniline from nitrobenzene by N.N. Zinin, a large number of various reducing agents were used to reduce nitro compounds: metals (Sn, Zn, Fe, etc.), metal sulfides and hydrogen sulphide, metal sulfites, hydrogen, hydrazine and its derivatives, hydrogen on catalysts [12, 14].

Amines can be obtained electrochemically by reduction of nitro compounds and nitriles of acids. The first method is usually used for the synthesis of aromatic amines and some aliphatic substituted amines, and hydroxylamines, the second method for the synthesis of aliphatic and fatty aromatic amines. In addition, some amines can be prepared by reduction of amides and oximes. It should be noted that the electrosynthesis of hexamethylenediamine from adiponitrile has undergone an experimental test, but this process is characterized by a significant specific electricity consumption and catalytic hydrogenation is used in the industry [12, 15, 16].

The main method for the preparation of primary aromatic amines and diamines is the catalytic reduction of nitro compounds by hydrogen in the vapor or liquid phase.

In the first way higher-boiling substances (dinitro-compounds, fats) are hydrogenated as their transfer to a gas form requires a large amount of hydrogen [17]. The second method is used for the reduction of substances, the volatility of which at a reaction temperature is sufficient to create the necessary partial pressure of substances in the vapor mixture. In this way, benzene, nitrobenzene, phenol can be hydrogenated [18, 19]. But in either case heterogeneous catalysis is used. The most commonly used catalysts are metals of Group VIII and mixed catalysts.

When carrying out the process in the vapor phase, copper is most often used on supports, since the hydrogenation of the aromatic ring does not occur when using this catalyst.

Advantages and disadvantages of the vapor phase hydrogenation catalysts used in industry are considered in the works [20, 21]. The authors consider that it is expedient to use modified heteropoly compounds for further improvement. According to the authors, film palladium catalysts are the best for the selective reduction of acetylenic compounds to olefins. The authors have presented data on the selective hydrogenation of aromatics over these catalysts.

It was proposed in [22] to obtain aniline in the presence of a catalyst: Pd or Pt, supported on lipophilic carbon. The promoter is alkali metal hydroxide, carbonate or bicarbonate, $Zn(OAc)_2$, $Zn (NO_3)_2$, at a temperature of 150-250°C. Significant improvements in the process consist in a continuous hydrogenation process with simultaneous removal of the water formed in the reaction. The disadvantage of these methods, in the opinion of the authors of [23], is a relatively low catalyst load, the use of a large excess of hydrogen, a short inter-regenerative period of operation of the catalyst. Performing a high-temperature regeneration operation results in partial destruction of the catalyst and a partial loss of its activity, as a result of which the yield of aromatic amine products decreases.

For the reduction of aromatic nitro compounds to aromatic amines are widely used catalytic hydrogenation. Synthesis of amines by catalytic hydrogenation of the corresponding nitro compounds is the most promising method [24, 41-54].

In general, the reduction reactions of organic compounds can be divided into two groups: the reduction by molecular hydrogen in the presence of hydrogenation catalysts and the reduction with other inorganic and organic reagents is “a chemical” reduction.

The most important way of obtaining amines from nitro compounds is catalytic reduction by hydrogen on catalysts. It was first realized by M. M. Zaitsev in 1872 with the passage of nitrobenzene and hydrogen vapor over platinum black. After 30 years, Sabatier showed that nickel and a number of other metals can be used as catalysts for this reaction [25]. A major contribution to the study of the catalytic reduction of nitro compounds was made by scientists from the USSR, the CIS, Russia and Kazakhstan [26-49].

The reduction of nitro compounds can be carried out in the presence of both heterogeneous and homogeneous catalysts. In recent years, both groups of processes has been given roughly equal attention, but in the industry to date use only solid-phase heterogeneous catalysts [50-52]. This is mainly due to the difficulty in isolating and regenerating the homogeneous catalyst for subsequent use.

When reduction on heterogeneous catalysts as catalysts most often group metals VIII and also the mixed catalysts like Ni-Cu-Fe are applied.

Heterogeneous hydrogenation catalysts for aromatic nitro compounds can be divided into the following groups:

1) catalysts containing nickel, copper and noble metals;
2) heterogeneous catalysts on a fiberglass woven matrix;
3) heterogeneous catalysts on a metal-polymeric matrix.

Most studies of the reduction of nitro compounds, as shown by the analysis of patents and literature data, are carried out using nickel catalysts [24, 27, 53-59].

Also, catalysts based on metals of the platinum group: metal black [60-62] and supported catalysts [4, 6, 8, 30-32, 41-50, 52, 53] have found wide application for the production of amines. Catalytic systems based on platinum group metals deposited on various sorbents reveal higher activity and stability than nickel catalysts. In the earliest works (50-70 years of XX century) the catalyst, regardless of its composition, was used in amounts equal to or exceeding several times the amount of hydrogenated nitro compound.

It should be noted that the black metal due to their properties, did not find practical application in the production of amines. At the same time, platinum metals deposited on various carriers, even at low contents, show high activity and selectivity of action during the reduction of aromatic nitro compounds [63, 64].

Despite the high cost, the catalysts based on platinum group metals are widely used in the hydrogenation of organic compounds, in particular, for the production of aromatic amines from the corresponding nitro compounds. A special role in this is played by the catalysts of the platinum group deposited on various carriers

Investigation of mechanism of the nitro group hydrogenation in nitrobenzene and intermediate products. In the literature, various variants of conversion schemes for substituted nitrobenzenes are given.

Haber in 1898-1900 for the first time proposed a general scheme for the formation of possible substances in the electrochemical reduction of nitrobenzene in the presence of strong bases or strong acids and in an almost neutral medium (in very weakly alkaline or slightly acidic) [65].

Debus and Jungers proposed a scheme for the catalytic reduction of nitrobenzene on Raney nickel (figure 3) [66]. They suggested the formation of azobenzene through the interaction of nitrobenzene and amine. Another scheme for the reduction of nitrobenzene, which is a continuation of the schemes of Debuss, Jungers and Haber, was created by I. Vishniyak and M.M. Klein [67].

V. P. Shmonina [68, 69], in order to determine the mechanism of catalytic reduction of nitro compounds, the reduction of nitrobenzene and twenty derivatives of it on skeleton nickel, Pt- and Pd-blacks studied with a wide variation of the process: catalyst charge, solvents, concentration of nitrocompounds, temperature, stirring intensity. The effect of various additives in the reaction mixture (nitrobenzene-aniline intermediates, acid, alkali, pyridine, aniline, etc.) was studied. In the work such control methods of the course of catalytic process as definition of saturating speed of hydrogen, measurement of potential of the catalyst by V. Drouz and D. V. Sokolsky [68] method, use of a polarography [69], a conductometric titration were applied.

It was found that the actual hydrogenation processes can be accompanied by the interaction and isomerization of the intermediate compounds. The ratio of hydrogenation rates and reactions of interaction of intermediate products affect the nature of intermediate stages and intermediate products, selectivity and depth of reduction.

Scheme of transformations of aromatic nitro compounds, proposed by V.P. Shmonina (figure 4), largely coincides with the schemes of F. Haber and V. O. Lukashevich [70], which were proposed for electrochemical and chemical methods for the reduction of aromatic nitrocompounds, but it has its own peculiarities. In the schemes proposed before the studies by V.P. Shmonina, there was no reaction of direct conversion of phenylhydroxylamine (PHA) to hydrazobenzene (HB), or isomerization of azoxybenzene (AOB) to oxyazobenzene. The reaction of the formation of azoxybenzene from nitrobenzene and phenylhydroxylamine under the conditions of the experiment, as in the scheme of V. Lukashevich, was also not noticed. Nor was the formation of azobenzene through the interaction of nitrobenzene with aniline and the formation of p-aminophenol from hydroxylamine indicated in the Debuss and Jungers scheme.

Three directions of course of process of reduction were found by Shmonina V. P. in the studied conditions. It follows from the scheme in fig.4 that the substituted nitrobenzenes (1) are converted to the corresponding amines (4) as a result of successive catalytic interaction of the nitro group with three moles of hydrogen through the formation of intermediate nitrosobenzenes (2) and arylhydroxylamines (3).

This first direction is purely hydrogenation direction, it is a sequential interaction of a nitro group with three hydrogen molecules. Intermediates may be nitrosobenzene and phenylhydroxylamine, but they do not accumulate in the reaction mixture and are reduced to aniline as they form.

Under certain conditions, for example, causing a decrease in surface concentrations of adsorbed hydrogen, homogeneous condensation of the intermediate reaction products becomes possible. Leading to the formation of substituted azoxy (6) or azobenzenes (7), which catalytically interact with hydrogen through intermediate hydrazobenzene (8), are converted to the corresponding amines.

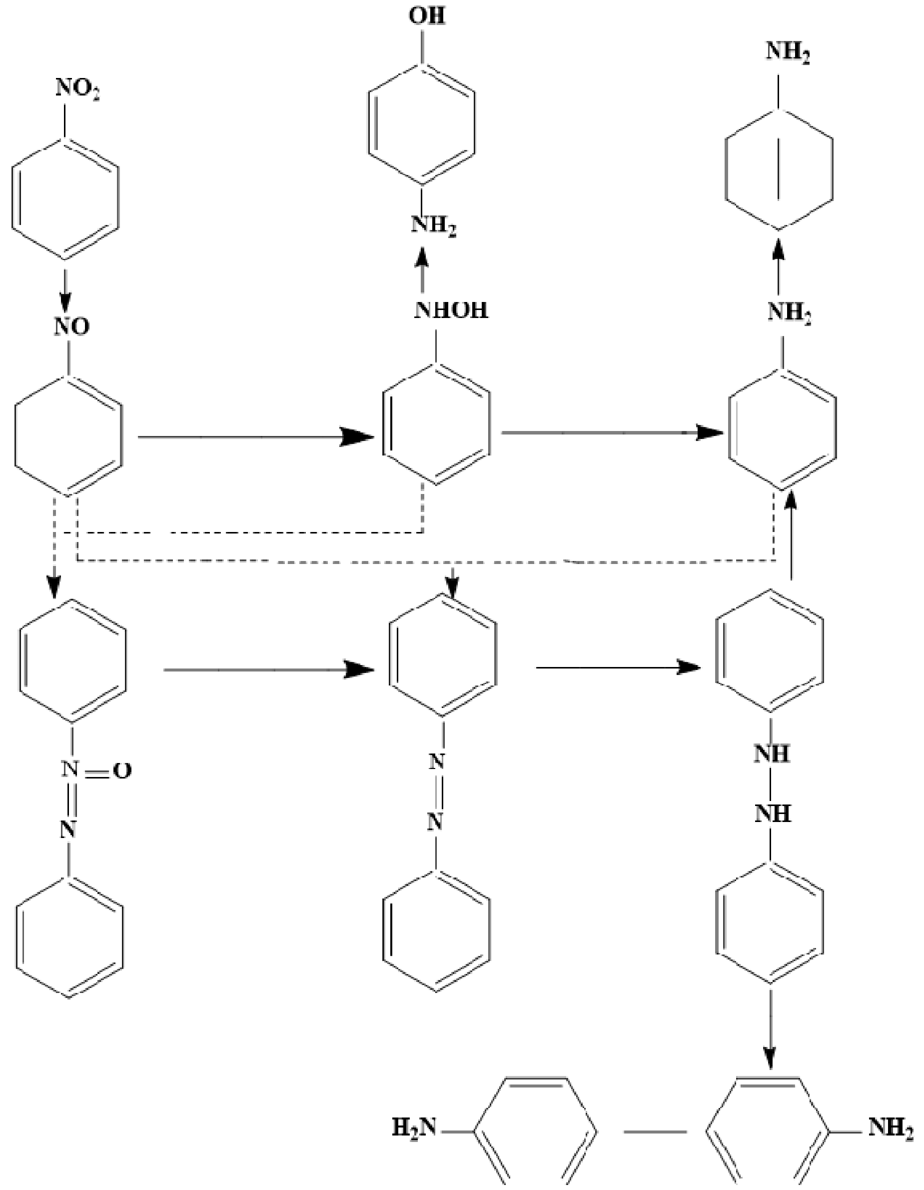

Figure 3 – Nitrobenzene reduction scheme [66]

The second direction is the interaction of nitrobenzene with phenylhydroxylamine, leading to azoxybenzene, which is further converted to aniline through azo and hydrazobenzene. The third direction is distinguished by the fact that the phenylhydroxylamine formed as a result of the reduction of nitrobenzene is subsequently converted to hydrazobenzene.

On catalytically active centers with low reactivity, the disproportionation of substituted arylhydroxylamines (9) into aminobenzenes and nitrosophenols is possible [71, 72], which, reacting with hydrogen, can be converted to aminophenols (9). The intermediate azoxy (6) and hydrazobenzenes (8) under certain processing conditions can be homogeneously rearranged to 4-hydroxyazobenzene (10) and benzidine (11), respectively. At elevated hydrogen pressures, the possibility of further hydrogenation of aniline (4) in cyclohexylamine (5) is not ruled out.

The transformation of the nitro group of substituted nitrobenzenes in the hydrogenation direction is carried out by reacting on platinum and palladium in water-organic and alkaline media, as well as on skeleton nickel in organic solvents, for example, in aqueous solutions of aliphatic alcohols [71-74].

An increase in the contribution of the hydrogenation direction to the overall hydrogenation rate is facilitated by a decrease in the concentration of the hydrogenated compound and an increase in the hydrogen pressure. The most rapid condensation of intermediate products leading to the formation of substituted azoxy- and azobenzenes occurs during the reaction on platinum black and skeletal nickel in solutions containing electron-donor additives or in strongly alkaline media at high initial concentrations of the hydrogenated compound [71-74].

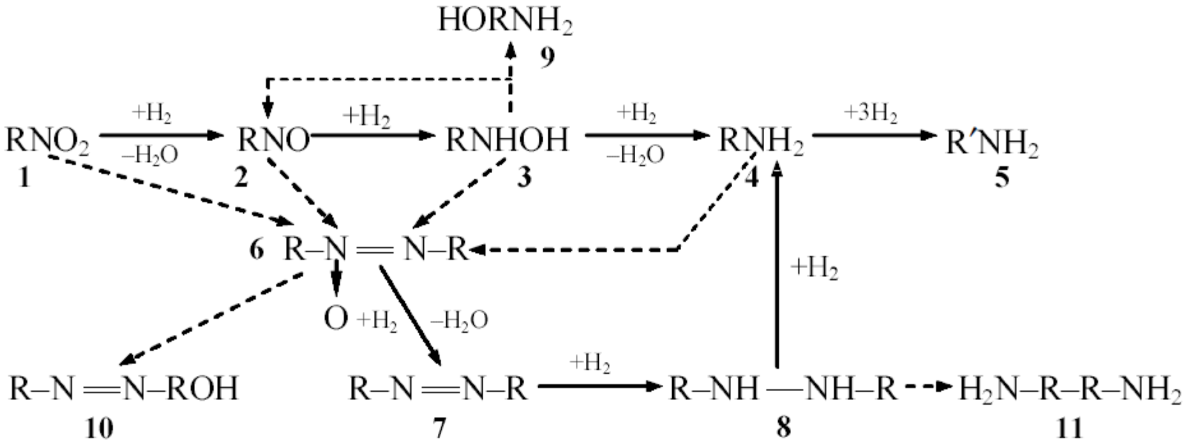

Figure 4 – The main products and stages of conversion of nitrobenzene and its substituted:
1 – nitrobenzene; 2 – nitrosobenzene; 3 – phenylhydroxylamine; 4 – aniline; 5 – cyclohexylamine; 6 – azoxybenzene;
7 – azobenzene; 8 – hydrazobenzene; 9 – 4-aminophenol; 10 – 4-hydroxyazobenzene; 11 – benzidine [71-77]

It should be noted that nitrosobenzene in reaction systems most often is not fixed as the intermediate product, but is introduced into nitrobenzene conversion schemes as a product preceding the formation of phenylhydroxylamine [78-88]. Most likely, the argument for including nitrosobenzene in the scheme for the conversion of nitrobenzene is the sequence of stages described in earlier works [76, 77], since there is no direct evidence of the presence of nitrosobenzene in the solution volume by the authors [79, 84]. In a number of papers [89], the data confirming the formation of nitrosobenzene as an intermediate product are given.

An analysis of the results presented in the works [90-93], allows us to state that in order to explain the kinetic regularities of the hydrogenation reactions of substituted nitrobenzenes, in most cases, the authors refer to the same type of chemical transformation schemes for the nitro group.

Representations of the chemisorption states of the nitro group and the results of kinetic studies of the transformations of intermediate products became the basis for the justification of the scheme proposed by E. Gelder (figure 5) [94]. The author rejects the traditional reaction mechanism proposed by Haber and Lukashevich, and suggests an alternative scheme, which, in their opinion, is valid for other metal-containing catalysts. Under this scheme, the intermediate product of the nitro group transformation is the hemi-hydrogenated form - $C_6H_5(OH)$, which takes part in all subsequent stages. Thus, during its catalytic interaction with hydrogen, azobenzene or phenylhydroxylamine is formed, and during the interaction of these forms, asoxybenzene is formed.

It is assumed that on the surface of the catalyst there is an intermediate intermediate for nitrobenzene and nitrosobenzene III (fig.5) which, in the case of hydrogenation of nitrobenzene, interacts with adsorbed hydrogen, successively converting to phenylhydroxylamine and aniline via intermediate V. Hydrogenation of nitrosobenzene reacts with 2 molecules of the intermediate to eliminate the molecule water and the formation of azoxybenzene (AOB), which is then converted to azobenzene (AB), hydrazobenzene (HB) and aniline.

Thus, in most works the classical scheme of the Haber-Lukashevich hydrogenation mechanism is confirmed and detailed by experimental methods [96, 97].

However, there are alternative judgments. The complexity of studying the mechanism of this reaction can be explained by the multistage character of the reduction of the nitro group (figure 5), as well as the influence on the rate of hydrogenation of a number of factors [96-106].

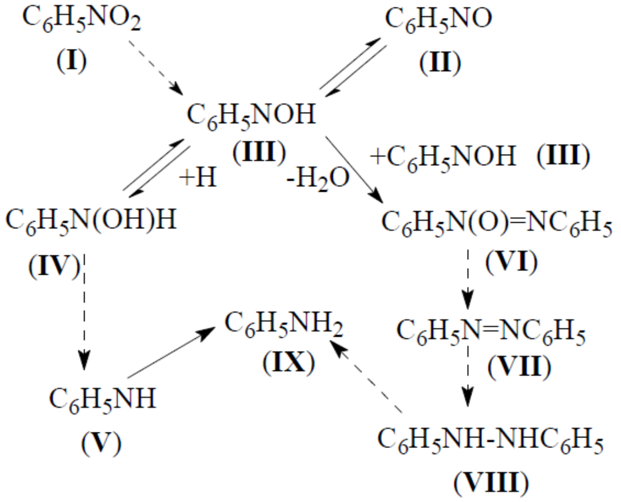

Figure 5 – The scheme of E. Gelder, describing the catalytic transformations of the nitro group [94, 95]

Possibly nitrobenzene hydrogenation proceeds in accordance with the Haber-Lukashevich scheme, regardless of the nature of the catalyst, solvent and substituents in the nitroarene molecule. However, the change in catalyst and solvent significantly affects the ratio of the rates of individual heterogeneous catalytic and homogeneous stages, changing their contribution to the overall reaction rate. Therefore, the mechanism of hydrogenation of nitro compounds on different catalysts requires additional studies.

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СҰЙЫҚ ФАЗАДА АРОМАТТЫ НИТРОҚОСЫЛЫСТАРДЫ МОЛЕКУЛЯРЛЫ СУТЕГІМЕН КАТАЛИЗДІК ТОТЫҚСЫЗДАНДЫРУДЫҢ ТЕОРИЯЛЫҚ ЖӘНЕ ЭКСПЕРИМЕНТТІК ЗЕРТТЕУЛЕРІ

Аннотация. Ароматты моно-, ди- және полиаминдер түрлі қосылыстардың өндірісінде қолданылады. Аминдерді, сәйкес нитроқосылыстармен катализдік гидрлеу арқылы (бу немесе сұйық фазада) синтездеу ең перспективті және экологиялық жағынан таза әдістердің бірі болып табылады. Бұл мақалада аминдерді, құнды аралық және соңғы өнімдерді алу үшін ароматты нитроқосылыстарды тотықсыздандыру қарастырылады.

Соңғы онжылдықтардағы әдеби және патенттік көздер туралы салыстырмалы деректер келтірілген. Нитротопты ароматты нитроқосылыстарды гидрлеу механизмінің әртүрлі нұсқалары келтірілген.

Әдебиеттердің анализі, ең алдымен, катализатордың құрамы мен дайындау әдістеріне, пайдаланылатын еріткіштің және нитроқосылыстар молекуласындағы орынбасарлардың болуына қарамастан, гидрлеу Хабер-Лукашевич схемасына сәйкес жүреді. Соған қарамастан, катализатордың және еріткіштің құрамының өзгеруі процестің жеке сатыларының жылдамдығын айтарлықтай өзгерте алады.

Түйін сөздер: катализ, ароматты нитроқосылыстар, аминдер, гидрлеу, қондырылған катализаторлар.

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ТЕОРЕТИЧЕСКИЕ И ЭКСПЕРИМЕНТАЛЬНЫЕ ИССЛЕДОВАНИЯ КАТАЛИТИЧЕСКОГО ВОССТАНОВЛЕНИЯ АРОМАТИЧЕСКИХ НИТРОСОЕДИНЕНИЙ МОЛЕКУЛЯРНЫМ ВОДОРОДОМ В ЖИДКОЙ ФАЗЕ

Аннотация. Ароматические моно-, ди- и полиамины используются в производстве различных соединений. Синтез аминов каталитическим гидрированием (в паровой или жидкой фазе) соответствующих нитросоединений является наиболее перспективным и экологически чистым методом. В этой статье рассматриваются вопросы восстановления ароматических нитросоединений для получения аминов, ценных промежуточных и конечных продуктов. Даны сравнительные данные литературных и патентных источников за последние десятилетия. Рассмотрены различные варианты механизма гидрирования нитрогруппы в ароматических нитросоединениях. Анализ литературы показывает, что вероятнее всего, независимо от состава и методов приготовления катализатора, применяемого растворителя и наличия заместителей в молекуле нитросоединения, гидрирование протекает в соответствии с схемой Габера-Лукашевича. Тем не менее изменение состава катализатора и растворителя может значительно изменять соотношение скоростей отдельных стадий процесса.

Ключевые слова: катализ, ароматические нитросоединения, амины, гидрирование, нанесенные катализаторы.

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