

CATALYTIC INTENSIFICATION
OF THE CYCLOHEXANE OXIDATION*Oleksandr Ivashchuk*^{1, *}<https://doi.org/10.23939/chcht11.04.430>

Abstract. Methods of intensification of the process of liquid-phase cyclohexane oxidation in the presence of complex catalytic systems, catalytic solutions and individual catalysts have been considered in the article. Quantitative and qualitative influences of binary catalytic systems which contain cobalt naphthenate and organic modifiers of different nature have been determined. The research confirmed the assumption of complexation involving components of the catalytic solutions in the reaction mixture. The structural formula of possible intermediate catalytic complex has been built.

Keywords: cyclohexane, oxidation, catalysis, catalytic systems.

1. Introduction

Liquid-phase oxidation of cyclohexane (CHX) to cyclohexanol (COL) and cyclohexanone (CON) is an important industrial process. The aim products (AP – COL, CON) are used as original materials for the synthesis of polyamide fibers – nylon and capron.

Like most liquid-phase hydrocarbons oxidation processes with air oxygen or molecular oxygen, the industrial cyclohexane oxidation is characterized by low selectivity for aim products and low feedstock conversion: $S_{AP} \approx 78\%$, $X_{CHX} \approx 4\%$. This is explained by the fact that the homogeneous catalytic hydrocarbons oxidation occurs by the radical mechanism that causes the formation of a wide range of by-products and limits the conversion process [1].

With further increase of conversion, there is a sharp decrease in selectivity due to accumulation of by-products, especially acids and esters in the oxidation mixture. Low conversion causes significant energy cost of recycling cyclohexane which has not been reacted. This determines the relevance of searching the capabilities of the intensification of CHX oxidation process.

It should be noted that an important criterion in the study of the oxidation of cyclohexane is, along with the aim products selectivity and the hydrocarbon conversion, the ratio of the aim products [COL]/[CON], which plays an important role in choosing the direction of use of the investigated process. In the case of a high [COL]/[CON] ratio it is appropriate to use the process in the production of adipic acid, and when the ration is low – in the production of caprolactam.

The researches of cyclohexane oxidation technical and economic parameters improvement are divided into two main areas – catalytic and non-catalytic ones. Non-catalytic CHX oxidation has been researched since the 60's of XX century [1, 2]. It was suggested to carry out non-catalytic oxidation of cyclohexane at elevated temperature (438–473 K) and low process time (1–10 min). The advantages of this method were small number of by-side reactions and quite high (85 %) selectivity of the aim products formation [2]. However, low hydrocarbon conversion leads to reduction of productivity of the reaction unit and high temperature causes significant energy costs.

A significant direction of the non-catalytic CHX oxidation research is inputting of various compounds into the reaction mixture, especially acids (lower aliphatic acids, boric acids, acetic acids, *etc.*) and their derivatives [3]. Using of these methods is difficult in the industry because of increasing different compounds in the reaction mixture and low productivity of the reaction unit.

Catalytic direction of the cyclohexane oxidation is also widely studied by scientists. Catalysis of the cyclohexane oxidation by the variable valence metal salts (VVM), mainly of cobalt, was chosen as the best way thereof [4]. This method is used in industry. The production process is carried out at 420–440 K under pressure (1–3 MPa) in the bubbling type reactor, usually in the reaction medium.

It should be noted that for the intensification of the oxidation of cyclohexane chemical and physico-chemical methods, including the ultrasound processing, have been widely studied [5]. However, this promising direction has not gained use in the industry as requiring complex production hardware.

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Low values of S_{AP} and X_{CHX} required new scientific research. Considering the economic factor, creation of a catalyst that would not demand major changes in the existing production scheme arose as the main issue.

At the end of XX century, the development of binary catalytic systems based on common industry catalysts, especially cobalt naphthenate (CoNph), has begun. An important contribution to this area has been made by scientists of Lviv Polytechnic National University. The Department of Technology of Organic Products carried out research and development the cyclohexane oxidation catalysts for this process.

So, the aim of this work is to compare the latest methods of liquid-phase cyclohexane oxidation process intensification in the presence of complex catalytic systems and individual catalysts.

2. Experimental

Cyclohexane oxidation was conducted at different temperatures (typically close to 413 K) and pressure $P = 1.0$ MPa in the bubbling type reactor. The study was carried out on an experimental autoclave installation with an electric heating of the reactor jacket (Fig. 1). A stable temperature mode was maintained by silicone oil in the reactor casing. Industrial oxygen has been used as oxidant.

Samples were collected into containers, which were previously filled with isopropyl alcohol. This was done to homogenize the samples and dissolve the adipic acid, which is formed in large quantities with increasing of the cyclohexane conversion. The composition of the products of the oxidation reaction was determined by titrimetric and gas chromatography.

Conditions of laboratory tests were similar to those used in the industrial process. The autoclave installation for the research process is shown in Fig. 1.

3. Results and Discussion

The study of the binary catalytic systems based on cobalt naphthenate and organic modifiers of different nature which were developed at Lviv Polytechnic National University [6-7] testifies to positive changes of the technical and economic parameters of the liquid-phase CHX oxidation (Table 1). It should be noted that for the analysis of the obtained experimental data the most important parameters of the process are those at the cyclohexane conversion close to $X = 4\%$, since this value is the closest to the parameters of the industry oxidation process. The results were compared with data obtained during the CHX oxidation with the individual industrial catalyst – CoNph.

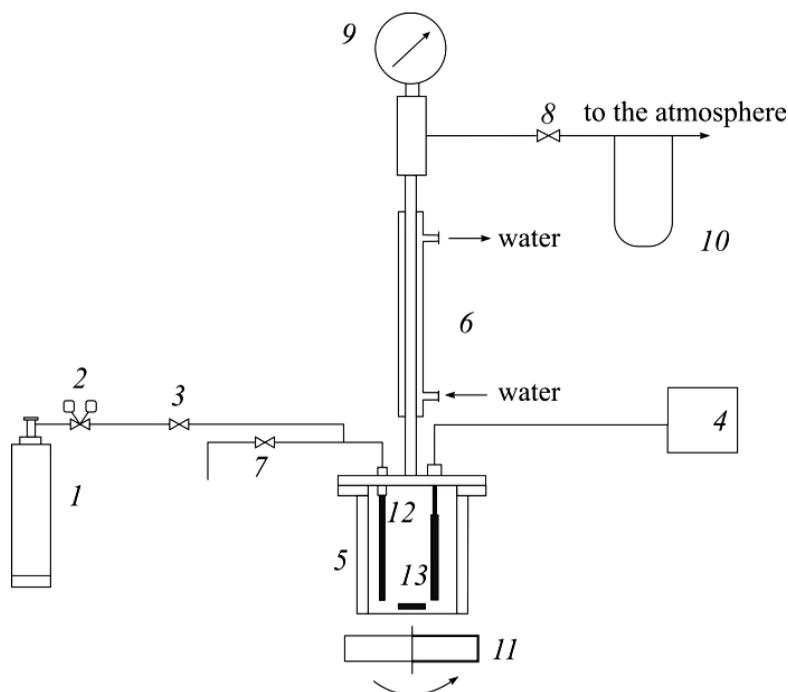


Fig. 1. The autoclave installation for the cyclohexane oxidation: 1 – oxygen cylinder; 2 – reducer; 3, 7, 8 – valves; 4 – control equipment; 5 – reactor for cyclohexane oxidation; 6 – shell-and-tube heat exchanger; 9 – pressure gauge; 10 – differential pressure gauge for the oxygen cost measuring; 11 – magnetic stirrer; 12 – capillary for oxygen; 13 – thermocouple

Table 1

Technological parameters of the catalytic cyclohexane oxidation in the presence of organic co-catalysts of different nature. $T = 413\text{--}418\text{ K}$; $P = 1.0\text{ MPa}$

Co-catalyst	t , min.	$\frac{\text{CoNph}}{\text{co-cat.}}$	$[\text{CoNph}] \cdot 10^4$, mol/l	X_{CHX} , %	S_{AP} , %	$\frac{\text{COL}}{\text{CON}}$
–	30	–	5.0	4.6	73.3	2.13
DBCR	40	5/1	5.0	4.2	75.8	1.75
15-CR-5	50	5/1	2.5	4.2	82.9	1.69
PPG425	50	5/1	5.0	4.5	85.1	1.11
PES4000	35	5/1	5.0	5.8	85.0	1.43
CHR	30	10/1	5.0	5.6	92.4	1.78
HMC	60	5/1	5.0	5.2	93.6	1.33

Notes: DBCR – dibenzo-18-Crown-6; 15-CR-5 – 15-Crown-5; PPG425 – polypropylene glycol with $M_{av} = 425$; PES4000 – polyethylene glycol succinate with $M_{av} = 4000$; CHR – chromoxane; HMC – hydroxymethylcellulose.

Table 2

Technological parameters of the catalytic cyclohexane oxidation in the presence of complex catalytic solution. $T = 413\text{ K}$; $P = 1.0\text{ MPa}$

Co-catalyst	t , min.	$\frac{\text{CoNph}}{\text{co-cat.}}$	$[\text{CoNph}] \cdot 10^4$, mol/l	X_{CHX} , %	S_{AP} , %	$\frac{\text{COL}}{\text{CON}}$
–	30	–	5.0	4.6	73.3	2.13
PEG2000 + CON	60	1/1	5.0	5.0	88.0	0.89

Note: PEG2000 + CON – solution of polyethylene glycol with $M_{av} = 2000$ in cyclohexanone.

The researches indicate that the most effective co-catalysts are the substances of ionic nature (Table 1). The use of binary catalytic systems allows to increase the selectivity for the aim products of the process and to regulate their correlation ratio. It was also determined that the use of ionic co-catalysts promotes the accumulation of cyclohexanone in the reaction medium. It is also important that the input of the binary catalytic systems in the industry does not require changes to existing technological scheme of production.

However, the use of systems [CoNph–organic modifier] has also the drawbacks. Experimental data showed that at the initial stages of oxidation, the effect of binary catalytic systems is not strongly pronounced and is accompanied by the induction period, after which the process rate sharply increases. The effect of additives is manifested in the conversion of more than 1% when the system accumulated sufficient oxygen compounds, which indicates the need for time for the formation and activation of a catalytic complex of variable valence metal salt and organic modifier in the reaction medium, as well as participation of oxygen-containing compounds in the process [7].

In view of this, it was suggested to study the influence of the pre-prepared catalyst solutions aimed at preliminary obtaining and activation of the catalytic

complex of the variable valence metal salt and an organic modifier. The studies have shown that the use of catalytic complex solutions [8] in one of the aim products – cyclohexanone – is rather effective and highly selective (Table 2).

On the basis of the research it was determined that a common feature of all effective modifiers is their ability to be part of the ligand surrounding of the catalyst central atom – the variable valence metal. Therefore, the positive effect of catalytic systems containing organic additives of different nature has been associated with the formation of complexes or ion associations between molecules of the catalyst and organic modifiers – intra- and inter-molecular coordination bonds of the electron acceptor cobalt atom and functional groups of the co-catalyst [9].

Conducted spectral analysis of the binary catalytic systems solutions (photocolorimetry, IR- and UV-spectroscopy) confirmed these assumptions. The results have shown the change of color of the solutions, shifts of their absorption peaks and the formation of OH...H-bonds, quantitative change of the C=O and –CH₃, –CH₂–, which indicate the formation of a complex compound or an ion association in the catalytic solution [9].

Thus, it was determined that improving of existing homogeneous catalysts through the use of organic

modifiers of different nature improves the technical and economic parameters of the liquid-phase CHX oxidation process. However, despite the numerous and long-term studies, the existing experimental data base is not enough to determine the mechanism of action of additives and to forecast their influence when used in various chemical processes. On the other hand, multiple components in the catalytic system lead to that situation when the ligand surrounding of the catalyst central atom in the oxidation may be subject to change, and such an unstable structure of the catalytic complex can lead to efficiency decrease.

In view of the intermediate complex formation during the oxidation process, another way of intensification was the use of individual catalysts that have the properties of the intracomplex compounds as well as related properties to the complex catalytic systems. Catalytic efficiency of cobalt chelates – cyclic complex compounds containing complexing agent (central metal ion – cobalt, which is part of the industrial catalyst) and organic ligands coordinated around it (Table 3, Fig. 2), was investigated [10].

The results indicate a common mechanism of action of cobalt oligomers and complex catalytic systems

in the oxidation of cyclohexane –using cobalt oligomers as individual catalysts allows to increase selectivity for the aim products of the process – cyclohexanone and cyclohexanol, and contributes to accumulation of ketone in the reaction medium.

Thus, it was found that oxygen- and nitrogen-containing compounds which are capable to form the complex compounds with the catalyst or ionic associations in the oxidation substrate, have influence on the regulation of the activity and selectivity of the catalytic cyclohexane oxidation. Therefore, it was planned to conduct researches on the effects of amino acids on the CHX oxidation. Initial studies were performed using glycine (GC) as an additive to cobalt naphthenate [11].

Glycine, as a component of the catalytic oxidation system, was chosen because of its accessibility, simple structure and relatively low cost.

As we can see (Table 4), in this case as well, the selectivity for the aim products increases and the ratio of target products decreases. To support this theory of the formation of complex compounds or ionic associations involving functional groups of additives with the molecule of the metal containing catalyst the spectral analyses of the catalytic solutions have been performed.

Table 3

Technological parameters of the catalytic cyclohexane oxidation in the presence of cobalt chelates
 $T = 413\text{--}418\text{ K}$; $P = 1.0\text{ MPa}$

Co-catalyst	t , min	$[\text{CoNph}] \cdot 10^4$, mol/l	X_{CHX} , %	S_{AP} , %	$\frac{\text{COL}}{\text{CON}}$
–	30	5.0	4.6	73.3	2.13
CoCh1	40	–	4.0	92.3	1.93
CoCh2	30	–	4.4	92.3	1.51

Notes: CoCh1 – cobalt pyrazole polychelate; CoCh2 – cobalt oligoperoxide complex, ligand: copolymer vinyl acetate (VA), 5-*tert*-butyl hydroperoxy)-5-methyl-1-hexen-3-in (VEP), butyl acrylate (BA), dimethylamine ethyl acrylate (DEA) (chelate Co, ligand: VA-VEP-BA-DEA (2:3:5:2))

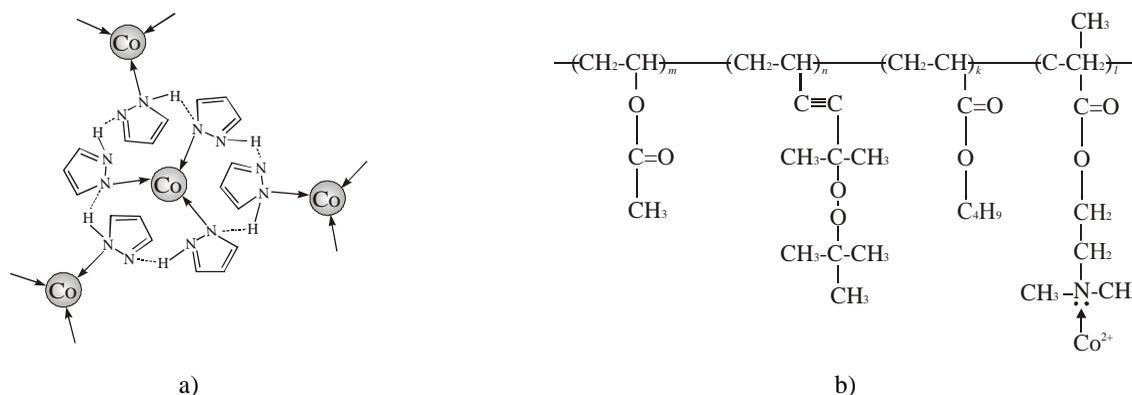


Fig. 2. Structural formulas of the cobalt chelates CoCh1 (a) and CoCh2 (b). Cobalt chelate (CoCh1): cobalt pyrazole polychelate. Cobalt chelate (CoCh2): cobalt oligoperoxide complex, ligand: copolymer vinyl acetate (VA), 5-*tert*-butyl hydroperoxy)-5-methyl-1-hexen-3-in (VEP), butyl acrylate (BA), dimethylamine ethyl acrylate (DEA) (chelateCo, ligand: VA-VEP-BA-DEA (2:3:5:2))

Table 4

Technological parameters of the catalytic cyclohexane oxidation in the presence of glycine
 $T = 413\text{ K}; P = 1.0\text{ MPa}$

Co-catalyst	t , min	$\frac{\text{CoNph}}{\text{co-cat.}}$	$[\text{CoNph}] \cdot 10^4$, mol/l	X_{CHX} , %	S_{AP} , %	$\frac{\text{COL}}{\text{CON}}$
–	30	–	5.0	4.6	73.3	2.13
GC	60	1/1	5.0	4.0	93.6	1.79

Note: CG – glycine

Table 5

IR-spectroscopic results of the prepared catalytic solutions

CoNph + CON		CoNph+ CON + GC		CoNph+ CON + GC*	
$\nu, \delta, \text{cm}^{-1}$	group	$\nu, \delta, \text{cm}^{-1}$	group	$\nu, \delta, \text{cm}^{-1}$	group
–	–	992	–C–O–	992 ⁵	–C–O–
–	–	–	–	920 ⁷	C–O–C
–	–	1040	C–OH	1040	–C–OH ³
1260 ¹	–CH ₃	1260 ²	–CH ₃	1260	–CH ₃
1296 ²	C–H	1296 ¹	C–H	1296	C–H
–	–	1664	–C=C–	1664	–C=C–
1640	C=O	1640 ³	C=O	1640	C=O
3300–2800	OH...H	3300–2800	OH...H	3300–2800 ⁴	OH...H
3700–3500	–	3700–3500	–OH	3700–3500	–OH
–	–	–	–	–	–

Notes: ¹ big, ² small, ³ increases, ⁴ decreases, ⁵ shifted, ⁶ appears(wide), ⁷ appeared.

*(CoNph+ CON + GC) solution after heating for $\tau = 10$ min at $T = 413\text{ K}$

The structure of metal complexes was confirmed by infrared spectroscopy. IR-spectroscopy of the analyzed catalytic systems colloidal solutions was carried out using spectrometer Specord M-80 with the cell thickness of 0.2 mm [12]. Analysis of the spectra was based on the tables of characteristic absorption frequencies [13, 14]. CON was used as a solvent, which in conditions of the oxidation process is presented in the reaction mixture. Also, it should be noted that under normal conditions cobalt naphthenate is better soluble into CON than into CHX and COL. The concentration of the VVM in the test solutions was $5.0 \cdot 10^{-5}$ mol/l. The total concentration of the catalyst solution was 5 wt %. The weight ratio between the components of the catalyst system was $[\text{CoNph}:\text{Additive}] = (1:1)$.

Comparing visible IR-spectrum of prepared catalytic solutions with the spectrum of CoNph solution, we see some significant changes in the absorption bands at certain frequencies (Table 5, Fig. 3).

There are two wide peaks within 3700–3500 and 3300–2800 cm^{-1} in the samples (CON + CoNph) and (CON + CoNph + GC) corresponding to the OH-groups in complexes with hydrogen bond. In the sample (CON + CoNph + GC) there is a large peak at 1296 cm^{-1} and a small peak at 1260 cm^{-1} , when in the sample (CON + CoNph) at 1296 cm^{-1} it is small and at 1260 cm^{-1} – large.

The peak at 1296 cm^{-1} corresponds to absorption of C–H in alkanes and has increased due to CH₂ presence in

the amino acid. Intensity of absorption in the sample (CON + CoNph + GC) has increased at 1640 cm^{-1} compared to (CON + CoNph), which corresponds to the C=O-group in amino acids. The peak at 1664 cm^{-1} , which corresponds to –C=C– in (CON + CoNph+ GC) increased as a result of possible interactions.

After heating of the sample (CON + CoNph+ GC), a peak appears at 920 cm^{-1} , corresponding to the C–O–C bonds – probably an interaction between the components of the catalytic solution took place. Maximum of the absorption (at 992 cm^{-1}) has been shifted toward longer wavelengths, which corresponds to C–O. After heating most of the hydrogen bonds have been destroyed – there are smaller peaks at 3400–3000 cm^{-1} compared with samples (CON + CoNph) and (CON + CoNph + GC) without heating. After heating intensity of all the peaks have increased, especially the absorption peak at 1040 cm^{-1} , corresponding to –C–OH group of atoms, that is the group the interaction took place by.

The research results of IR-spectroscopy allows us to make the conclusion that interaction with complex formation occurred involving C–OH groups of the additives and reaction products. It is also clear that heating of the sample (CON + CoNph+ GC) contributes to the destruction of hydrogen bonds presented in (CON + CoNph) and (CON + CoNph+ GC).

The results of spectral studies allow to offer the following structural formula of the catalytic complex (Fig. 4).

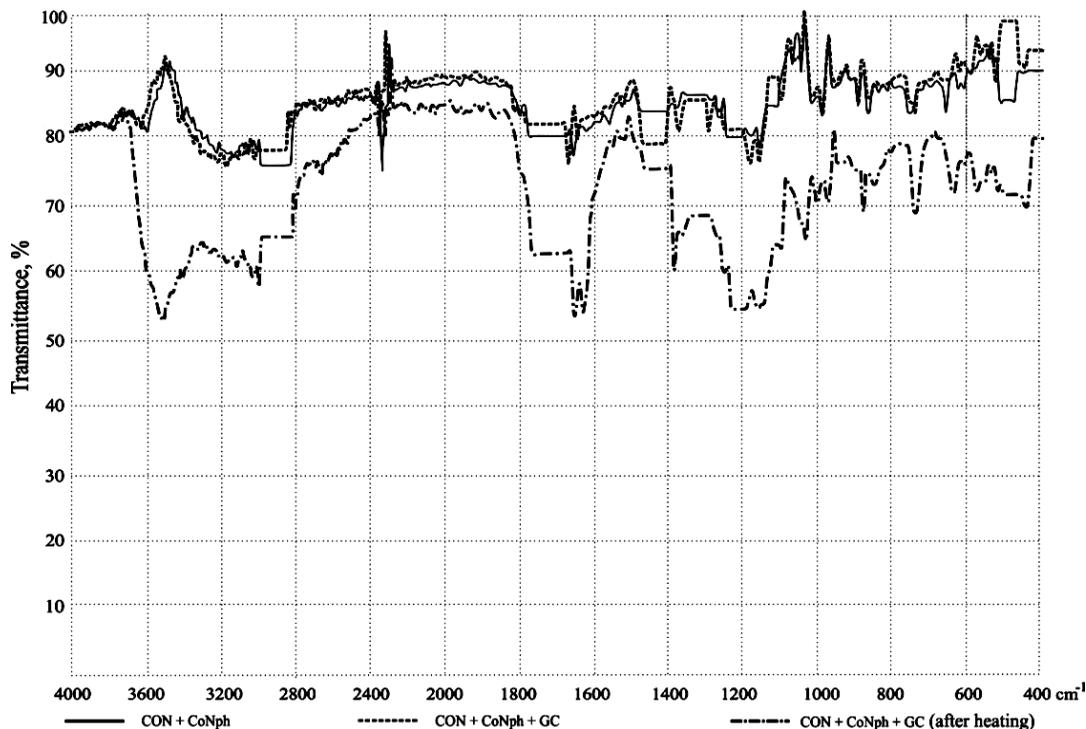


Fig. 3. The infrared spectrography results of the prepared catalytic solutions

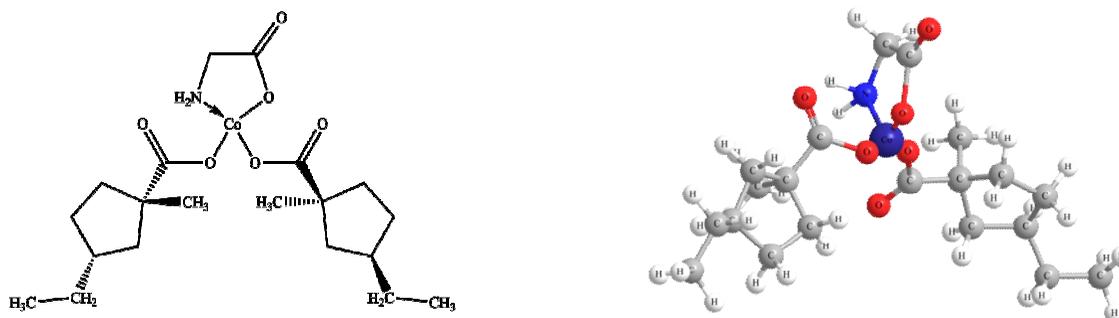


Fig. 4. Expected catalytic complex of cobalt naphthenate with glycine

4. Conclusions

The experimental results indicate the right direction of the scientific search for new methods for intensifying the liquid-phase oxidation of cyclohexane. Development and research of new individual catalysts with properties of intracomplex compounds are promising and require careful study and search for optimal catalyst. At the same time, further studies of single-component catalysts will expand the current understanding of the impact of the structure of organic compounds in cyclohexane oxidation.

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Received: March 16, 2017 / Revised: March 28, 2017 /
Accepted: June 02, 2017

ІНТЕНСИФІКАЦІЯ КАТАЛІТИЧНОГО ОКИСНЕННЯ ЦИКЛОГЕКСАНУ

Анотація. Розглянуто методи інтенсифікації процесу рідиннофазного окиснення циклогексану в присутності складних каталітичних систем, каталітичних розчинів та індивідуальних каталізаторів. Визначено кількісний та якісний вплив бінарних каталітичних систем, до складу яких входить нафтенат кобальту та органічні модифікатори різної природи. Проведені дослідження підтверджують припущення про комплексоутворення за участю компонентів каталітичних розчинів у реакційному середовищі. Побудовано структурну формулу ймовірного проміжного каталітичного комплексу.

Ключові слова: циклогексан, окиснення, каталіз, каталітичні системи.