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*A.M. Ludyn, V.V. Reutskyy, Vol.V. Reutskyy***BINARY CATALYTIC SYSTEMS FOR THE INDUSTRIAL CYCLOHEXANE OXIDATION PROCESS****Lviv Polytechnic National University, Lviv, Ukraine**

This paper proposes the possibility of creating an efficient binary catalytic system for the industrial oxidation process of cyclohexane based on a compound of a metal of variable valence and a salt of perfluorinated sulfonic acid. Two-component binary mixtures of the main component and additive were used for the study. In addition to industrial cobalt naphthenate, other salts of metals of variable valences, such as manganese naphthenate, as well as stearates of copper, nickel, and cerium, were used as the main component of the binary mixture. A number of salts of perfluorinated sulfonic acids were used as an additive to the binary mixture. Chromoxane is shown to be the most efficient additive to cobalt naphthenate. In the presence of this binary system at the 50th minute of the process, the conversion of raw materials increased to 10.4 mol.%, which is 22% more than the oxidation of pure cobalt naphthenate, while the selectivity with respect to the target products remains high (79.5 mol.%). It is shown that of a number of compounds of metals of variable valence, the most effective main components of binary systems are cobalt naphthenate and cobalt-cerium catalyst. Carrying out the oxidation of cyclohexane in the presence of such systems allows increasing the conversion of the initial cyclohexane by 1.13 to 1.5 times and thus increasing the rate of oxidation of the hydrocarbon in comparison with the industrial process. It is also important that the use of such catalysts allows conducting the oxidation of cyclohexane to high conversions without losing the yield of the target products.

Keywords: oxidation, cyclohexane, binary catalytic system, conversion of raw material, selectivity.

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Introduction

Oxidation processes are one of the groups that play key role in the modern chemical industry. Oxidation processes are usually carried out under industrial conditions in the gas phase using heterogeneous catalysts and in the liquid phase using homogeneous catalysts.

Liquid-phase oxidation processes mainly proceed by a radical-chain mechanism and imply formation of a wide range of products and relatively low selectivity with respect to the aim products. Homogeneous catalysts are involved in all stages of radical-chain oxidation: nucleation, continuation, degenerate branching and chain breakage. However, in a stationary continuous industrial process, the decisive factor is the effect of the catalyst on the

composition of the products, i.e. primarily the effect at the stage of degenerate branching and chain breakage.

The catalyst in any industrial process can be used under condition that meets the requirements for activity and selectivity. The cost of raw materials and energy for its production, environmental protection and utilization of production waste play a significant role.

One of catalysts that are used in industrial oxidation processes are organic salts of metals of variable valence. They have a number of disadvantages, among which are low selectivity towards the aim products and low conversion values of raw materials. All this entails energy consumption in production, which is associated with the recycling of unreacted raw materials.

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Binary catalytic systems for the industrial cyclohexane oxidation process

Studies of single-component catalysts in oxidation processes have shown that they, while affecting the ratio of formed products and oxidation rate, cannot increase the yield of target products, as well as increase the oxidation rate of hydrocarbons compared to industrial catalyst [1].

One way to solve this problem is to develop efficient binary catalytic systems, which are often more efficient than single-component catalysts. The study of the mechanism of action of such systems and kinetic patterns of formation of reaction products with the participation of binary catalysts will increase the technical and economic performance of the oxidation process. Therefore, the problem of creating efficient binary catalyst systems for the oxidation process of cyclohexane remains extremely relevant.

Recent studies [1,2] have shown that the parameters of the catalytic oxidation process are significantly influenced by oxygen and nitrogen compounds, which in small quantities with a catalyst are able to regulate the selectivity of products through the formation of intermediate complexes or associations. The effectiveness of organic modifiers depends on their properties and characteristics of the metal ion that is a part of the main catalyst. The results of the research revealed a wide range of opportunities for the purposeful creation of new promising catalytic and initiation systems for oxidation processes. The use of oxygen-containing additives of different nature in the oxidation of cyclohexane (CH) allows influencing the composition of the obtained products and the relationship between them [4].

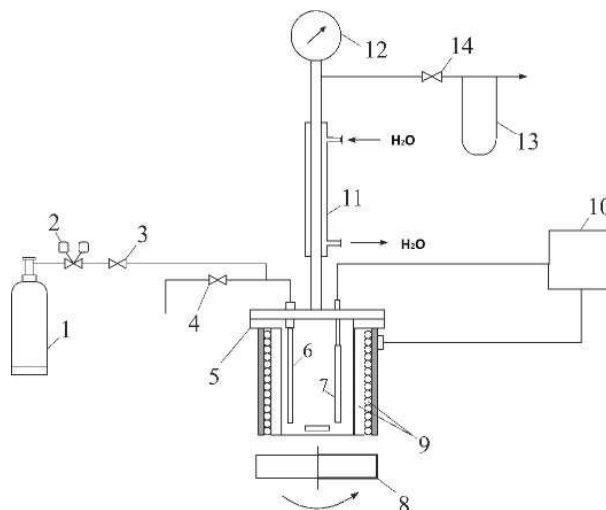
Our goal was to create a binary catalyst system based on a compound of variable valence metal (SVVM) and a salt of perfluorinated sulfonic acid (SPSA), which would prevail in its activity and selectivity over an industrial catalyst for the oxidation process of CH.

The main aim of this work was to establish the dependences of efficiency of organic modifiers on the nature of metal in the main catalytic salt. Determining those dependences will allow us to create binary catalytic system based on SVVM and SPSA with activity and selectivity higher than of industrial catalyst for CH oxidation process.

Experimental

The study was performed using a laboratory installation for cyclohexane oxidation, the oxidation reactor of which was operated at high temperatures and pressures and made from stainless steel Ch18N9T.

The scheme of the experimental laboratory installation is shown in Figure. The installation works



Autoclave installation for oxidation of cyclohexane: 1 – oxygen tank; 2 – reducer; 3, 4, 14 – valves; 5 – reactor for oxidation of cyclohexane; 6 – thermocouple; 7 – capillary for oxygen supply; 8 – magnetic stirrer; 9 – oil jacket and electric heater; 10 – control and measuring device ARIES TRM-1; 11 – shell-and-tube heat exchanger; 12 – manometer; 13 – differential pressure gauge for measuring oxygen consumption

in the following way. Technical oxygen from the cylinder 1 through the reducer 2 and the valve 3 enters the reactor 5. The reactor is pre-loaded with CH in the amount of 100 cm³. Heating begins with an electric heater 9. When the reactor reaches the required technological parameters (temperature of 418 K and pressure of 1.0 MPa), the oxidation process begins.

Stable temperature is maintained by silicone oil in the reactor casing. The reaction mixture is stirred with a magnetic stirrer 8, as well as by intensive bubbling of oxygen through the capillary 6.

Solutions of cobalt naphthenate in cyclohexanone (basic) and solutions of various binary catalysts (studied) were used as catalysts. The concentration of cobalt naphthenate in the reaction medium was 10⁻⁴ mol/L. The oxidant was technical oxygen. Experimental data on the oxidation of cyclohexane in the presence of the studied catalysts were compared with those achieved by the oxidation of cyclohexane with the base catalyst.

The temperature in the reactor was measured by chromel-copel thermocouple ChC-68 (Ukraine) 7 and recorded by the control and measuring device ARIES TRM-1 (Ukraine) 10. The pressure in the system was measured by a manometer 12, and gas flow at the outlet was measured by a differential pressure gauge 13.

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

During the process, samples were periodically taken and analyzed for the concentration of the main products of liquid-phase catalytic oxidation of cyclohexane: cyclohexyl hydroperoxide (CHH), cyclohexanol (COL), cyclohexanone (CON), and acids which mainly contained adipic acid. Concentrations of CH by-products (including CO, CO₂, lower dicarboxylic and monocarboxylic acids, cyclohexyl formate) did not exceed the error of analysis and therefore were not determined.

Two-component binary mixtures in the main component and additive were used for the study. In addition to industrial cobalt naphthenate, other salts of metals of variable valence, such as manganese naphthenate, as well as stearates of copper, nickel and cerium, were used as the main component of the binary mixture. A number of the following salts of perfluorinated sulfonic acids were used as an additive to the binary mixture:

- chromoxane –
 $\text{CF}_3\text{CF}_2\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_3\text{K}$,
- oxane – $\text{CF}_3\text{CF}_2\text{OCF}_2\text{SO}_3\text{K}$,
- fluoroxane –
 $\text{CF}_3\text{CF}_2\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_3\text{K}$,
- carboxane –
 $(\text{CF}_3\text{CF}_2\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_3)_2\text{Ca}$,
- aminoxane –
 $\text{CF}_3\text{CF}_2\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{NH}_2$.

Results and discussion

At the first stage of research, the combined effect of various salts of metals of variable valence in the binary catalyst system on the oxidation of cyclohexane was determined. Cobalt and manganese naphthenate, as well as copper, nickel and cerium stearates were used for this purpose. A salt of perfluorinated sulfonic acid, chromoxane, was used as an additive. Two groups of experiments were performed: in the presence of individual SVVM and under the action of binary mixtures with a ratio of components [SVVM]/[chromoxane] of 10/1.

The results of the experiments showed (Table 1) that only the presence of a binary catalyst system based on cobalt naphthenate or cerium stearate with the addition of chromoxane causes an increase in the oxidation rate of cyclohexane. If we consider the change in selectivity for the target products in the presence of SVVM and chromoxane, then only binary catalyst systems based on cobalt and cerium salts lead to an increase in this parameter. In the process of oxidation of CH in the presence of cerium stearate with the addition of chromoxane, the selectivity of the formation of CHH and acids significantly increases, the selectivity of the formation of COL and CON slightly increases (18.8 and 13.7%, respectively), and the formation of esters decreases as compared with the oxidation on pure cerium stearate. It should be noted that the increase in the content of hydroperoxide in this case due to the explosiveness of this product impairs the safety of the process.

In the process of oxidation of CH under the influence of cobalt naphthenate and chromoxane, the selectivity of the formation of hydroperoxide and acids decreases, the selectivity of the formation of the desired CHH and CON, as well as undesirable esters increases compared to the oxidation without

Table 1
Composition of cyclohexane oxidation products in the presence of chromoxane and salts of various metals of variable valence. T=413 K, P=1 MPa, [cat.]=5·10⁻⁴ mol/l, [SVVM]/[chromoxane]=10/1

Catalyst		τ, min	Selectivity, mol.%					Conversion, mol.%
main comp.	additive		CHH	acids	ethers	CON	COL	
CoNaf ₂	–	30	11.2	13.8	2.0	24.2	49.8	4.6
CoNaf ₂	chromoxane	30	5.5	9.7	8.1	32.5	44.2	5.4
MnNaf ₂	–	60	27.6	5.4	10.1	21.7	35.2	4.0
MnNaf ₂	chromoxane	80	36.5	9.4	13.2	15.7	25.2	3.4
CuSt ₂	–	90	43.0	6.5	23.3	13.0	14.2	4.2
CuSt ₂	chromoxane	90	52.3	5.2	18.1	13.9	10.5	3.1
NiSt ₂	–	120	21.7	13.4	19.8	19.5	25.6	4.4
NiSt ₂	chromoxane	120	46.0	7.8	11.2	15.5	19.5	4.2
CeSt ₃	–	65	28.4	4.0	44.2	9.9	13.5	4.0
CeSt ₃	chromoxane	90	36.6	11.1	19.8	13.7	18.8	4.5

chromoxane. For this reason, the following binary catalyst system may be of practical interest: cobalt naphthenate–chromoxane.

The addition of chromoxane to other metals of variable valence inhibits the oxidation of CH.

Thus, cobalt is a necessary component of catalytic systems for the oxidation of cyclohexane. Therefore, the combined effect of various salts of perfluorinated sulfonic acids on the oxidation of CH as additives to cobalt naphthenate or cobalt-cerium catalyst was further investigated. The binary catalyst mixture was created with a ratio of components [Co]/[SPSA]=10/1. As a result of the research, the conversion of the transformed raw material and the selectivity of all reaction products were similarly determined, in addition, the selectivity for the target products of the process was calculated. The results of experiments on the oxidation of CH in the presence of cobalt naphthenate and PSA are given in Table 2.

These data indicate that the same regularities exist for all studied salts of perfluorinated oxysulfonic acids: an increase in the oxidation rate, an increase in the selectivity of the formation of esters, and a decrease in the selectivity of the formation of CHH and acids. The selectivity of the oxidation process of

CH with respect to the target products during oxidation in the presence of binary catalyst systems is 70–80% (for 50 min of the experiment), and remains at this level until the CH conversion of 10.4%, whereas during oxidation in the presence of convert more than 5%, there is a sharp decrease in the selectivity of the process towards the target products which reaches 58%.

As can be seen from the results of experiments, the most effective additive to cobalt naphthenate is chromoxane. In the presence of this binary system at the 50th minute of the process, the conversion of raw materials increased to 10.4 mol.%, which is 22% more than the oxidation of pure cobalt naphthenate, while the selectivity for the target products remains high (79.5 mol.%).

For a complete analysis of the efficiency of the catalytic action of the binary system cobalt naphthenate–chromoxane, we present the results of the complete cycle of oxidation of CH in the presence of this system (Table 3).

According to the results of experiments, the binary system NC–chromoxane is an effective catalyst for the oxidation of CH, in the presence of which the selectivity with respect to the target products does not decrease lower than 73.9 mol.%,

Table 2

Composition of cyclohexane oxidation products in the presence of cobalt naphthenate and salts of perfluorinated sulfonic acids*. T=413 K, P=1 MPa, [cat.]= $5 \cdot 10^{-4}$ mol/l, [NC]/[SPSA]=10/1

Catalyst		τ , min	Selectivity, mol.%					K, mol.%	Sap, %
main comp.	additive		CHH	acids	ethers	CON	COL		
CoNaf ₂	–	50	4.4	20.3	21.5	23.3	30.5	8.5	58.2
CoNaf ₂	oxane	50	7.9	10.7	13.5	25.2	35.9	4.8	69.0
CoNaf ₂	chromoxane	50	6.5	9.2	11.2	31.3	41.7	10.4	79.5
CoNaf ₂	fluoroxane	50	7.7	10.6	14.6	29.8	37.5	9.1	75.0
CoNaf ₂	carboxane	50	10.2	11.3	12.3	27.9	38.3	9.1	76.4

Note: * – K, mol.% is the conversion of the raw material in mole percentage; and Sap is the selectivity towards the end products.

Table 3

Composition of cyclohexane oxidation products in the presence of cobalt naphthenate and chromoxane*. T=413 K, P=1 MPa, [cat.]= $5 \cdot 10^{-4}$ mol/l, [NC]/[chromoxane]=10/1

Catalyst		τ , min	Selectivity, mol.%					K, mol.%	Sap, %
main comp.	additive		CHH	acids	ethers	CON	COL		
CoNaf ₂	chromoxane	10	31.5	5.9	18.5	14.8	29.6	1.5	75.5
CoNaf ₂		20	15.7	9.6	12.0	22.1	40.6	4.8	78.4
CoNaf ₂		30	4.3	9.9	8.1	30.0	47.8	6.3	82.1
CoNaf ₂		40	5.0	10.7	12.3	29.0	42.9	7.9	76.9
CoNaf ₂		50	6.5	9.2	11.2	31.3	41.7	10.4	79.5
CoNaf ₂		60	8.3	10.2	15.9	27.5	38.1	12.1	73.9

Note: * – K, mol.% is the conversion of the raw material in mole percentage; and Sap is the selectivity towards the end products.

and this value is maintained until the conversion of 12 mol.%. It should also be noted that at the 30th minute of the reaction, there is a maximum at which the conversion of raw materials increases to 6.3% and while maintaining the highest value of selectivity for the target products (82.1 mol.%).

For comparison, the following data 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% and the selectivity towards the target products decreases to 49.0%.

During the oxidation of CH in the presence of binary catalytic systems in the cobalt–cerium catalyst and salts of various perfluorinated oxysulfonic acids, the oxidation rate also increases, albeit to a lesser extent, in comparison with the oxidation on pure cobalt–cerium. However, their influence on the selectivity of the oxidation process is different: the selectivity of the process with respect to acids increases, whereas the selectivity of the formation of CHH and esters decreases (Table 4). The dependence of the efficiency of action on the structure of sulfonic acid is less detailed than in the case of catalytic systems based on cobalt naphthenate. In this system, in addition to chromoxane, oxane is also an effective additive.

In order to explain the mechanism of the binary catalytic system NC–chromoxane, we investigated the individual constituents of it as compared with

the similar compounds.

Structural comparison of the “ligand” part of the catalytic system chromoxane with other SPSA shows that chromoxane is a “medium”, in size, compound. Therefore, we cannot explain its influence by the possibility of more “loose” coordination around complex creating metal, or by possibility of increase (or decrease) of the numbers of coordinated ligands. In addition, it is worth mentioning that it is not the only compound containing potassium, so solubility of SPSA cannot explain such effectiveness in the oxidation process either.

Next step of our research was investigation of characteristics of the individual metals that are used in the formation of catalytic system. Main characteristics of metals are given in Table 5.

As can be seen from Table 5, all characteristics of cobalt, in comparison with similar variable valence metals, are in the «middle» range. Influence of cobalt cannot be explained by the size of ion, as it is neither the biggest nor the smallest from the researched. Electronegativity does not take part in the efficiency of cobalt as a catalyst either. Both more electronegative and less electronegative metals showed weaker results than cobalt. In terms of coordination numbers and ability to form complex compounds, cobalt as well demonstrates characteristics similar to other researched metals.

In case of CH oxidation process, we cannot

Table 4

Composition of cyclohexane oxidation products in the presence of cobalt-cerium catalyst and salts of perfluorinated sulfonic acids*. T=413 K, P=1 MPa, [cat.]=5·10⁻⁴ mol/l, [Co–Ce]/[SPSa]=10/1

Catalyst		τ, min	Selectivity, mol.%					K, mol.%	Sap, %
main comp.	additive		CHH	acids	ethers	CON	COL		
Co–Ce	–	50	10.7	15.5	31.0	20.9	21.9	5.4	53.5
Co–Ce	oxane	60	21.9	13.0	26.0	14.8	24.3	6.2	61.0
Co–Ce	chromoxane	60	7.8	23.0	31.7	17.9	19.6	6.3	45.3
Co–Ce	fluoroxane	50	9.8	22.9	19.1	21.3	26.9	5.4	58.0
Co–Ce	aminoxane	60	5.0	25.0	26.0	19.8	24.2	5.6	49.0

Note: * – K, mol.% is the conversion of the raw material in mole percentage; and Sap is the selectivity towards the end products.

Table 5

Main characteristics of the metals of variable valences used for the research

Element	Group	Family	Coordination number	Ion radius, pm	E potential, V	Electronegativity
Co	4 VIII B	d	4; 6	63 (+3); 72(+2)	–0.277	1.88
Mn	4 VII B	d	4	46(+7); 80(+2)	–1.18	1.55
Cu	4 I B	d	6	73(+2); 77(+1)	0.337	1.9
Ni	4 VIII B	d	4; 6	69(+2)	–0.25	1.91
Ce	6 lant.	f	6	92(+4); 103(+3)	–2.34	1.08

explain difference of the impact of different metals by structure of the surface of researched metals, as it is not a heterogeneous but homogeneous catalytic process.

Our hypothesis for the mechanism of catalytic reaction is that cobalt naphthenate forms a highly reactive, short-term complex with SPSA and reaction media that has relatively low energy of activation and under reaction conditions transforms into the aim products, mainly CHH. This hypothesis is also confirmed by a higher percentage of ethers found in the products of reaction. However, very specific conditions of creation and high instability of the catalytic complexes does not allow us to identify their presence and exact composition by any accessible to us methods of analysis. Developing new methods of identification of such catalytic complexes in the reaction media under the high reaction conditions becomes very relevant and can help to find new highly effective catalytic systems for industrial processes.

Conclusions

Conducted experiments and researches of the influence of organic modifiers of different nature on organic catalysts with different composition for the CH oxidation proved that the most efficient catalysts are based on the cobalt naphthenate.

Therefore, binary catalyst systems based on industrial cobalt naphthenate as the main component and salts of perfluorinated sulfonic acids as additives can be effective catalysts in the process of liquid-phase oxidation of cyclohexane. Carrying out the oxidation of cyclohexane in the presence of such systems allows increasing the conversion of the original cyclohexane by 1.13–1.5 times and thus increasing the rate of oxidation of the hydrocarbon in comparison with the industrial process. It is also important that the use of these catalysts allows performing the oxidation of cyclohexane with high conversions without decreasing the yield of the target products.

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БІНАРНІ КАТАЛІТИЧНІ СИСТЕМИ ДЛЯ ПРОМИСЛОВОГО ПРОЦЕСУ ОКИСНЕННЯ ЦИКЛОГЕКСАНУ

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В даній статті запропонована можливість створення ефективною бінарною каталітичною системою для промислового процесу окиснення циклогексану на основі сполуки металу змінної валентності та солі перфторованої сульфокислоти. Для дослідження брались двокомпонентні бінарні суміші в складі основного компоненту та добавки. Як основний компонент бінарної суміші використовувались, крім промислового нафтенату кобальту, також інші солі металів змінної валентності такі, як нафтенат марганцю, а також стеарати міді, нікелю та церію. Як добавка до бінарної суміші використовувалась низка солей перфторованих сульфокислот. Встановлено, що найефективнішою добавкою до нафтенату кобальту є хромоксан. В присутності цієї бінарної системи на 50-ій хвилині перебігу процесу конверсія сировини зросла до 10,4 мол.%, що є на 22% більше, ніж при окисненні на чистому нафтенаті кобальту, при цьому селективність за цільовими продуктами залишається високою і складає 79,5 мол.%. Показано, що з низки сполук металів змінної валентності найефективнішими основними компонентами бінарних систем є нафтенат кобальту та кобальт-церієвий каталізатор. Проведення окиснення циклогексану в присутності таких систем дозволяє підвищити конверсію вихідного циклогексану в 1,13–1,5 рази і таким чином збільшити швидкість окиснення вуглеводню в порівнянні з промисловим процесом. Важливим також є те, що застосування таких каталізаторів дозволяє вести процес окиснення циклогексану до високих конверсій і при цьому не втрачати показники з виходу цільових продуктів.

Ключові слова: окиснення, циклогексан, бінарна каталітична система, конверсія сировини, селективність.

BINARY CATALYTIC SYSTEMS FOR THE INDUSTRIAL CYCLOHEXANE OXIDATION PROCESS*A.M. Ludyn**, *V.V. Reutskyy*, *Vol.V. Reutskyy*

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This paper proposes the possibility of creating an efficient binary catalytic system for the industrial oxidation process of cyclohexane based on a compound of a metal of variable valence and a salt of perfluorinated sulfonic acid. Two-component binary mixtures of the main component and additive were used for the study. In addition to industrial cobalt naphthenate, other salts of metals of variable valences, such as manganese naphthenate, as well as stearates of copper, nickel, and cerium, were used as the main component of the binary mixture. A number of salts of perfluorinated sulfonic acids were used as an additive to the binary mixture. Chromoxane is shown to be the most efficient additive to cobalt naphthenate. In the presence of this binary system at the 50th minute of the process, the conversion of raw materials increased to 10.4 mol.%, which is 22% more than the oxidation of pure cobalt naphthenate, while the selectivity with respect to the target products remains high (79.5 mol.%). It is shown that of a number of compounds of metals of variable valence, the most effective main components of binary systems are cobalt naphthenate and cobalt-cerium catalyst. Carrying out the oxidation of cyclohexane in the presence of such systems allows increasing the conversion of the initial cyclohexane by 1.13 to 1.5 times and thus increasing the rate of oxidation of the hydrocarbon in comparison with the industrial process. It is also important that the use of such catalysts allows conducting the oxidation of cyclohexane to high conversions without losing the yield of the target products.

Keywords: oxidation; cyclohexane; binary catalytic system; conversion of raw material; selectivity.

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