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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

PREPARATION OF GRAPHITE-TYPE CARBON NITRIDE COMPOSITES AND STUDY OF THEIR CATALYTIC PROPERTIES

Specialty: 2316.01 – Chemical kinetics and catalysis

Field of science: Chemistry

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The work was performed at Laboratory "Nanocomposite catalysts" of the Institute of Catalysis and Inorganic Chemistry named after academician M.Nagiyev of Ministry of Science and Education Republic of Azerbaijan

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GENERAL CHARACTERISTICS OF WORK

Relevance of the topic and the degree of development. Most of the catalytic processes currently used in the chemical industry are carried out on heterogeneous catalysts containing metals or metal oxides. The processes involving these systems are characterized by high-energy consumption and intake of a large amount of precious metals and cause environmental pollution.

Catalysis research over the past 100 years has shown that the microstructure of a catalyst (including its geometry and electronic structure) can directly change its adsorption properties, which are crucial for its catalytic activity[1]. In this regard, the preparation and research of graphite-type polymer carbon-nitrides (g-C_3N_4), which are formed on the basis of cyclic triazine molecules and are proposed as a new heterogeneous catalyst without metal, are of great theoretical and practical importance. Formed as a result of the combination of carbon and nitrogen elements, which are abundant in nature, layered graphite-type carbon nitride is a material with high chemical and thermal stability due to the strong covalent bonds formed between carbon and nitrogen atoms[2]. Carbon nitrides have basic and π-donor-acceptor properties as a result of the interaction of functional groups such as -NH-, NH_2- and N-C=N on their surface with a nanoscale structure. This allows them to be used as efficient heterogeneous organic catalysts in reactions with a range of electrophilic and nucleophilic mechanisms without the presence of metals. g-C_3N_4 was first shown to be a metal-free catalyst capable of

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[1] Xie, C. Defect chemistry in heterogeneous catalysis: Recognition, understanding, and utilization / Xie, C., Yan, D.F., Li, H., // ACS Catal., - 2020, v. 10, - p. 11082-11098

[2] Mohammed I. A review on graphitic carbon nitride (g-C_3N_4) based nanocomposites: Synthesis, categories, and their application in photocatalysis // Journal of Alloys and Compounds, – 2020, v. 846, – p. 156446

unusual Friedel–Crafts-type aromatic substitution reactions[3].

Carbon nitride is intensively studied in many practical photocatalytic processes, such as water splitting, wastewater treatment, solar cell preparation, CO_2 reduction, and H_2O_2 synthesis[4].

The property of catalytic activation of the hydrogen molecule without any metal presence of graphite-type polymer carbon nitrides was discovered in the laboratory "Nanocomposite catalysts" at the Institute of Catalysis and Inorganic Chemistry. This phenomenon was successfully applied by us for the first time in the process of selective hydrogenation of phenylacetylene to styrene. In the dissertation, it was shown that metal-free carbon-nitride-based catalysts are capable of hydrogenating acetylene to ethylene and phenol to cyclohexanone with equally high selectivity.

Studying the catalytic properties of nano-sized carbon-nitride-based materials capable of selective hydrogenation of organic compounds with -C=C- and -C≡C- related groups without the presence of metals based on inexpensive raw materials such as urea, melamine and dicyandiamide is promising. Also, the possibility of preparing new catalysts based on urea produced on an industrial scale in the Republic and studying their catalytic properties is an urgent issue in terms of expanding the application areas of this raw material.

The work objective and subject – The hydrogen molecule and the group of hydrocarbons containing double and triple carbon-carbon bonds are the object of study. The subject of the work is the effective implementation of the processes related to this object by activating the hydrogen molecule with a new progressive method.

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[3] Thomas, A., Graphitic carbon nitride materials: variation of structure and morphology and their use as metal-free catalysts / Arne Thomas, Anna Fischer, Frederic Goettmann [et al.] // Journal of Materials Chemistry – 2008, v. 18, – p. 4893–4908.

[4] Tian, Y. Hierarchical acro-mesoporous g-C_3N_4 with an inverse opal structure and vacancies for high-efficiency solar energy conversion and environmental remediation / Tian, Y., Zhou, L., Zhu, Q. [et al.] // Nanoscale, – 2019, v. 43, –p. 20638-20647.

The work aims and tasks. The main goal of the research is the synthesis and selection of non-metal graphite-type carbon nitrides and their various modifications for the selective hydrogenation of phenylacetylene to styrene, the experimental study of the kinetic regularities of this reaction on an active catalyst, the selection of the step-by-step scheme of the likely mechanism of the reaction, and it consists of developing a theoretically based kinetic model of this process. Also, the possibility of selective hydrogenation of acetylene to ethylene and phenol to cyclohexanone on these catalysts was shown in order to confirm the property of activating the H_2 molecule of the new carbon-nitride-based catalysts without metal content and to reflect the possibilities of the unique effect being applied on a wider scale.

In order to achieve the aim of the research, the tasks set are planned as follows:

- synthesis of carbon nitride samples by the method of thermolysis of various primary substances (melamine, urea and dicyandiamide);
- determining the catalytic efficiency of the synthesized carbon nitride samples in hydrogenation reactions of phenylacetylene, acetylene and phenol;
- preparation of composites containing Pt/mpg-C_3N_4 to study the effect of the metal on the catalytic properties of graphite-type carbon-nitride and the study of the hydrogenation reaction of phenylacetylene to styrene on them;
- study of physico-chemical properties of catalyst samples selected by modern research methods;
- study of the kinetic regularities of the hydrogenation reaction of phenylacetylene to styrene over an optimal graphite-type carbon-nitride catalyst;
- development of a kinetic model of the process based on the probable mechanism of the hydrogenation reaction of phenylacetylene to styrene.

The research methods. The composition of the synthesized and modified carbon-nitride catalyst samples, as well as the physico-chemical properties of these catalysts were determined by X-ray

Phase Analysis (XRD), Scanning Electron Microscope (SEM), Thermogravimetry (TGA), Brunauer-Emmett-Teller (BET) and Fourier Transform. ‖ studied by Infrared Spectroscopy (FTIR) methods, raw materials and reaction products taken for the hydrogenation process were analyzed by means of an Agilent 7820A gas chromatograph with flame ionization detector.

The main provisions defended are as follows:

– Preparation of catalysts based on melamine, dicyandiamide, including urea produced in the Republic and research of their catalytic properties in hydrogenation processes of phenylacetylene, acetylene and phenol;

– Preparation of purpose-built catalysts by modifying carbon nitrides;

– Investigating the physico-chemical properties of the synthesized catalysts with modern research methods;

– Studying the activity of metal-free and metal-containing mesoporous carbon-nitride samples in the selective hydrogenation reaction of phenylacetylene to styrene;

– Study of the kinetic regularities of the reaction of selective hydrogenation of phenylacetylene to styrene over a carbon-nitride catalyst with a mesoporous graphite structure, calculation of the numerical values of the constants of the theoretically based kinetic model of the process according to the possible mechanism.

Scientific novelty of the research. The property of catalytic activation of hydrogen molecule was discovered by carbon nitrides with a graphite-type polymer structure without any metal presence, and this phenomenon was experimentally confirmed for the first time in the process of selective hydrogenation of phenylacetylene to styrene. It was found that the new catalysts have the property of hydrogenating acetylene to ethylene and phenol to cyclohexanone with equally high selectivity. A step-by-step scheme of the probable mechanism of the process of selective hydrogenation of phenylacetylene to styrene on metal-free mesoporous carbon-nitride was proposed and the values of the parameters of the kinetic model were calculated.

Theoretical and practical significance of research. In recent years, intensive research works have been carried out in chemical and photo-catalysis in order to create new promising environmentally friendly technologies by activating small molecules such as O_2, CO_2 and H_2O in mild conditions on carbon nitrides of graphite type without metal content. The fact of catalytic activation of the H_2 molecule without metal presence of carbon nitrides expands the range of small molecules that can be difficult to activate under mild conditions and opens up new possibilities for the creation of practically significant hydrogenation processes. The selective hydrogenation of phenylacetylene, acetylene, and phenol over metal-free carbon nitrides enables the environmentally friendly synthesis of valuable monomers such as styrene, ethylene, and cyclohexanone. Urea-based synthesis of heterogeneous catalysts of organic origin with great potential of non-metal carbon nitride type expands the possibilities of use of the material produced in our Republic.

Published works and approbation of the work.

The main results of the dissertation work were presented and discussed at the following international and national scientific conferences:

- XII European Congress on Catalysis —Catalysis: Balancing the use of fossil and renewable resources», (Kazan 2015);
- Akademik Toğrul Şahtaxtinskinin 90 illik yubileyinə həsr olunmuş Respublika Elmi Konfransı, (Bakı, 2015);
- IX Бакинская Международная Конференция по Нефтехимии, ИНХП, (Баку 2016);
- AMEA-nın akademik M.Nağıyev adına Kataliz və Qeyri-üzvi Kimya İnsti-tutunun 80 illik yubileyinə həsr olunmuş Respublika Elmi Konfransı, (Bakı, 2016);
- The 13th European Congress on Catalysis (EUROPACAT 2017), august 27 to 31, 2017, Florence, Italy;
- The 8th Tokyo Conference on Advanced Catalytic Science and Technology (TOCAT8), 2018, (Yokohama, Yaponiya);
- AMEA-nın akademik Y.H.Məmmədəliyev adına Neft-Kimya Prosesləri İnstitutunun 90-illik yubileyinə həsr

olunmuş ″Müasir kimyanın aktual problemləri″ mövzusunda Beynəlxalq Elmi Konfrans, (Bakı, 2019).

The name of the organization where the dissertation work was carried out. The dissertation work was performed in the "Nanocomposite catalysts" laboratory of the Institute of Catalysis and Inorganic Chemistry named after academician M. Nagiyev of the Ministry of Science and Education Republic of Azerbaijan.

The structure and scope of the dissertation work. Dissertation work including introduction (12391 symbols), 4 chapters (chapter I – 45092 symbols, chapter II – 36414 symbols, chapter III – 48360 symbols, chapter IV – 21168 symbols), main results (1660 symbols), and 196 citied references. The total volume of the work, including 30 pictures, 12 tables and 7 schemes, consists of 130 computer printed sheets and 165085 symbols.

Research publication rate. 20 scientific works have been published on the subject of the dissertation work. 9 of them are articles (4 of them are included in the international summarizing and indexing systems), abstracts of 9 reports, and 2 are patents of the Republic of Azerbaijan. Six of thesis were published in international and three national scientific conference materials.

The author's personal contribution covers the formulation of the aim of the dissertation, the development of a methodological approach for its solution, the implementation of the majority of experimental studies and their generalization.

CONTENT OF THE WORK

The introduction shows the relevance of the research topic, the purpose of the work, the issues to be solved, scientific innovations, the practical significance of the work, and the main propositions defended.

In the first chapter, information on the structural features, isomers and physico-chemical properties of graphite-type carbon nitrides was provided, and the current state of research conducted in the field of using their various modifications in catalysis was analyzed [17].

In the second chapter, the methods of preparation of graphite-type carbon-nitride-based catalysts used in research and their various modifications are given, the results of physico-chemical analysis of catalyst samples, reagents and reaction products analysis are analyzed, and the flow-type laboratory experiment facility where the hydrogenation process is studied is described.

Synthesis of carbon nitride catalysts.

For the synthesis of graphite-type carbon nitride samples with various morphologies, it was performed by the method of thermal polycondensation of inexpensive substances such as melamine, dicyandiamide, and urea produced in our Republic.

1) For the synthesis of carbon nitride samples with a dense morphology, a certain amount of melamine (or urea or dicyandiamide) is heated to 500-550°C in a programmed mode in a semi-closed vessel made of aluminum oxide. Synthesized carbon nitride samples are stored in a desiccator and used as a catalyst [1].
2) Mesoporous carbon nitride is synthesized by heating the complex of pre-prepared melamine with cyanuric acid in a 1:1 molar ratio [14, 19] in an inert gas environment in a programmed mode to a temperature of 550°C.
3) In order to compare the catalytic activity, composites containing Pt/mpg-C_3N_4 with a mass fraction of 0.46-2.86% on the carbon nitride surface and their analogues modified with triphenylphosphine, triphenyl phosphite and 2,2`-bipyridine were synthesized.
4) In order to enhance the base function of the surface of mesoporous carbon nitrides, they have been modified with strong alkaline agents such as KOH and NaOH [20].

Study of physical and chemical properties of carbon nitride catalysts.

Figure 1 shows the X-ray diffraction spectra of the synthesized carbon nitride-based catalyst samples [14, 18]. The samples show a two-dimensional single phase with an interplanar spacing of 3.24 Å and approximately 40% partially crystallized, which is in agreement with values theoretically calculated by Teter and Hemley for the graphite-like form of carbon nitride[5].

The BET surface area of the sample is 54-60 m^2g^{-1} and the pore volume varies between 0.44-0.55 cm^3g^{-1}, depending on the presence of mesoporous graphite type carbon nitride in the free and composite components. Most of the mesopores are composed of 22-35 nm diameter pores.

The mesoporous carbon nitride and nanocomposite samples exhibit two peaks: a weak diffraction peak at 13.1° indexed in the (100) plane, corresponding to the in-plane stacking of tri-s-triazine rings with periodicity of 6.91 Å; a strong reflection at 27.4°, indexed in the (002) plane, corresponds to the interlayer stacking of connected aromatic systems with an interlayer distance of d = 3.26 Å. These parameters are in full compliance with the accepted standards for graphite-type structures.

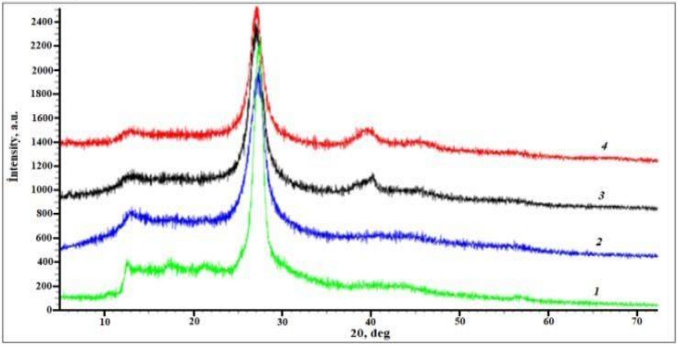

Figure 1. mpg-C_3N_4 (1) and Pt/mpg-C_3N_4 nanocomposites: Pt/mpg-C_3N_4-0.46 (2); Pt/mpg-C_3N_4-0.91 (3); X-ray diffraction lines for Pt/mpg-C_3N_4-2.86 (4) [14, 18].

As can be seen from the SEM (Scanning Electron Microscope) images of the surfaces of undoped mesoporous carbon nitride and Pt/mpg-C_3N_4 nanocomposite (Figure 2. (a and b)), the metal particles

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[5] Teter, D. M., Hemley, R. J. Low-Compressibility Carbon Nitrides // Science, – 1996, v. 271, – p. 53-55.

are arranged in the form of additional spheres on the carbon nitride nanosheets. The nanoparticle shape is almost spherical, and the size of Pt^0 particles ranges from 17 to 42 nm [18].

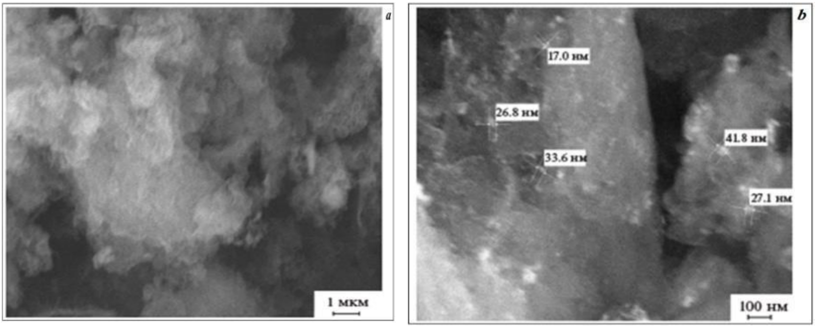

Figure 2. SEM analysis images of mpg-C_3N_4 (a) and Pt/mpg-C_3N_4 -2.86 (b) [18].

Figure 3 shows the FTIR spectra of the doped mpg-C_3N_4 compound and metal-containing composites [18]. All spectra show bands typical of undoped carbon nitride. The spectra at 1637, 1570, 1541, and 1458 cm-1 correspond to attached C-N bonds in the heterocycle. The location of these bands in the spectra of Pt/mpg-C_3N_4-0.46, Pt/mpg-C_3N_4-0.91 and Pt/mpg-C_3N_4-2.86 nanocomposites almost completely coincides with the bands typical of their doped carbon nitride. This indicates that the morphology of carbon nitride remains unchanged during the formation of mesoporous hybrids.

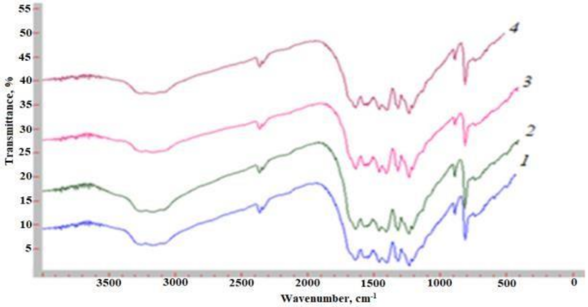

Figure 3. mpg-C_3N_4 (1) and Pt/mpg-C_3N_4-0.5 (2), Pt/mpg-C_3N_4(3), FTIR spectra of Pt/mpg-C_3N_4-3 (4) nanocomposite catalysts [18].

As can be seen in Figure 4, which shows the results of the analysis of carbon nitride by thermogravimetric method, the catalyst does not undergo thermal decomposition in the temperature range of

150-250°C, where the hydrogenation reactions of phenyl-acetylene to styrene, acetylene to ethylene, and phenol to cyclohexanone were carried out in the study.

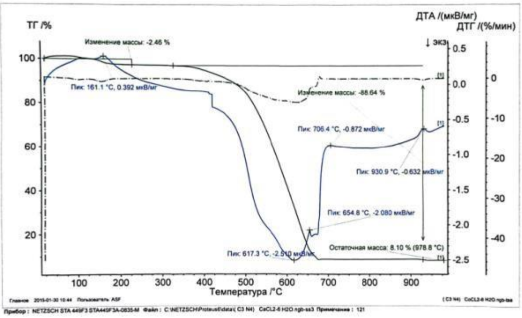

Figure 4. Spectrum of analysis of carbon nitride by the thermogravimetric method.

In the third chapter, the results of experimental experiments are presented, which show the confirmation of the effect of graphite-type polymer carbon nitrides being able to catalytically activate the hydrogen molecule without the presence of metal in the selective hydrogenation reactions of phenylacetylene to styrene, acetylene to ethylene, and phenol to cyclohexanone. Carbon nitrides can be successfully used as heterogeneous catalysts of organic origin for the selective hydrogenation of phenylacetylene to styrene, acetylene to ethylene, and phenol to cyclohexanone without the presence of metals. This chapter also investigated the hydrogenation reaction of phenylacetylene on platinum-modified carbon nitride composites.

Catalytic hydrogenation of phenylacetylene over metal-free carbon nitrides.

In this section, the order of experiments, the analysis of reagents and reaction products, the results of the preliminary tests of the catalytic activity of the samples used in the process of hydrogenation of phenylacetylene are reflected. The experiments were carried out in a flow-type microreactor at a temperature range of 150-250°C and by passing a 20-50% hexane solution of phenylacetylene in the gas phase with a molar ratio of C_8H_6:H_2=1:(1.2-3.0) over mpg-C_3N_4 through a syringe pump. All reaction products and unreacted raw materials and solvent were analyzed using an Agilent 7820A gas chromatograph equipped with a 30 m long 0.53 mm ID HP-5 and HP Plot Q capillary column with a FID detector. In the laboratory, 85-86% catalytic conversion of phenylacetylene and 89-94% selectivity hydrogenation to styrene were determined on samples of carbon nitride synthesized. As shown in figure 5, the initial high catalytic activity during the hydrogenation of phenylacetylene on densely shaped g-C_3N_4 samples decreases sharply in a short time [11].

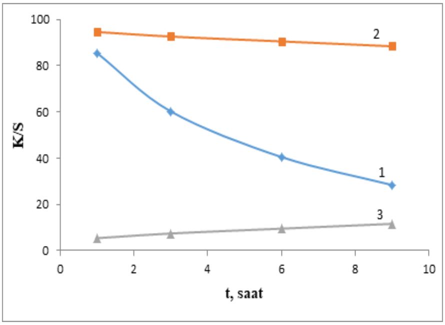

Figure 5. Hydrogenation of phenylacetylene over g-C_3N_4 at 250°C [11]
Cat - 0.4 g, H_2: PhA = 2:1, V= 2240 s^{-1}. Solvent - n-heptane.
(1-Phenylacetylene conversion; 2-Styrene selectivity; 3-Ethylbenzene selectivity).

In contrast to g-C_3N_4, porous mpg-C_3N_4 with a large surface area keeps its catalytic activity stable for a long time, and the selectivity of styrene is above 90% even in the conditions of high concentration of hydrogen in the reaction medium (Figure 6). Based on these results, the kinetic regularities of the hydrogenation of phenylacetylene to styrene were studied on the example of mpg-C_3N_4 catalyst [11, 18].

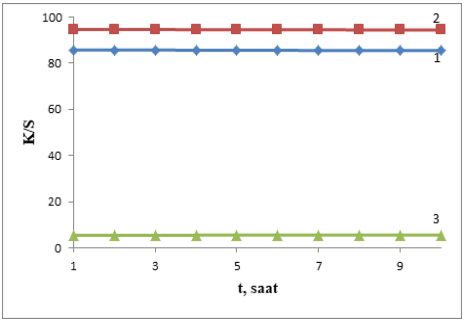

Figure 6. Hydrogenation of phenylacetylene over mpg-C_3N_4 at 250°C [11, 18] Cat - 0.4 g, H_2: PhA = 2:1, V= 2240 s^{-1}. Solvent - n-heptane. (1-Phenylacetylene conversion; 2-Styrene selectivity; 3-Ethylbenzene selectivity).

When the reaction temperature is increased from 50˚C to 250˚C, the conversion of phenylacetylene increases sharply from 35.9% to 85.5%, while the selectivity for styrene shows a slight decrease (Figure 7) [11].

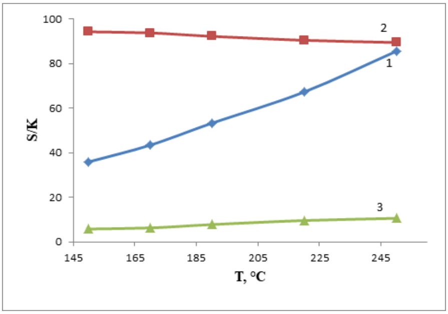

Figure 7. Hydrogenation of phenylacetylene over mpg-C_3N_4 at 250°C [11] Cat - 0.4 g, H_2: PhA = 2:1, V= 2240 s^{-1}. Solvent - n-heptane. (1-Phenylacetylene conversion; 2-Styrene selectivity; 3-Ethylbenzene selectivity).

Catalytic hydrogenation of acetylene over metal-free carbon nitrides.

The possibility of selective hydrogenation of acetylene to ethylene on graphite-type carbon nitrides in the liquid phase and at room temperature without the presence of metal has been established by us for the first time. In this section, the results obtained during the investigation of the selective hydrogenation process of acetylene in the liquid phase over environmentally clean catalysts based on graphite-type carbon nitrides modified with alkali are discussed. Currently, heterogeneous catalysts of inorganic origin containing Pd and other precious metals are used in the industry for selective hydrogenation of acetylene. In addition to hydrogenation of acetylene to ethylene, the process is accompanied by undesirable side reactions such as hydrogenation of ethylene to ethane, conversion of acetylene to green oil and carbon deposits. In the dissertation, it was shown that graphite-type carbon nitrides are effective catalysts for the partial hydrogenation of acetylene, as well as in the selective hydrogenation of phenylacetylene to styrene. Acetylene hydrogenation process using mpg-C_3N_4 and mpg-C_3N_4 composites modified with NaOH and KOH as catalysts using polar substances such as dimethylformamide (DMF), dimethyl sulfoxide (DMSO) or n-methyl-2-pyrrolidone (NMP). Table 1 shows the catalytic indicators of the synthesized catalyst samples in the hydrogenation process of acetylene in the presence of a polar solvent in the liquid phase. As can be seen from the results, the process of hydrogenation of acetylene takes place in polar solvents in the liquid phase at -20 -(+ 50°C) temperature and under 10-15 atm pressure and H_2/C_2H_2=1-3 molar ratios. In the process of hydrogenation, the conversion of acetylene is 81-91%, the selectivity for ethylene is 83-90%, and the yield of ethane is 10-15% [20].

Table 1

Efficiency of mpg-C_3N_4 and mpg-C_3N_4/X (X= KOH, or NaOH) samples in the process of hydrogenation of acetylene in the liquid phase [20]

Catalyst	Decisive	Temperature/ Pressure, °C/atm	Conver-sion,%	Selectivity, %	
				Ethyle-ne	Etha-ne
mpg-C_3N_4	DMF	25/10	85.0	84.7	15.3
mpg-C_3N_4	DMSO	25/10	81.0	86.4	13.6
mpg-C_3N_4/ KOH	DMF	25/10	90.5	90.2	9.8
mpg-C_3N_4/ KOH	DMSO	25/15	95.7	81.4	18.6
mpg-C_3N_4/ KOH	DMF	50/10	97.3	80.2	19.8
mpg-C_3N_4/ KOH	NMP	25/15	91.5	80.7	19.3
mpg-C_3N_4/ NaOH	DMF	-10/15	86.6	90.3	9.7

Table 1 is next

mpg-C_3N_4/ NaOH	NMP	-5/15	88.3	90.1	9.9
mpg-C_3N_4 / KOH	DMF	-20/15	82.6	90.2	9.8

60 mmol acetylene; 100 ml solvent; Cat.-0.4g, Reaction time- 60 min.

Under the conditions described in table 1, the hydrogenation process of acetylene on C_3N_4/KOH composite was continuously tested for 10 days, and during this period it was determined that the catalyst maintained its stable activity and selectivity.

Catalytic hydrogenation of phenol over metal-free carbon nitrides.

The effect of graphite-type carbon nitrides being able to activate hydrogen molecules without the presence of metal has also been confirmed in the selective hydrogenation reactions of phenol to cyclohexanone. In this research work, it was established for the first time that carbon nitrides can be used as efficient heterogeneous catalysts of organic origin for hydrogenation of phenol in gas phase to cyclohexanone without metal presence. In this section, experimental results of our study on the hydrogenation of phenol to cyclohexanone on graphite-like carbon nitride samples are discussed. The carbon nitride samples discussed in the previous sections were used to study the reaction of hydrogenation of phenol to cyclohexanone without metal presence. Hydrogenation of phenol was studied in the gas phase in the temperature range of 190-250°C. As a reagent, 5% solution of phenol in hexane was used. Table 2 shows the relative activities of the prepared samples [4, 9].

Table 2

Hydrogenation of phenol over graphite-type carbon nitrides [4, 9].

Catalyst	Temperature, °C	Conversion, %	Product distribution, %	
			Cyclohexanone	Cyclohexanol
DCA	190	10.4	83.4	16.6
	200	25.7	80.1	19.9
	220	50.4	74.6	25.4
	250	71.3	66.3	33.7
M	190	16.8	74.8	25.2
	200	23.6	70.4	29.6
	220	41.8	67.3	32.7
	250	68.4	59.6	40.4

Table 2 is next

M+K	190	33.3	87.5	12.5
	200	55.3	75.8	24.2
	220	76.9	71.1	28.9
	250	97.4	48.6	51.4

DSA - dicyandiamide, M-melamine, K-urea, Catalyst - 0.5 g; H_2: F = 2: 1

As in the partial hydrogenation of phenylacetylene, mesoporous mpg-C_3N_4 catalyst samples show higher activity and selectivity than g-C_3N_4. The reaction results in an increase in the conversion of phenol and a sharp decrease in the selectivity to cyclohexanone with increasing temperature. The process of hydrogenation of phenol over mpg-C_3N_4 is likely to follow the route shown in Figure 8 [9].

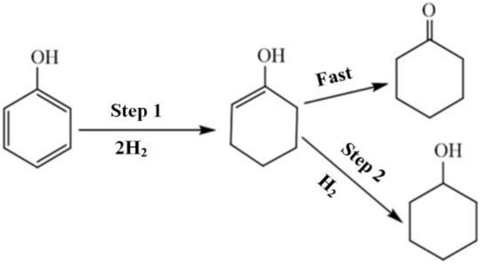

Figure 8. Probable scheme of phenol hydrogenation reaction [9].

Catalytic hydrogenation of phenylacetylene over graphite-type Pt/ mpg-C_3N_4 composites.

Despite its unique chemical, physical, and electronic properties, the Lewis base function created by nitrogen-rich ternary and aromatic amines on its surface provides g-C_3N_4 with multiple active sites in metal-free catalysis and makes it an effective platform for immobilization of metal nanoparticles. In this study, in order to compare the carbon nitride-based catalysts with high selectivity in the partial hydrogenation reaction of phenylacetylene without the presence of metal, with their metal-containing analogues, graphite-type Pt/mpg-C_3N_4 composites were synthesized and studied in the same reaction. The results of the experiments show that at 150°C, FA:H_2=1:2 and the flow rate of FA is 0.02 mol hour^{-1}, complete conversion of phenylacetylene is observed on the samples containing 0.46-2.86% Pt mass fraction. The rate of hydrogenation based on 1 g of platinum reaches 43.4 mol•h^{-1} on the Pt/mpq-C_3N_4-0.46 catalyst at a 2:1 mol ratio of hydrogen to phenylacetylene and a variable flow rate of phenylacetylene solution in hexane in the range of 0.005-0.02mol·h^{-1}. The selectivity for styrene increases from 1.7% to 25.8%.

Figure 9 shows the effect of the nature of the diluent on the hydrogenation reaction of phenylacetylene over the Pt/mpq-C_3N_4-0.46 catalyst. When hexane is replaced by tetrahydrofuran, ethanol, triethylamine, dioxane or chloroform, the selectivity towards styrene increases dramatically. The selectivity to styrene was 91.1%, 91.5%, and 91.7%, respectively, in the experiments in ethanol, tetrahydrofuran, and chloroform. 92.2% selectivity of styrene is observed when a mixture of ethanol and water is used as a diluent [15, 18].

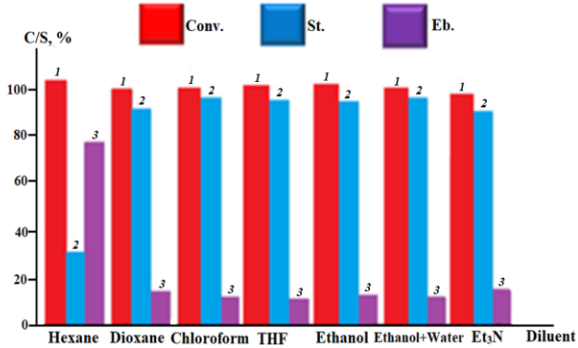

Figure 9. Effect of various diluents on the hydrogenation reaction of phenylacetylene over Pt/mpq-C_3N_4-0.46 catalyst [15, 18].
(150°C, H_2/Ph = 2 mol/mol; V=2240 s^{-1}).
(1-Phenylacetylene conversion; 2-Styrene selectivity; 3-Ethylbenzene selectivity).

In this study, we also determined for the first time that nitrogen-containing organic ligands can significantly influence the catalytic properties of Pt/mpg-C_3N_4 composites during the gas phase hydrogenation of phenylacetylene. As shown in Figure 10, when a small amount of pyridine (0.3–0.4 ml) is added to a solution of phenylacetylene in hexane, hydrogenation occurs with near 100% conversion and 90–91% selectivity to styrene. The addition of morpholine, piperidine, and triethylamine has a similar effect on the selectivity of the Pt/mpq-C_3N_4 catalyst [15, 18].

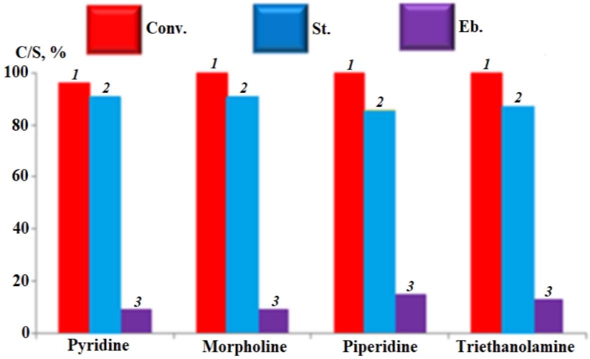

Figure 10. Effect of various nitrogen-containing organic ligands on the hydrogenation reaction of phenylacetylene over Pt/mpq-C_3N_4-0.46 catalyst. (150°C, H_2/Ph = 2 mol /mol; V=2240 s^{-1}) [15, 18]. (1-Phenylacetylene conversion; 2-Styrene selectivity; 3-Ethylbenzene selectivity)

New $P(C_6H_5)_3$ Pt/mpq-C_3N_4, P(O $C_6H_5)_3$ Pt/mpq-C_3N_4 and Bipyridyl Pt/mpq- C_3N_4 composites were synthesized and studied as catalysts in gas phase hydrogenation of phenylacetylene. The results show that the hydrogenation on the catalyst samples obtained by means of $P(C_6H_5)_3$ and $P(OC_6H_5)_3$ at the L/Pt = 1 ratio is close to 100% conversion and 74% and 72.4% selectivity for styrene, respectively. Under similar reaction conditions, the conversion of phenylacetylene on the bipyridine-containing composite was 97%, and the selectivity for styrene was 81%. Samples tested at Pt/L = 2 ratio showed low catalytic activity [15].

From the obtained results, it is clear that the effect of organic modifiers on the catalytic efficiency of Pt/mpg-C_3N_4 does not differ significantly from their known effect observed for Pd-containing catalysts in the liquid phase. It can be assumed that a wide variety of polar solvents such as ethanol, tetrahydrofuran, chloroform and others are not directly involved in the hydrogenation of phenylacetylene over Pt/mpg-C_3N_4. They form a dense layer on the Pt surface, which prevents styrene from adsorbing on the active center and increasing the concentration of H_2 on the catalyst surface.

Thus, deep hydrogenation is prevented. The increase in the selectivity of hydrogenation of phenylacetylene by nitrogen-containing compounds can be explained by the ability of these compounds to change the electronic properties of the active metal. Pyridine, piperidine and morpholine molecules act as σ-donors and form weak coordination bonds with Pt, which prevents the adsorption of styrene on the active center. Most likely, modification of the catalyst surface by ligands with electron-donor, electron-acceptor or chelating properties increases the yield of ethylbenzene due to the long-term stay of styrene on Pt particles through strong electronic and steric effects.

It was determined that the activity of Pt/mpq-C_3N_4 catalyst is $8{\bullet}10^3{\bullet}$(molar amount of product)•(molar amount of Pt)$^{-1}{\bullet}s^{-1}$. The resistance of the new catalyst to metal loss was tested in a flow process (150°C, atmospheric pressure, tetrahydrofuran as diluent) for 10 hours, during which no change in the activity and selectivity of the catalyst was observed.

The synthesized Pt/mpg-C_3N_4 composites were also found to have effective catalytic activity for the hydrogenation of phenylacetylene at a lower temperature (50-70°C) in the liquid phase [16].

In the fourth chapter, the results of the performed studies related to the study of the kinetic regularities of the catalytic hydrogenation reaction of phenylacetylene to styrene without the presence of metal on mesoporous graphite-type carbon-nitride of organic origin in the gas phase, the probable mechanism and the formulation of the kinetic model of the process are given. The kinetic parameters of the phenylacetylene hydrogenation process were determined based on the observed changes in the initial reaction rates depending on the temperature and the partial pressures of phenylacetylene and hydrogen. From the results of the experiments performed at different H_2/FA molar ratios shown in Table 3, it is clear that mpg-C_3N_4 efficiently provides selective hydrogenation of phenylacetylene to styrene in the temperature range of 150-250˚C and atmospheric pressure [11]. The conversion of phenylacetylene and the yield of hydrogenation products increase proportionally with the mass of mpg-C_3N_4 in the reaction zone.

Table 3

Hydrogenation of phenylacetylene over mpg-C_3N_4 [11]

№	**T, °C**	N_1^0, **mol/s (FA)**	N_2^0, **mol/s (H_2)**	**G_{cat} /** N_1^0, **g /mol**	**Conversion, FA, %**	**Yield % (St)**	**Yield % (Eb)**
1	150	0.0135	0.027	14.8	17.4	16.4	1.0
2	170	0.0135	0.027	14.8	22.4	20.8	1.6
3	190	0.0135	0.027	14.8	25.6	23.5	2.1
4	220	0.0135	0.027	14.8	31.7	28.6	3.1
5	250	0.0135	0.027	14.8	39.5	35.2	4.3
6	150	0.0135	0.027	22.2	26.7	25.2	1.5
7	170	0.0135	0.027	22.2	32.2	30.1	2.1
8	190	0.0135	0.027	22.2	38.4	35.5	2.9
9	220	0.0135	0.027	22.2	48.3	43.7	4.6
10	250	0.0135	0.027	22.2	57.9	51.8	6.3
11	150	0.0135	0.027	29.6	35.9	33.8	2.1
12	170	0.0135	0.027	29.6	42.6	39.9	2.7
13	190	0.0135	0.027	29.6	53.7	49.5	4.2
14	220	0.0135	0.027	29.6	66.7	60.3	6.4
15	250	0.0135	0.027	29.6	85.5	76.4	9.1
16	150	0.018	0.04	16.6	22.4	21.1	1.3
17	170	0.018	0.04	16.6	25.8	24.1	1.7
18	190	0.018	0.04	16.6	30.5	28.1	2.4
19	220	0.018	0.04	16.6	38.4	35.1	3.2
20	250	0.018	0.04	16.6	47.2	42.3	4.9
21	150	0.027	0.054	11.1	14.9	14.1	0.8
22	170	0.027	0.054	11.1	19.3	18.1	1.2
23	190	0.027	0.054	11.1	23.2	21.6	1.6
24	220	0.027	0.054	11.1	26.1	24.1	2.0
25	250	0.027	0.054	11.1	30.5	27.9	2.6

FA-phenylacetylene; St-styrene; Eb-ethylbenzene, - molar amount of phenylacetylene, - molar amount of hydrogen, V=2240 h^{-1}

The rate of phenylacetylene conversion and styrene formation increases with the increase in the volume of phenylacetylene. Along with an increase in the partial pressure of phenylacetylene due to hydrogen, the same changes are observed in the conversion and yields of hydrogenation reaction products (Figure 11) [11].

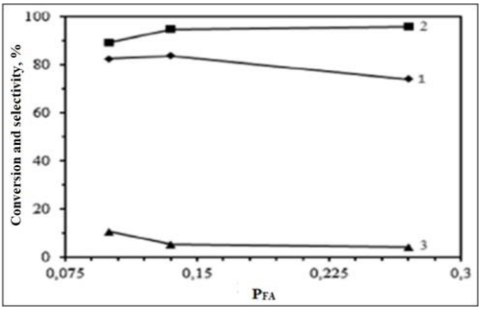

Figure 11. The effect of the partial pressure of phenylacetylene on the rate of the hydrogenation reaction of phenylacetylene over mpg-C_3N_4 at 250°C (V = 2240 h^{-1}) [11].
(1-Phenylacetylene conversion; 2-Styrene selectivity; 3-Ethylbenzene selectivity)

Increasing the partial pressure of hydrogen with respect to phenylacetylene does not significantly affect the rate and selectivity of the H_2/PhA>2 reaction (Figure 12) [11].

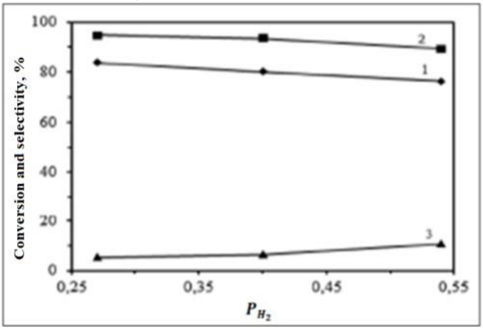

Figure 12. Effect of hydrogen partial pressure on the rate of hydrogenation reaction of phenylacetylene on mpg-C_3N_4 at 250°C (V = 2240 h^{-1}) [11].
(1-Phenylacetylene conversion; 2-Styrene selectivity; 3-Ethylbenzene selectivity)

The results of the performed experiments were used in the preparation of the kinetic model of selective hydrogenation of phenylacetylene to styrene on mesoporous carbon nitrides.

Possible mechanism of activation of H_2 molecule on graphite-type carbon-nitride

Selective hydrogenation of chemicals with -C=C- and -C≡C- linked groups is one of the most important practical processes widely used in organic chemical synthesis [1]. Therefore, the problem of molecular hydrogen activation is of great interest from the theoretical and practical point of view and has been intensively studied. Regardless of the research object, the hydrogenation process is accompanied by the stages of dissociation of the hydrogen molecule into hydrogen atoms on the surface of the catalyst and their combination into -C=C- and -C≡C- groups. The mechanism of activation of the hydrogen molecule is different depending on the composition and structure of the used catalyst.

In the scientific literature, the general conclusion of the published research studies on the chemical activation of the H_2 molecule on heterogeneous catalysts containing transition metals can be described as shown[6] in Scheme 2.

Depending on the electronic structure of the metal, the H_2 molecule is subjected to dissociative adsorption on the electrophilic or nucleophilic heterolysis or homolysis routes, and individual hydrogen atoms are formed on the metal surface. In the next step, the formed active metal-hydrogen complex combines with the substrate molecule (for example, alkyne or alkene) with -C=C- and -C≡C- linked groups adsorbed on the catalyst surface, and the catalytic cycle is realized. It is believed that in the hydrogenation reaction of acetylene on palladium, the H_2 molecule is chemisorbed on the surface of the catalyst, undergoing dissociative adsorption and forming an active complex with Pd[7]. The activation energy for the 1st and 2nd stages of the process is 7 and 28 kcal/mol, respectively, that is, acetylene is adsorbed on Pd more easily than ethylene. For

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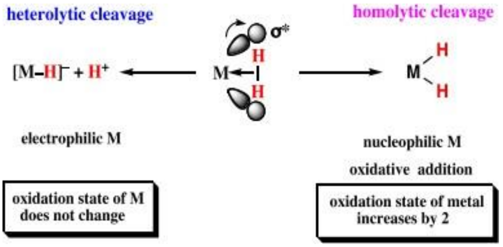
[6] Kubas, G. J. Activation of dihydrogen and coordination of molecular H_2 on transition metals // Journal of Organometallic Chemistry, - 2014, v. 751, - p. 33-49.

[7] Nakatsuji, H., Hada, M. and Yonezawa, T. Theoretical study on the catalytic activity of palladium for the hydrogenation of acetylene // Surface Science, - 1987, v. 185, - p. 319- 342.

this reason, hydrogenation of ethylene is not observed until the complete conversion of acetylene to ethylene, and hydrogenation to ethane is difficult.



Scheme 2. Activation of hydrogen molecule on transition metals[6].

In addition to transition metals, the H_2 molecule can also be activated by many donor and acceptor compounds. For example, the H_2 molecule is activated under mild conditions in aprotic medium in SO_2, SO_2ClF solution of SbF_5 superacid[8].

At this time, the ionization energy of the activated H_2 molecule is 259.2 kC/mol, significantly reduced compared to the normal molecule (436.4 kC/mol). Activation of hydrogen also occurs on compounds with basic properties (OH-, KNH_2, K). At this time, as explained by the Molecular Orbit theory, the placement of an electron in an empty orbital of hydrogen reduces the dissociation energy of the H-H bond to 17.14 kC/mole as a solvent activation factor[9]. Apparently, in both cases, the H_2 molecule can participate in chemical transformations in milder conditions.

As widely discussed in the scientific literature in recent years,

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[8] Темкин, О. Н. Химия молекулярного водорода // изд. Химия, Москва, - 2000; http://www.pereplet.ru/obrazovanie/stsoros/1090.html

[9] Витковская, Н. М. Метод молекулярных орбиталей: Основные идеи и важные следствия // Соросовский Образовательный Журнал, - 1996, v. 6, - ст. 58-64.

organic compounds consisting of an isolated Lewis acid and Lewis base pair enable heterolytic cleavage of the H_2 molecule without metal presence in a homogeneous medium[10].

It is believed that Lewis-type positively and negatively charged isolated groups can be formed on the surface of heterogeneous catalysts due to defects of different physical and chemical nature[1]. In this regard, it can be concluded that carbon nitride can be a promising platform for creating metal-free catalytic systems. Carbon nitrides are capable of activating various substrates (CO_2, O_2, H_2O) under mild conditions through the donor-acceptor interaction of a large number of nitrogen-containing functional groups on their surface[3]. It can be assumed that the hydrogenation of phenylacetylene takes place through the dissociative adsorption of the H_2 molecule on the donor-acceptor type centers formed due to the surface defects of carbon nitride and at the next stage reacting with the alkyne adsorbed on the surface.

Development of a kinetic model of the catalytic hydrogenation of phenylacetylene to styrene in the gas phase over carbon nitride.

As mentioned above, catalytic conversion of phenylacetylene to styrene with high selectivity in the gas phase temperature range of 150-250°C and normal pressure is observed on mpg-C_3N_4, which does not contain metal. mpg-C_3N_4 exhibits very weak catalytic activity in the process of hydrogenation of styrene to ethylbenzene, and it is assumed that a small amount of ethylbenzene is formed during the process as a result of the direct hydrogenation of

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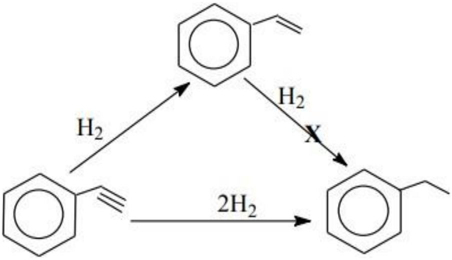
[10] Stephan, D. W. Frustrated Lewis pairs: a new strategy to small molecule activation and hydrogenation catalysis.// Dalton Trans., - 2009, v. 17, - p. 3129–3136.

phenylacetylene by $2H_2$ molecule over the catalyst (Scheme 3) [11].



Scheme 3. Scheme of hydrogenation of phenylacetylene over mpg-C_3N_4 [11].

Based on these experimental results, the scheme of the step-by-step mechanism of the hydrogenation reaction of phenylacetylene to styrene and ethylbenzene on the surface of the mpg-C_3N_4 catalyst can be described as follows.

$$H_2 + 2Z \longrightarrow 2HZ \qquad (k1)$$

$$PhA + 2HZ \longrightarrow PhA(2HZ) \qquad (k2)$$

$$PhA(2HZ) \longrightarrow St + 2Z \qquad (k3)$$

$$PhA + 2(2HZ) \longrightarrow PhA2[(2HZ)] \qquad (k4)$$

$$PhA2[(2HZ)] \longrightarrow Eb + 4Z \qquad (k5)$$

Here, PhA, St and Eb stand for phenylacetylene, styrene and ethylbenzene, respectively. "Z" is active center; PhA(2HZ) is an active center intermediate of adsorbed phenylacetylene that retains an adsorbed hydrogen molecule to be followed by dissociation, while PhA2[(2HZ)] is an intermediate of adsorbed phenylacetylene with two (2HZ) intermediates. Using the initial molar amounts of phenylacetylene (N_1^0) and hydrogen (N_2^0), as well as the yields of the reaction products of styrene (A_1) and ethylbenzene (A_2), the available molar rates of the reactants in the stream can be determined. A simplified stepwise scheme for the formation of styrene can be described as follows:

$$\left.\begin{array}{l} H_2 + 2Z \xrightarrow{k_1} 2ZH \\ 2ZH + PhA \xrightarrow{k_2} (2ZH)PhA \\ (2ZH)PhA \xrightarrow{k_3} St + 2Z \\ \hline H_2 + PhA = St \end{array}\right| \begin{array}{l} 1 \\ 1 \\ 1 \\ \\ \end{array}$$

Assuming their elementary nature, the following expressions can be written for the rates of all stages of the formation of styrene:

$$r_1 = k_1P_2\theta_1^2,\ r_2 = k_2P_1\theta_2^2,\ r_3 = k_3\theta_3 \qquad \textbf{(1)}$$

where, θ_1^2, θ_2^2, θ_3 are atomic hydrogen, phenylacetylene molecules, and parts of the free sites of the catalyst covered by the surface intermediate; k_1, k_2, k_3 are the rate constants of the corresponding stages; P_1, P_2 are partial pressures of phenylacetylene and hydrogen; r_1, r_2, r_3 are the speeds of the corresponding stages.

In a stationary setting

$$r_1 = r_2 = r_3 = r_{St} \qquad \textbf{(2)}$$

where, rst is the total rate of styrene formation. Proceeding from these equations and the constancy of the total number of surface regions of formations, the overall reaction rate θi can be described as a function of reactant concentrations:

$$\theta_1 + \theta_2 + \theta_3 = 1 \qquad \textbf{(3)}$$

$$\theta_2 = \sqrt{\frac{k_1P_2}{k_2P_1}} \cdot \theta_1 \qquad \theta_3 = \frac{k_1P_2}{k_3} \cdot \theta_1^2$$

$$\frac{k_1P_2}{k_3} \cdot \theta_1^2 + \theta_1 + \sqrt{\frac{k_1P_2}{k_2P_1}} \cdot \theta_1 - 1 = 0 \qquad \textbf{(4)}$$

Substituting the expressions θ_2, θ_3 into equation (4), we get:

$$\frac{k_1\,P_2}{k_3} \cdot \theta_1^2 + \left(1 + \sqrt{\frac{k_1P_2}{k_2P_1}}\right) \cdot \theta_1 - 1 = 0 \qquad \textbf{(5)}$$

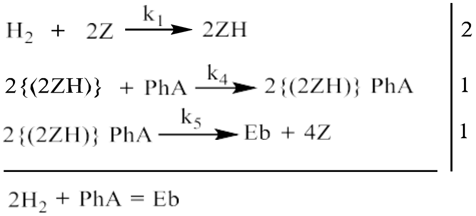
By solving equation (5), the following expression for θ_1 is obtained:

$$\theta_1 = \frac{-\left(1+\sqrt{\frac{k_1P_2}{k_2P_1}}\right)+\sqrt{\left[-\left(1+\sqrt{\frac{k_1P_2}{k_2P_1}}\right)\right]^2-4\cdot\frac{k_1P_2}{k_3}(-1)}}{2\frac{k_1P_2}{k_3}} \qquad \textbf{(6)}$$

Thus, the rate equation for the formation of styrene can be expressed as:

$$r_{St} = \frac{dA_1}{d\left(\frac{G_{cat}}{\theta_1}\right)} = k_2P_1\theta_1^2 \qquad \textbf{(7)}$$

According to the proposed mechanism, the direct hydrogenation of phenylacetylene to ethylbenzene occurs via a phenylacetylene molecule adsorbed on two active intermediates that hold two adsorbed hydrogen molecules that will result in dissociation. Accordingly, a simplified stepwise scheme for the formation of ethylbenzene can be given as follows:



The kinetic equation corresponding to the indicated mechanism has the following form:

$$r_1 = k_1P_2\theta_1^2,\ r_4 = k_4P_1\theta_2^2,\ r_5 = k_1\theta_4 \qquad \textbf{(8)}$$

$$r_1 = r_4 = r_5 = r_{Eb}$$

$$\theta_1 + \theta_2 + \theta_4 = 1 \qquad \textbf{(9)}$$

$$\theta_2 = \frac{k_1P_2\theta_1}{k_4P_1},\ \theta_4 = \frac{k_1P_2\theta_1^2}{k_5}$$

By substituting the expressions θ₂, θ₄ into equation (9), the following equation is obtained:

$$\theta_1 + \frac{k_1P_2\theta_1}{k_4P_1} + \frac{k_1P_2\theta_1^2}{k_5} = 1$$

$$\frac{k_1P_2\theta_1^2}{k_5} + \left(\frac{k_1P_2\theta_1}{k_4P_1} + 1\right)\theta_1 - 1 = 0 \qquad \textbf{(10)}$$

After solving the equation (10), the following expression can be obtained for θ_1:

$$\theta_1 = \frac{-\left(\sqrt{\frac{k_1 P_2}{k_4 P_1}}+1\right)+\sqrt{\left(\sqrt{\frac{k_1 P_2}{k_4 P_1}}+1\right)^2-4\frac{k_1 P_2}{k_5}\cdot(-1)}}{2\frac{k_1 P_2}{k_5}} \qquad \textbf{(11)}$$

The equation for the rate of formation of ethylbenzene can be given as follows:

$$\tau_{Eb} = k_4 \cdot P_1 \cdot \theta_1^2 \qquad \textbf{(12)}$$

In order to calculate the ki constants, the formula $k = k_0 \cdot e^{-\frac{E}{RT}}$ was used. Thus, according to the mechanism of the above-mentioned hydrogenation reaction, the yields of the reaction products, and the initial molar amounts of phenylacetylene N_1^0 and hydrogen N_2^0, it is possible to determine the available molar amounts n_1-n_4 for phenylacetylene, H_2, St, and Eb, respectively, in the reaction component stream based on the following equations:

$$n_1 = N_1^0 - (A_1 N_1^0 + A_2 N_1^0) = N_1^0 - N_1^0(A_1 + A_2)$$

$$n_2 = N_2^0 - (A_1 N_1^0 + A_2 N_1^0) = N_2^0 - N_1^0(A_1 + A_2)$$

$$n_3 = N_1^0 A_1,\ n_4 = N_1^0 A_2,\ n_{hek} = n_{hek}^0,\ n_{N_2} = n_{N_2}^0$$

where A_1 and A_2 are derivatives of St and Eb, respectively.

Total number of moles of substances:

$$\sum n_i = n_1 + n_2 + n_3 + n_4 + n_{hek}^0 + n_{N_2}^0$$

Partial pressure of substances:

$$P_i = \frac{n_i}{\sum n_i} P;\ \text{ümumi təzyiq } P = 1\ atm$$

Equations (7) and (12) form a kinetic model of the selective hydrogenation of phenylacetylene over mpg-C_3N_4. The developed kinetic model of the reaction was calculated based on statistical analysis based on kinetic data. Calculation of $\ln k_1^0$ and activation energies (E_1^0) of the pre-exponential multiplication of the reaction constants was carried out using the "Slide tolerance" and Powell methods using the "Search" software system based on the following formula:

$$F = \min \sum_{j=1}^{m} \sum_{i=1}^{n} \left(\frac{A_{ji}^{exp} - A_{ji}^{ca}}{A_{ji}^{exp}}\right)^2 ,$$

where A_{ji}^{exp} is the experimental and calculated values of the subtraction of component i in A_{ji}^{cal} experiment j, m is the number of experiments, n is the number of components.

The numerical values of the parameters of the kinetic model of the process (pre-exponential impact and activation energy) are presented in table 4 [11].

Table 4.

Kinetic parameters of a model of the partial hydrogenation of phenylacetylene [11]

Pre-exponential factors		**Activation energies, kcal/mol**	
In k_1^0	2.427 x 10^{-2}	E_1	3.396
In k_2^0	16.143	E_2	3.967
In k_3^0	28.728	E_3	3.044
In k_4^0	19.850	E_4	3.082
In k_5^0	0.840	E_5	6.545

CONCLUSIONS

1. Graphite-type carbon nitride samples with various morphologies were synthesized on the basis of cheap substances such as melamine and dicyandiamide, as well as urea produced in our Republic, and their ability to activate the hydrogen molecule without the presence of metal was discovered. This phenomenon was confirmed experimentally for the first time in the hydrogenation reaction of phenylacetylene and styrene was synthesized with 94-95% selectivity [19].
2. For the first time, the property of hydrogenation of acetylene to ethylene with 90-91% selectivity in the liquid phase of -20-(+50°C) temperature of graphite-type nanoscale carbon-nitride-based catalysts

without metal or modified with alkali (KOH or NaOH) was determined was done [20].

3. It was shown for the first time that metal-free graphite-type nanoscale carbon-nitride-based catalysts are capable of hydrogenating phenol to cyclohexanone with high selectivity [4].
4. In order to study the effect of metal on the catalytic properties of graphite-type carbon-nitride, composites containing Pt/mpg-C3N4 were prepared, and the effect of various donor-acceptor ligands on the hydrogenation of phenylacetylene to styrene was studied on them [16].
5. The composition, structure and physico-chemical properties of the optimal catalyst samples were determined by modern research methods [1, 4, 9, 11, 14, 15, 16, 18].
6. The kinetic regularities of the hydrogenation reaction of phenylacetylene to styrene on mesoporous graphite-type carbon-nitride were studied in a wide temperature range (150-250°C), at volume velocities of 2000-2500 s-1 of reagents and at different mole ratios [11, 19].
7. Based on the determined kinetic regularities, a possible mechanism of the hydrogenation reaction of phenylacetylene to styrene was proposed, and a theoretically based kinetic model of the process was developed according to this mechanism [11].

The main results of the dissertation work were published in the following articles and abstracts:

1. Ahmadov, Vs. M. / Metal-Free Heterogeneous Catalyst for Selective Hydrogenation of Phenylacetylene / Vs. M. Ahmadov, V.M. Akhmedov, İ.D. Ahmadov [et al.] //Azərbaycan Kimya Jurnalı, Bakı, – 2014, №4, – səh. 116-118.

2. Ahmadov, Vs. M. Metal-Free Polymer Catalyst for Selective Semihydrogenation of Alkynes / Vs. M. Ahmadov, V.M. Akhmedov, İ.D. Ahmadov [et al.] // XII European Congress on Catalysis ―Catalysis: Balan-cing the use of fossiland renewable resources». Kazan, Russia, – 30th August–4th September, – 2015, – p. 1359-1360.

3. Ahmadov, Vs. M. Metal-Free polymer catalyst for selective partial hydrogenation of phenylacetylene / Vs. M. Ahmadov, V.M. Akhmedov, İ.D. Ahmadov [et al.] // Akademik Toğrul Şahtaxtinskinin 90 illik yubileyinə həsr olunmuş respublika elmi konfransı/ Bakı, – 2015 oktyabr, – səh 211.

4. Ahmadov, Vs. M. Metal-free graphitic carbon nitrides as a catalysts for hydrogenation of phenol / Vs. M. Ahmadov, V.M. Akhmedov, İ.D. Ahmadov [et al.] // Azərbaycan Kimya Jurnalı №2, Bakı, – 2016, – səh 21-25.

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