

# Effect of nitrogen- and oxygen-containing additives on the efficiency of the catalytic oxidation of cyclohexane

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**Abstract** – The research of influence of oxygen- and nitrogen- containing organic catalytic additives to the general parameters of the process of cyclohexane oxidation have been conducted. Investigated additives can change the composition of the products of oxidation and the ratio between them. The most effective additives was bis-2-cyanethyl ether and polyethylene glycol with a molecular weight of 400 g/mole. This effect is explained by research results of IR- spectra. With the use of modern computer technology built spatial model of intermediate active complex consisting of organic additives and cobalt naphthenate.

Key words – oxidation, cyclohexane, catalyst, additive, cyclohexanol, cyclohexanone, homogeneous, acid, peroxide, ether.

## I. Introduction

Much of the industrial chemical productions associated with the catalytic oxidation of hydrocarbons. Their profitability directly depends on the efficiency of the applied catalytic systems.

Homogeneous catalytic oxidation of cyclohexane (CyH) to cyclohexanone (CON) and cyclohexanol (COL) is widely used today. These products are used as raw materials for the synthesis of polyamide fibers – nylon and kapron [1-5, 12].

Existing catalytic system is low-effective, which makes it impossible to carry out oxidation of CyH at high conversion. This leads to significant energy loss associated with recirculation of unreacted raw materials [1]. Increasing of conversion of hydrocarbons leads to decrease of selectivity of the process due to the accumulation of by-products, primarily – acids and ethers. Increase values of selectivity and conversion and selectivity of the process at least  $0,5 \div 2\%$  (abs.) will significantly reduce expenditure coefficients for raw materials and energy [6]. Therefore creation of new effective catalytic systems for the process of homogeneous catalytic oxidation CyH is relevant [2, 7, 8].

It is known that the processes of oxidation of hydrocarbons passing with higher selectivity for not chain mechanism in the coordination sphere of homogeneous catalyst. Application of additives of different nature (donors and acceptors of electrons) to cobalt naphthenate (NC) leads to increase selectivity of process and change the ratio between products in the required direction, which determines the direction of their future use [9-11].

Therefore it makes sense to continue the study of binary catalytic systems consisting of NC and organic additives containing oxygen and nitrogen, and compounds based on polyglycols different structure and composition.

## II. Experimental

The process of oxidation of cyclohexane studied at pressure 1.0 MPa and temperature of 418K in the autoclave reactor bubbling type of stainless steel (Fig. 1). Oxidation was carried out by molecular oxygen, which bubbled under pressure through a liquid phase. Molar ratio between [NC] / [organic additive] was 1:1. The concentration of NC is equal to  $5,0 \cdot 10^{-4}$  mol / l.

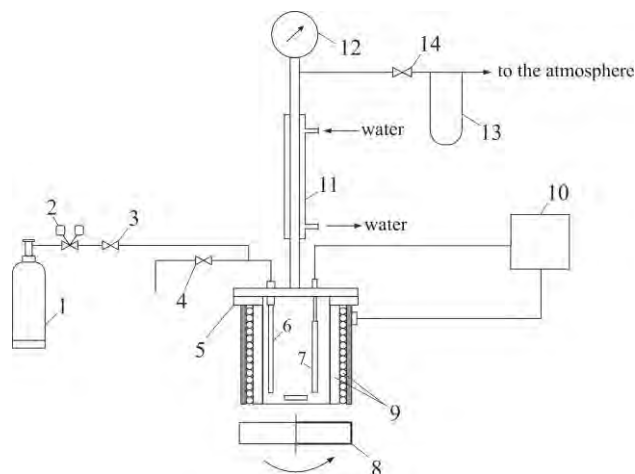


Fig. 1. Autoclave plant for the oxidation of cyclohexane.

1 – Oxygen cylinder; 2 – reducer; 3, 4, 14 – valves; 9 – electric heating reactor; 10 – control-measuring device; 5 – reactor for the oxidation of cyclohexane; 11 – inverse heat exchanger; 12 – pressure gauge; 13 – manometer for measuring oxygen consumption; 8 – magnetic stirrer; 6 – capillary for oxygen; 7 – thermocouple

At fixed intervals samples were taken from liquid phase for analysis. The samples was analyzed titrimetric and chromatographic methods [13]. The main products of liquid-phase oxidation of cyclohexane is peroxide compounds (most cyclohexil hydroperoxide (CHP)), cyclohexanol, cyclohexanone, acids (most of adipic acid (AA)) and ethers (including dicyclohexyadipic (DCHA)). The concentrations of CO and CO<sub>2</sub> are not measured because their contents do not exceed the error of analysis.

## III. Results and Discussion

Investigation of liquid-phase homogeneous catalytic oxidation of cyclohexane in the presence of binary catalytic systems was conducted. Binary catalytic systems consisting of NC and additives. As additives used a wide range of nitrogen and oxygen- containing compounds, and compounds based on polyglycols with varying molecular weight. For comparisons were taken the results are significantly different from similar in the presence of NC. Experimental results obtained in the presence of such additives: tetraethylammonium iodide (TEAI), cetyl thremethyl ammonium bromide (CMAB), polyethylene glycol with a molecular weight  $M = 400$  g/mol (PEG400), polyethyleneglycol succinate with a molecular weight  $M = 1000$  g/mol and  $M = 4000$  g/mol (PEGS1000 and PEGS4000 respectively), bis-2-cyanethyl ether (CEE), polyethyleneglycol adipic with a molecular weight

M = 4000 g/mol (PEGA4000), tetrabenzoate pentaerythrit (TBPE) and tetrabutylammonium bromide (TBAB) (Fig 2-9).

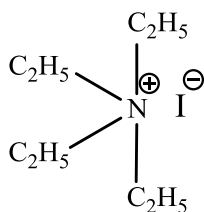


Fig. 2. Structural formula of tetraethylammonium iodide

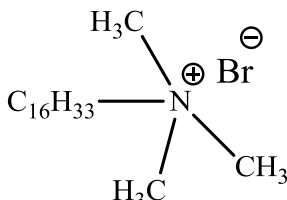


Fig. 3. Structural formula of cetyl threemethyl ammonium bromide

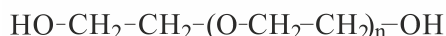


Fig. 4. Structural formula of polyethylene glycol

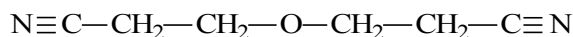


Fig. 5. Structural formula of bis-2-cyanethyl ether

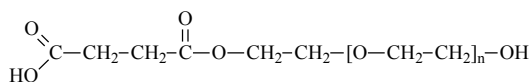


Fig. 6. Structural formula of polyethyleneglycol succinate.

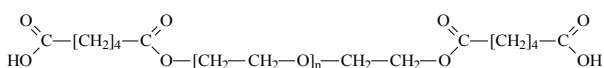


Fig. 7. Structural formula of polyethyleneglycol adipic

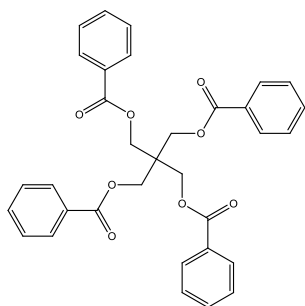


Fig. 8. Structural formula of tetrabenzoate pentaerythrit

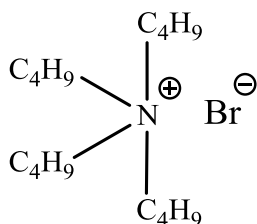


Fig. 9. Structural formula of tetrabutylammonium bromide

During the liquid-phase catalytic oxidation of hydrocarbons the composition and properties of the reaction environment significantly changing due to the accumulation of intermediate compounds. They are able to further transformation and interaction with the catalyst, affecting its activity. Therefore it is necessary to investigate the influence of additives on the selectivity for specific products at low conversion of raw material ( $K = 1 \div 2\%$ ), and values close to industrial ( $C \approx 4\%$ ). It helps to analyze the dynamics of change the basic parameters of the oxidation process of and consider the influence of intermediate products of oxidation on the activity of the catalytic system.

Influence on the process of oxidation of investigated additives varies depending to their nature. At the initial stages of oxidation of cyclohexane all nitrogen-containing additives (CMAB, CEE, TEAI and TBAB) and some oxygen (TBPE and PEGA4000) led to slower reactions of deep oxidation and formation of acids in solution. Selectivity of acid did not exceed  $S_{AA} \leq 7,6\%$ , while in the presence of individual NC and binary catalytic systems based on polyglycols (PEG400, PEGS4000 and PEGS1000)  $S_{AA} = 12 \div 16\%$ . At the same time, all the investigated additives changed the ratio between COL/CON towards CON accumulation compared to individual NC. Note that the CEE and PEGS1000 facilitated the rise of peroxide compounds ( $S_{CHP} = 20 \div 28\%$ ) and CMAB and PEGS4000 to decrease it ( $S_{CHP} = 2 \div 6\%$ ) (Table 1).

TABLE 1

SELECTIVITY OF CYCLOHEXANE OXIDATION AT CONVERSION OF RAW MATERIALS  $K = 1 \div 2\%$ .  $C(\text{NC}) = 5,0 \cdot 10^{-4}$  MOL/L. MOLAR RATIO BETWEEN  $[\text{NC}] / [\text{ADDITIVE}] = 1:1$

Catalytic systems	$S_{AA}, \%$	$S_{DCHA}, \%$	$S_{CHP}, \%$	$S_{COL}, \%$	$S_{CON}, \%$
NC	12,5	18,5	11,6	40,7	16,7
NC+CMAB	7,6	5,9	33,1	38,3	15,1
NC+CEE	7,2	28,1	11,8	33,3	19,5
NC+TEAI	2,2	6,9	47,5	24,6	18,8
NC+TBAB	7,5	18,7	35,0	25,4	13,4
NC+TBPE	5,1	16,6	41,8	22,7	13,9
NC+PEGA4000	5,5	14,6	50,4	19,8	9,7
NC+PEGS4000	16,1	2,3	5,4	49,8	17,5
NC+PEG400	13,4	7,7	8,8	43,0	27,0
NC+PEGS1000	12,1	20,5	0,0	44,6	22,8

$S_{AA}$  – selectivity of acids, %;  $S_{CHP}$  – selectivity of peroxide compounds, %;  $S_{DCHA}$  – selectivity of ethers, %;  $S_{COL}$  and  $S_{CON}$  – selectivity of cyclohexanol and cyclohexanone respectively, %.

Selectivity of complex ethers in the mixture varied in a wide range of values depending on the nature of the additive. In the presence of oxygen additive PEGS1000 formation of ethers in the mixture not observed, and the application of PEGA4000 and TEAI, the value of selectivity for esters was 5 times higher compared with individual NC. This suggests that the presence of organic additives in the reaction mixture, due to the peculiarities of their structure and chemical properties has an influence on the stage of formation of radical chains and the speed of the individual stages of oxidation.

At higher values of conversion of raw material situation has changed. All investigated organic additives except CEE and PEG400 led to a reduction selectivity for acids, along with the observed accumulation esters in solution. For example: CMAB additive reduced the selectivity of acid to 8.9%, while the selectivity of esters increased to 29.1%. Selectivity for peroxide compounds significantly increased only in the presence of TBAB, TBPE, PEGA4000 and PEGS1000 and is 12.7%, 14.7%, 10.5% and 12.1%, respectively, that in  $2 \div 3$  times higher compared to NC (Table 2).

TABLE 2

SELECTIVITY OF CYCLOHEXANE OXIDATION AT CONVERSION OF RAW MATERIALS  $K \approx 4\%$ .  $C(\text{NC})=5,0 \cdot 10^{-4}$  MOL/L. MOLAR RATIO BETWEEN  $[\text{NC}] / [\text{ADDITIVE}] = 1:1$

Catalytic systems	$S_{\text{AA}}, \%$	$S_{\text{DCHA}}, \%$	$S_{\text{CHP}}, \%$	$S_{\text{COL}}, \%$	$S_{\text{CON}}, \%$
NC	15,7	5,1	15,9	42,9	20,3
NC+CMAB	8,9	5,8	29,1	38,6	17,6
NC+CEE	18,8	6,8	7,5	41,6	25,3
NC+TEAI	5,7	8,9	29,6	36,3	19,5
NC+TBAB	10,6	12,7	25,5	36,6	14,6
NC+TBPE	9,1	14,7	29,8	30,2	16,2
NC+PEGA4000	7,6	10,5	48,3	22,6	11,1
NC+PEGS4000	6,5	6,0	21,2	36,3	30,1
NC+PEG400	17,8	4,3	6,8	34,2	36,8
NC+PEGS1000	13,0	12,1	12,1	36,2	26,6

It is interesting that the binary catalytic systems based on NC and additives CEE, PEGS4000 and PEG400 accelerate the reaction of formation the primary products of oxidation, such as peroxide compounds and mixtures of COL and CON. Their presence made the total selectivity of primary oxidation products 73.7%, 72.4% and 75.3% respectively (calculated as  $S_{\Sigma} = S_{\text{CHP}} + S_{\text{COL}} + S_{\text{CON}}$  in the conversion of raw materials close to 4%). It is important for industrial processes when on the certain stages deep oxidation products are undesirable.

Based on the above data, the most effective were binary catalytic systems containing organic additives such as CEE, PEGS4000 and PEG400. Therefore, they were chosen for the following studies.

Through analysis of experimental data over the range achieved conversion of raw materials could monitor the dynamic process of the passage of time and accumulation relevant trends of certain products in the early stages and during the advanced oxidation. The total selectivity  $S_{\Sigma}$  of COL, CON and CHP throughout the oxidation time is within  $70 \div 85\%$  (mol) in the application of additives CEE and PEG400, which is higher by  $10 \div 15\%$  (abs.) compared with similar data obtained in the presence of pure NC (Fig. 10). In this case, the curves for these catalytic systems have maxima at conversions within the limits of  $0,5 \div 1$ .

A similar situation is observed with the dependence of accumulation ethers in the reaction mixture from the conversion of raw materials in the presence of additives CEE and PEG400 (Fig. 11).

It is noteworthy that in the presence of oxygen additive PEGS4000 observed significant accumulation of primary

oxidation products in the conversion of less than 3%, and at higher values curve of accumulation mixtures COL, CON and CHP was similar to that obtained without the use of additives to the catalyst (Fig. 10).

It is interesting that the binary catalytic systems with additives CEE and PEG400 with high selectivity for the primary products of oxidation also allowed to receive higher values of selectivity for acids compared with pure NC (Fig. 12). It is likely that these catalytic systems accelerate the oxidation reaction of esters with subsequent formation of acids.

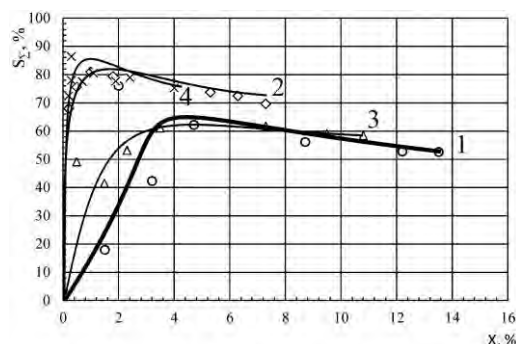


Fig. 10. The curve of the total selectivity of primary oxidation products for all values of the conversion of raw materials. 1- NC; 2- NC+CEE; 3- NC+PEGS4000; 4- NC+PEG400

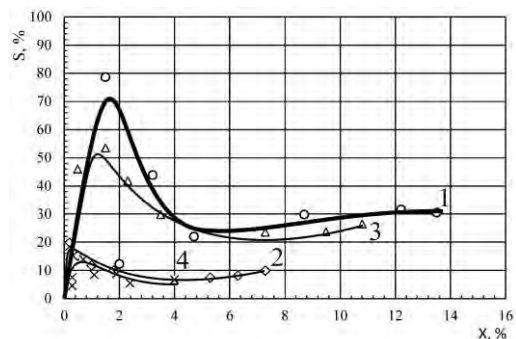


Fig. 11. The curve of the selectivity of ethers for all values of the conversion of raw materials. 1- NC; 2- NC+CEE; 3- NC+PEGS4000; 4- NC+PEG400

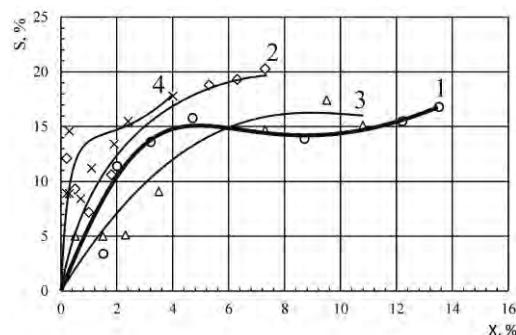


Fig. 12. The curve of the selectivity of acids for all values of the conversion of raw materials. 1- NC; 2- NC+CEE; 3- NC+PEGS4000; 4- NC+PEG400

The difference between character influence of additives on the cyclohexane oxidation process at low and high values of the conversion of raw materials due to the fact that with prolonged oxidation in the reaction mixture

present oxygen-containing intermediate products also react with the catalytic system and affect its activity.

Catalytic influence of nitrogen-containing additives associated with the presence of these groups:  $-C\equiv N$ ,  $-COR$  that exhibit electrophilic properties. This leads to a shift of the electron cloud to their side, which can greatly affect the coordination of variable valence metal (cobalt) during the formation of the active complex [8].

Investigation of infrared absorption spectra of created model compounds to identify new chemical bonds and formation of complexes between CEE (as the most effective additive, given the highest selectivity for COL and CON) and NC were conducted. As the solvent used CON that is present in the reaction mixture in the process of oxidation, and there is better dissolve NC under normal conditions.

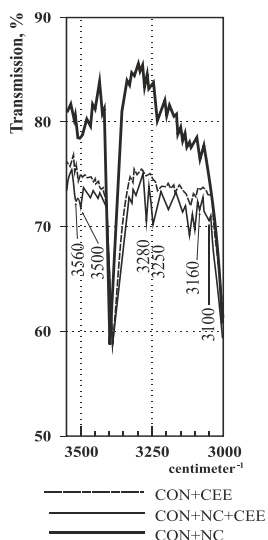


Fig. 13. Infrared absorption spectra of the investigated solutions.

Increasing the the intensity of absorption in  $\delta_{OH} = 3560 \div 3500 \text{ cm}^{-1}$  may indicate the formation of intermolecular hydrogen bonds with polar compounds, namely, the polar additive CEE. Boost absorption at frequencies  $\delta = 3250, 3160$  and  $3100 \text{ cm}^{-1}$  indicates the complexation involving  $-OH$  groups of naphthenic acids contained in NC, and  $-C\equiv N$  group comprising additive CEE [9].

Note that the above-mentioned absorption bands observed only in the model solution [CON + NC + CEE] and absent in the [NC + CON] and [CEE + CON], indicating that the interaction of NC and CEE involving CON.

## Conclusion

Based on the experimental data confirmed the effectiveness of nitrogen-containing compounds and polyglycols as additives in catalytic oxidation of cyclohexane.

Effect of catalytic activity of cobalt naphthenate under the influence of the studied additives grounded by re-

sults of research IR- absorption spectra created model solutions.

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