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PERFLUORINATED SULFAMIDES IN THE TECHNOLOGY OF COMPLEX UTILIZATION OF CYCLOHEXANE OXIDATION PRODUCTS

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This article discusses the use of perfluorinated sulfamides in various technological processes. The potential of aminotoxane as a catalyst in the cyclohexane oxidation process was studied. The use of aminotoxane significantly shifts the distribution of target products in cyclohexane oxidation, favoring increased alcohol formation. This catalytic system is distinct from those involving crown ethers and polyglycols, suggesting a specific mechanism of influence by perfluorinated sulfamides on the intermediate stages of radical-chain oxidation. For the by-product adipic acid, which is formed in significant amounts, a complex method of utilizing cyclohexane oxidation products is proposed. Specifically, esterification of adipic acid with alcohol was performed, resulting in the production of dibutyl adipinate, a valuable raw material for plasticizer manufacturing. The yield of dibutyl adipinate was 57.6%. The study found that cyclohexane oxidation in the presence of a binary catalyst, cobalt naphthenate−aminotoxane, results in an increased oxidation rate, a threefold reduction in ester and acid selectivity, and a twofold increase in cyclohexanol selectivity compared to oxidation with cobalt naphthenate alone.

Introduction

Amides of sulfonic acids are formed as a result of the action of ammonia on sulfochlorides [1]. Sulfamides are used as emulsifiers, bleaching agents, surface-active substances in metal processing, etc. [1]. Perfluorinated sulfonic acid amides or perfluorinated sulfamides can be of even greater value in industry.

Perfluorooctanesulfonamide (PFOSA), a synthetic organofluorine compound with an eight-carbon chain and a terminal sulfonamide functional group, has been used to repel grease and water in food packaging, as well as for other consumer applications [2]. The main technology for the production of PFOSA and related substances is electrochemical fluorination (ECF). This reaction yields perfluorooctanesulfonyl fluoride (PFOSF) which is the main intermediate product in the synthesis of PFOSA and PFOSA-related substances. This production of PFOSF is currently highly developed in China. N-ethyl- and N-methyl PFOSA can be obtained from PFOSF by further reaction with methyl- or ethylamine, and then by reaction with ethylene carbonate, N-ethyl- and N-methylperfluorooctanesulfamideethanol (N-EtFOSE and MeFOSE). These compounds are metabolized through acetates to PFOSA [4]. In addition, PFOSA is believed to be the biologically active form of the insecticide Sulfluramide (N-ethylperfluorooctanesulfonamide) [5].

Perfluorinated substances with a carbon chain structure, including PFOSA, have fat- and water-repellent properties. Due to the above, all compounds related to PFOSA are used for various purposes as surfactants. The extreme stability of these compounds allows their use at high temperatures, as well as in the presence of strong acids or alkalis. The reason for this stability is the exceptional strength of the fluorocarbon bonds. The above-mentioned compounds are used in

many fields: for example, for anti-erosion additives to liquids of aircraft hydraulic systems; in the composition of ingredients for the manufacture of semiconductors and similar parts by the micro photolithographic method; to reduce surface tension, electrostatic properties, and adhesiveness in the production of analog and digital photo and film films, photo paper and contact plates, etc. [6,7].

Fluorinated sulfonated polyesteramides (SPA) were synthesized for their use in fuel cells on a proton exchange membrane [8]. Most SPA membranes with a degree of sulfonation of 90% showed high proton conductivity. The influence of the chemical structure on the membrane properties was systematically studied by comparing fluorinated polymers with their hydrogenated counterparts. The results indicate that the inclusion of fluorinated fragments in the polymer base of the membrane reduces water absorption [8].

Membranes based on perfluorinated sulfonic acid resin have been used as catalysts for various Ritter transformations involving the treatment of alkenes or alcohols with nitriles in the presence of sulfuric acid. The acid catalyst based on perfluorinated sulfonic acid resin NafionH is effective in a wide range of liquids and gases for carrying out various transformations [9]. This catalyst allows you to lower the temperature and speed up the reaction of benzyl alcohols with nitriles to obtain N-benzylamides [9].

The most popular perfluorinated cyclic tertiary amine in the composition of perfluorocarbon emulsions is perfluoro-N-(4-methylcyclohexyl)piperidine (PMCP), which, along with perfluorodecalin, is the basis of the drug Perftoran. These compounds can be used to obtain perfluorocarbon emulsions capable of carrying oxygen. Perfluorocarbon emulsions are used mainly in medicine as blood substitutes, MRI contrast agents, and also as media for preserving isolated organs [10]. The literature describes a method of oxidizing cellulose with nitrogen dioxide using a perfluorinated tertiary amine solvent. Cellulose changes into the form of oxidized cellulose, which has the property of biological absorption, which allows it to be used for medical purposes for healing stitches, and wounds, stopping bleeding, etc. [10].

It is common to use a solution of perfluoropolyoxaalkylene sulfonic acid amide to prepare a polymeric anti-friction coating, resulting in simplification of the method of creating a coating with increased wear resistance. Fluorinated quaternary ammonium salts were synthesized for their use as catalysts for interphase transfer of halide substitution reactions in extremely nonpolar fluorinated solvents [11].

There is information about the use of amino acids of different structures as catalysts in the processes of homogeneous-catalytic liquid-phase oxidation of cyclohexane [13]. The oxidation process of cyclohexane (CH) provides an important raw material for the production of polyamide fibers and therefore plays an important role in the chemical industry. Cobalt naphthenate catalyst is used in industrial processes of CH oxidation, which has several disadvantages, among which are low selectivity indicators for target products and low conversion values of raw materials. As by-products in this process, esters are formed, the main part of which is dicyclohexyl adipinate and acids, mainly adipic acid. Therefore, the problem of inefficient use of by-products, which are mainly burned, remains relevant, which leads to an increase in production cost factors.

Recent studies [14,15] established that the parameters of the process of catalytic oxidation of cyclohexane are significantly affected by the addition of organic compounds (amino acids, crown ethers, polyglycols), which in small quantities in the composition of the binary system can regulate the selectivity of the process products due to the formation of intermediates complexes or associates, as well as affect the colloidal state of the catalyst.

A representative of the class of amides of perfluorinated sulfonic acids is a compound such as aminotoxane (N-tetraethyl-perfluoro-4-methyl-3,6-dioxahexanesulfonamide) with the following chemical formula:

$$CF_3CF_2OCF_2CF(CF_3)OCF_2CF_2SO_3)[N(C_2H_5)_4].$$

The above-mentioned compound has the properties of hydro- and oleophobization characteristic of perfluorinated sulfonamides, therefore it is an effective surface-active substance and can lower the surface tension at the interface of the hydrocarbon phase and air or oxygen. Therefore, it is expedient to study aminotoxane as a catalyst for the oxidation of CH, as well as to create a technology based on it for the complex use of the obtained oxidation products of CH. This will make it possible to solve the problem of disposal of by-products, and therefore to increase the selectivity of the process.

Experimental

The study was conducted at a laboratory installation for the oxidation of cyclohexane, the reactor for oxidation was operated at high temperatures and pressures and was made of stainless steel 321 (X18H9T).

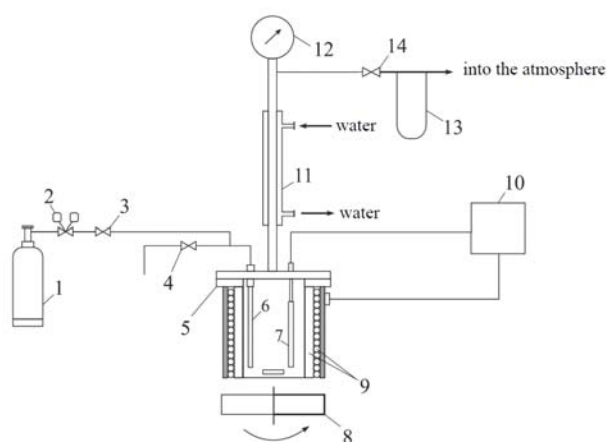The scheme of the experimental laboratory installation is shown in Fig. 1.

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Fig. 1. Autoclave installation for cyclohexane oxidation:
1 − reservoir with oxygen; 2 − reducer; 3, 4, and 14 − valves;
5 − reactor for cyclohexane oxidation; 6 − thermocouple;
7 − capillary for oxygen; 8 − magnetic mixer; 9 − oil shell
and electrical heater; 10 − control-measuring instrument
OVEN TRM-1; 11 − shell-and-tube heat exchanger;
12 − manometer; 13 − flowmeter for measurement of
oxygen consumption

The installation works as follows. Technical oxygen from cylinder 1 enters reactor 5 through reducer 2 and valve 3. Cyclohexane in the amount of 100 cm³ is preloaded into the reactor. Heating begins with the help of an electric heater 9. When the required technological parameters are reached in the reactor, temperature of 418 K and pressure of 1.0 MPa, the oxidation process begins.

A stable temperature regime is maintained by silicone oil located in the reactor casing. The reaction mixture is stirred with a magnetic stirrer 8, as well as with the help of intensive bubbling of oxygen through a capillary 6. The temperature in the reactor is measured by a chromel-copel thermocouple XK-68 (Ukraine) 7 and recorded by a control and measuring device OVEN TRM-1 (Ukraine) 10. The pressure in the system is measured by pressure gauge 12, and the gas flow rate at the exit from it is measured by differential pressure gauge 13.

A return shell-and-tube cooler 11 with water cooling is used for steam condensation. The sample for analysis is taken with valve 4 open and valve 3 closed.

The prepared reaction mixture consisted of 100 cm³ cyclohexane and the catalyst (aminotoxane and the binary system: cobalt naphthenate−aminotoxane were used at various stages of research). The concentration of the catalyst in the reaction medium was 0.0005 mol/l. The oxidant was technical oxygen.

The target products of CH oxidation are cyclohexanol (COL), cyclohexanone (COH), as well as cyclohexyl hydroperoxide (CHHP), which at further stages decomposes with the formation of COH and COl. As by-products in this process, esters are formed, the main part of which is dicyclohexyl adipinate and acids, mainly adipic acid.

During the process, samples were periodically taken and analysis was carried out for the concentration of the main products of the liquid-phase catalytic oxidation of cyclohexane.

The analysis of the target products of COH and COL was carried out on an LHM-80 chromatograph with a thermal conductivity detector. A 2 m long and 3 mm diameter stainless steel column was packed with a plug containing 10% polyethylene glycol sebacinate coated on Chromaton N-AW. The concentration of TSO and TSO was determined by the method of absolute calibration. The concentration of HCG was determined by the iodometric method [15].

The content of carboxylic acids, among which adipic acid occupies the main place (95−97%), is more expedient to determine by titration, because when determining their concentration using gas chromatographic analysis, the error is higher. The concentration of acids in terms of AC was determined according to the method described in ref. [15].

The middle ester (dicyclohexyl adipinate) is well soluble in cyclohexane, so it accumulates in the organic layer during oxidation. The acidic ester is much less soluble in cyclohexane, so its main amount is in the aqueous-acidic layer. The content of DCA is more than 95% of the total number of esters. DCA was analyzed by reverse titration according to the method described in ref. [15].

The concentrations of cyclohexane oxidation by-products (in particular, CO, CO_2, lower dicarboxylic and monocarboxylic acids, and cyclohexylformate) did not exceed the analytical errors and therefore were not determined.

Results and discussion

At the first stage of research, the oxidation of CH was carried out in the presence of an industrial catalyst, cobalt naphthenate, the concentration of which in the reaction mixture was 0.0005 mol/l by analogy with the industrial process. The results of the study are given in Table 1.

Among the representatives of perfluorinated sulfonamides, aminotoxane (AmO), which was added to the original hydrocarbon in the same concentration as NC, was used as a catalyst for the oxidation of CH for further research. The results of the study of the catalytic effect of AmO are given in Table 2.

According to the results of the study, it can be concluded that although aminotoxane helps to preserve the selectivity of target products in the process of oxidation of CH. The conversion of raw materials under the action of AmO reached 4.4 mol.% only at the 100th minute of the experiment, i.e., the rate of the process is lower than during oxidation using NC. In addition, an important conclusion of this study is that the activating effect of aminotoxane is manifested only after the accumulation of a certain amount of oxygen-containing compounds in the oxide when the conversion of the raw material exceeds 1 mol.%. Until the accumulation of oxygen-containing compounds, the rate of oxidation is low, and the so-called induction period is observed.

To improve this process and obtain additional valuable compounds, it is advisable to use a complex method of using the oxidation products of CH. For this reason, it is necessary to dispose of the obtained acids.

One of the methods of disposal of the obtained acids is to prepare esters from acids by their esterification with alcohol. Future, the obtained esters can be used as plasticizers for polymers. In the case of esterification with lower alcohols, the resulting esters can be separated by boiling point and used as raw materials for the isolation of individual acids.

To carry out the esterification process, the oxidate with the largest amount of acids, obtained by oxidation of CH in the presence of aminotoxane, was taken. The composition of oxidation products is given in Table 3.

The obtained acids from the mixture of the remaining products were separated by washing with water. The obtained aqueous solution of organic acids was concentrated by evaporation of water. The composition of the resulting acid solution was as follows: HPCH 0.008 mol/l; acids 0.167 mol/l; esters 0.010 mol/l; TsOH 0.013 mol/l; and TsOL 0.011 mol/l.

Esterification of the aqueous layer of acids in an excess of n-butanol in the presence of KU-2 (КУ-2) ion exchange resin was carried out at the boiling point of the formed water−n-butanol azeotrope (T=365 K).

After the esterification process, distillation of

Table 1

Composition of cyclohexane oxidation products in the presence of cobalt naphthenate, T=413 K, P=1.0 MPa, [cat.]=0.0005 mol/l

τ, min	Selectivity, mol.%					K, mol.%	Sap, mol.%	COL/CON
	HPCH	Acids	Esters	CON	COL			
10	17.0	10.4	14.2	19.8	38.6	1.1	75.4	1.95
20	20.0	11.5	12.5	21.0	35.0	2.1	76.0	1.67
30	5.0	11.5	14.0	23.0	46.5	3.8	74.5	2.02
40	5.1	13.1	13.4	27.6	42.8	4.8	65.5	1.55
50	4.4	20.3	21.5	23.3	30.5	8.5	58.2	1.31
60	3.5	25.6	25.2	21.2	24.5	11.3	49.2	1.16

Table 2

Composition of cyclohexane oxidation products in the presence of aminotoxane, T=413 K, P=1.0 MPa, [cat.]=0.0005 mol/l

τ, min	Selectivity, mol.%					K, mol.%	Sap, mol.%
	HPCH	Acids	Esters	CON	COL		
20	25.0	20.0	5.0	25.0	25.0	1.0	75.0
40	15.8	11.5	9.3	32.0	31.2	1.1	79.2
60	4.3	16.1	11.0	29.5	39.1	2.3	72.9
100	3.1	17.2	10.4	32.1	37.2	4.4	72.4

Table 3

Composition of cyclohexane oxidation products in the presence of aminotoxane, K=1.0 mol.%, t=20 min, T=413 K, P=1.0 MPa, [cat.]=0.0005 mol/l

Selectivity, mol/l and mol.%										Sap, mol.%
HPCH		Acids		Esters		CON		COL		
mol/l	%	mol/l	%	mol/l	%	mol/l	%	mol/l	%	
0.209	25.0	0.167	20.0	0.042	5.0	0.209	25.0	0.209	25.0	75.0

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water and unreacted n-butanol was carried out. The composition of the obtained cube of esterification of adipic acid and n-butanol was as follows: acids 0.032 mol/l; esters 0.29 mol/l; and HPCH, CON, COL 0.000 mol/l. The yield of esters was 57.6%.

Thus, the by-product formed during the oxidation of CH in the presence of AmO was used as a raw material to obtain an additional amount of target products, namely dibutyl adipinate.

At the second stage of research, aminotoxane was used as an additive to the main catalyst, cobalt naphthenate, at three different component ratios: [NC]/[AmO]=5/1; 10/1; and 20/1. Experiments on the oxidation of CH were carried out at a temperature of 413 K and a binary catalyst content in the reaction mixture of 0.0005 mol/l. The change in the conversion of raw materials and the selectivity of the target products depending on the time of the CH oxidation reaction in the presence of the binary system NC−AmO are shown in Figs. 2 and 3.
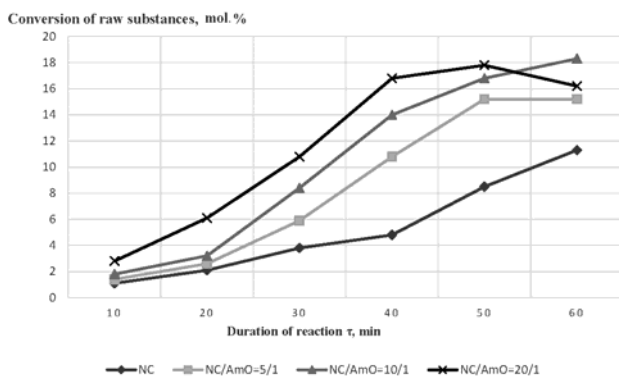

Fig. 2. Dependence of the conversion of raw materials on the duration of CH oxidation in the presence of NC and the binary catalytic system NC−AmO at different ratios of components

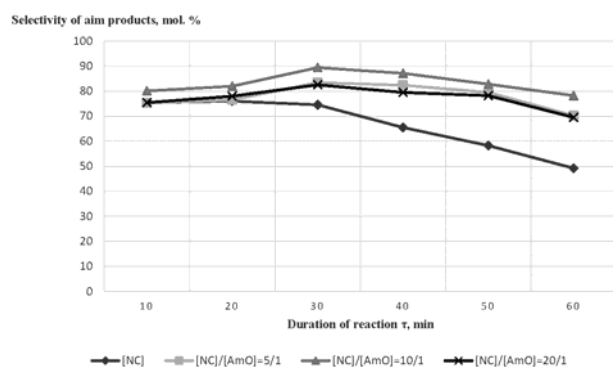Fig. 3. Dependence of the selectivity of the target products on the duration of CH oxidation in the presence of NC and the binary catalytic system NC−AmO at different ratios of components

As the results of the experiments showed, the presence of aminotoxane in the binary system has a positive effect on the conversion of the raw material compared to oxidation on pure cobalt naphthenate. As can be seen from Fig. 2, at the lowest ratio of components ([NC]/[AmO]=20/1), the rate of growth of conversion is the greatest, but already at the 45th minute of the reaction, the value of conversion begins to decrease in comparison with the ratio [NC]/[AmO]=10/1. For that reason, although the conversion of raw materials increases as the proportion of AmO in the binary catalyst decreases, the optimal ratio of components should be taken as [NC]/[AmO]=10/1.

An important technological parameter of the industrial process of CH oxidation is the selectivity of the target products, S_{AP}. During the oxidation of CH on a binary catalyst with the addition of aminotoxane, the selectivity of the target products begins to decrease slightly after reaching a conversion value of 12 mol.% (25−30 min of the experiment). The most optimal is the ratio [NC]/[AmO]=10/1, at which the S_{AP} value reaches a maximum (90 mol.%) at 25 min of the experiment and decreases to the value of 79 mol.% at 50 min of the reaction (Fig. 3). At the same time, in the process of CH oxidation using an industrial catalyst, an increase in the conversion of raw materials above 4 mol.% causes a decrease in the selectivity of the target products to 50 mol.%. In addition, the activating effect of aminotoxane must not require the accumulation of a certain amount of oxygen-containing compounds in the oxidized, in other words, the so-called induction period.

As can be seen from the results of the study, the most optimal ratio of components in the binary catalytic system, which ensures an increase in the conversion of raw materials with high selectivity of the target products, is the ratio of components [NC]/[AmO]=10/1. Therefore, the analysis of the catalytic activity of the binary system NC−AmO in the process of oxidation of CH was carried out using the above ratio of components (Table 4).

We will analyze the composition of oxidation products both in the presence of a binary catalyst with the addition of perfluorinated sulfamide and in the presence of pure cobalt naphthenate. Figures 4 and 5 show the diagrams of comparative data of the composition of the products of both oxidation processes at two conversion values, 2 and 8.5 mol.%.

As can be seen, at the initial stage of oxidation, aminotoxane additives slightly reduce the formation of esters and significantly inhibit acid formation compared to oxidation in the presence of NC. From the target products, with the presence of the AmO

Table 4

Composition of cyclohexane oxidation products in the presence of a binary catalyst cobalt naphthenate−aminotoxane, [NC]/[AmO]=10/1, T=413 K, P=1 MPa, [cat.]=0.0005 mol/l

τ, min	Selectivity, mol.%.					К, mol.%.	Sap, mol.%	COL/CON
	HPCH	Acids	Esters	CON	COL			
10	13.5	4.7	15.2	12.8	53.8	1.8	80.1	4.20
20	14.7	4.5	20.5	19.2	41.1	3.2	75.0	2.14
30	4.6	5.2	5.4	24.1	60.7	8.5	89.4	2.52
40	3.2	5.2	7.7	29.5	54.4	13.9	87.1	1.84
50	4.5	6.5	10.7	30.4	47.9	16.9	82.8	1.58
60	5.5	7.3	12.7	31.2	34.5	18.3	71.2	1.11

additive, the selectivities of the formation of HPCH and COL decrease, and the amount of TSO increases by approximately 1.3 times. In the later stages of oxidation, when the conversion of raw materials exceeds 8 mol.%, the formation of acids and esters decreases several times, and the target products of the process (especially TSO, the amount of which increases by 2 times) are formed in larger quantities than in the process using pure NC. The optimal stage, where the catalytic activity of AmO is manifested to the greatest extent, is the 30th minute of the reaction when the conversion of raw materials reaches 8.5 mol.% and at the same time, the selectivity of the target products of the process is maintained at the level of 89.4 mol.%. At this stage, of the formed target products, the largest share falls on TSO (Fig. 6).

For the CH oxidation processes, such a parameter as the ratio of target products COL/CON is important. As follows from our results, the addition of aminotoxane shifts this ratio towards the formation of COL, which is 4.2 at the initial stages of oxidation and decreases to 1.2 at the final stage of the reaction, and at the 60th minute of the experiment, the ratios of COL/CON equalize compared to by oxidation on pure NC (Fig. 7). Therefore, the binary systems NC−AmO can be effective catalysts in the oxidation processes of CH, which are included in the structure of industrial production of adipic acid, hexamethyldiamine and polyamide synthetic fiber, nylon.

As the results of the experiments showed, the binary system NC−aminotoxane is an effective catalyst for the oxidation of CH, in the presence of which the selectivity for the target products is 79−90%, and the value is 79.0 mol.% is maintained even at a conversion of 16 mol.% (for a 50-minute experiment). The given data show that the oxidation process of CH in the presence of a binary catalyst cobalt naphthenate−aminotoxane exhibits an increase in the rate of oxidation, a 3-fold decrease in the selectivity of the
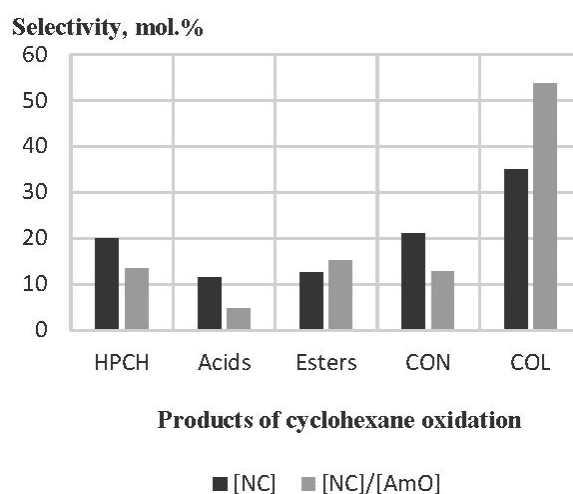

Fig. 4. Comparative composition of CH oxidation products in the presence of NC and a binary catalytic system NC−AmO at the conversion of raw materials of 2 mol.%
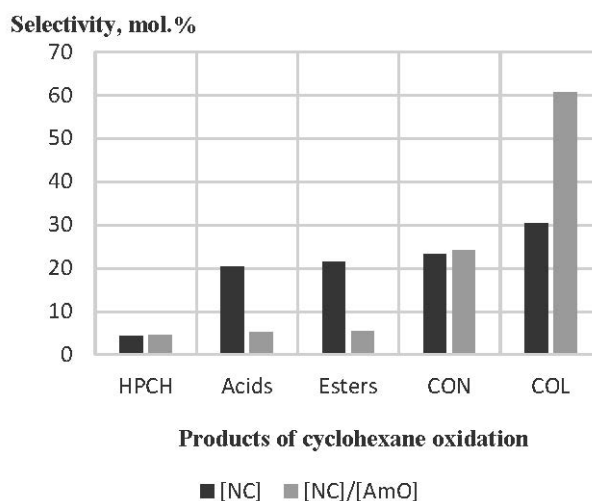

Fig. 5. Comparative composition of CH oxidation products in the presence of NC and a binary catalytic system NC−AmO at the conversion of raw materials of 8.5 mol.%
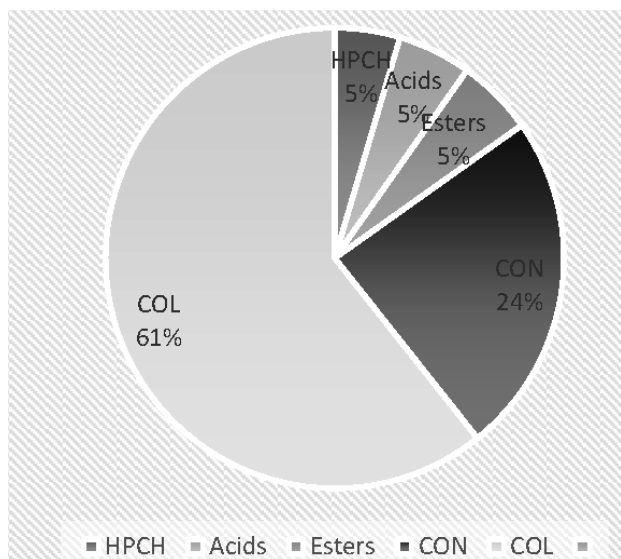
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Fig. 6. Distribution of the products of the CH oxidation process in the presence of a binary catalytic system NC−AmO at the conversion of raw materials of 8.5 mol.%
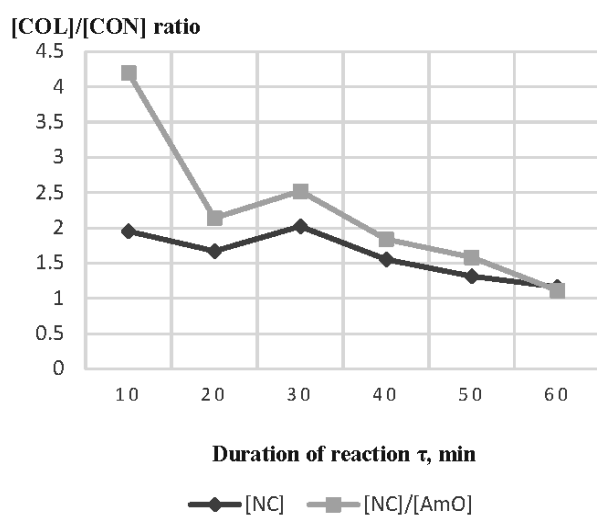

Fig. 7. Dependence of the ratio of the target products COL/CON on the duration of CH oxidation in the presence of NC and the binary catalytic system NC−AmO

formation of unwanted esters and acids, and a 2-fold increase in the selectivity of the formation of the target cyclohexanol. For comparison, the following values can be given: the conversion of raw materials during the oxidation of CH in the presence of cobalt naphthenate at the 60th minute of the experiment barely reaches 5.6%, while the selectivity for the target products drops to 49.0%.

Conclusions

Aminatoxane (N-tetraethyl-perfluoro-4-methyl-3,6-dioxahexanesulfonamide) as a representative of the class of perfluorinated sulfonamides can be used in the oxidation of cyclohexane.

The active catalytic action of an individual aminotoxane during the oxidation of cyclohexane is manifested only after the accumulation of a certain amount of oxygen-containing compounds in the reaction mixture. The use of aminotoxane allows significantly shifting the share of the target products of the cyclohexane oxidation process in the direction of increasing the formation of alcohol, which distinguishes this catalytic system from catalysts with additives of crown ethers and polyglycols and indicates the mechanism of the effect of perfluorinated sulfonamides on the intermediate stages of radical chain oxidation.

For the by-product, adipic acid, which is formed in this process in a significant amount, it is possible to apply the technology of a complex method of using cyclohexane oxidation products. For this, esterification with alcohol can be carried out with the obtained acid, as a result of which dibutyl adipinate was obtained (a valuable raw material for the production of plasticizers). In this way, the problem of disposal of by-products is solved, which means that the selectivity of the process increases.

The oxidation of cyclohexane in the presence of a binary catalyst cobalt naphthenate−aminotoxane is characterized by an increase in the rate of oxidation, a 3-times decrease in the selectivity of the formation of esters and acids, and a 2-times increase in the selectivity of the formation of cyclohexanol compared to oxidation on cobalt naphthenate. The optimal conditions for the oxidation of cyclohexane in the presence of a binary catalytic system cobalt naphthenate−aminotoxane are as follows: the concentration of the catalyst in the reaction mixture of 0.0005 mol/l, the process temperature of 413 K, and the ratio of components [NC]/[AmO]=10/1.

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ПЕРФТОРОВАНІ СУЛЬФАМІДИ В ТЕХНОЛОГІЇ КОМПЛЕКСНОГО ВИКОРИСТАННЯ ПРОДУКТІВ ОКИСНЕННЯ ЦИКЛОГЕКСАНУ

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В даній статті розглянуто шляхи використання перфторованих сульфамідів в різних технологічних процесах. Досліджено можливість використання амінатоксану як каталізатора в процесі окиснення циклогексану. Використання амінатоксану дозволяє значно зсунути частку цільових продуктів процесу окиснення циклогексану в бік збільшення утворення спирту, що відрізняє дану каталітичну систему від каталізаторів з добавками краун-етерів і полігліколей і свідчить про механізм впливу перфторованих сульфамідів на проміжні стадії радикально-ланцюгового окиснення. Для побічного продукту – адипінової кислоти, що утворюється в даному процесі в значній кількості, запропонована технологія комплексного методу використання продуктів окиснення циклогексану. Для цього з одержаною кислотою проводили естерифікацію зі спиртом, в результаті чого було одержано дибутиладипінат – цінну сировину для виробництва пластифікаторів. Вихід дибутиладипінату становив 57,6%. Показано, що для процесу окиснення циклогексану в присутності бінарного каталізатора нафтенат кобальту–амінатоксан є характерними збільшення швидкості окиснення, зменшення селективності утворення естерів та кислот в 3 рази, збільшення селективності утворення циклогексанолу в 2 рази у порівнянні з окисненням на нафтенаті кобальту.

Ключові слова: перфторовані сульфаміди, амінатоксан, циклогексан, окиснення, конверсія сировини, селективність за цільовими продуктами, нафтенат кобальту.

PERFLUORINATED SULFAMIDES IN THE TECHNOLOGY OF COMPLEX UTILIZATION OF CYCLOHEXANE OXIDATION PRODUCTS

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This article discusses the use of perfluorinated sulfamides in various technological processes. The potential of aminotoxane as a catalyst in the cyclohexane oxidation process was studied. The use of aminotoxane significantly shifts the distribution of target products in cyclohexane oxidation, favoring increased alcohol formation. This catalytic system is distinct from those involving crown ethers and polyglycols, suggesting a specific mechanism of influence by perfluorinated sulfamides on the intermediate stages of radical-chain oxidation. For the by-product adipic acid, which is formed in significant amounts, a complex method of utilizing cyclohexane oxidation products is proposed. Specifically, esterification of adipic acid with alcohol was performed, resulting in the production of dibutyl adipinate, a valuable raw material for plasticizer manufacturing. The yield of dibutyl adipinate was 57.6%. The study found that cyclohexane oxidation in the presence of a binary catalyst, cobalt naphthenate–aminotoxane, results in an increased oxidation rate, a threefold reduction in ester and acid selectivity, and a twofold increase in cyclohexanol selectivity compared to oxidation with cobalt naphthenate alone.

Keywords: perfluorinated sulfamides; aminotoxane; cyclohexane; oxidation; raw material conversion; selectivity for target products; cobalt naphthenate.

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