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CYCLOHEXANE OXIDATION IN THE PRESENCE OF VARIABLE VALENCY METALS CHELATES

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Abstract. Influence of individual catalysts – oligomeric chelate complexes of cobalt and copper in the cyclohexane oxidation process was investigated. The method of of metal-complex catalysts synthesis was shown. The influence of complex oligomers and their ligands on the parameters of the cyclohexane oxidation process was analyzed.

Keywords: cyclohexane, oxidation, catalysis, chelates, complex compounds.

1. Introduction

Using complicated catalytic systems based on compounds containing variable valency metal is the weel-known and effective method of intensification of the liquid phase cyclohexane (CYH) oxidation process [1]. Modern research is often aimed at search of efficient catalysts and the oxidation process conditions among metal-compounds or binary catalytic systems [metal salt–organic modifier] based on industrial catalysts [2-8]. Experimental data shows the increase of the process selectivity relative to the main products (cyclohexanol (COL) and cyclohexanone (CON)), as well as the possibility of regulating the ratio between main products (COL/CON) [2, 3, 6-8]. However, the obtained results do not satisfy industry requirements for safety or productivity of the reactive volume [2-6].

The common feature of all effective organic co-catalysts is the ability to be a member of ligand surrounding of the catalyst central atom – variable valency metal. That's why, in literature the positive effect of catalytic systems containing organic additives of different nature is linked with the formation of complexes or ionic associates between molecules of the catalyst and organic agent – intra- and intermolecular bonds coordination of cobalt electron-acceptor atom and co-catalyst functional groups [9]. But bicomponent catalytic system leads to the changes of ligand surrounding of catalyst central atom, so the unstable composition of the catalytic complex can decrease its efficiency.

Taking this fact into consideration, it was reasonable to investigate the influence of individual cyclohexane oxidation catalysts, which have innercomplex compounds properties and probably have related properties with aforesaid catalytic systems. For this purpose, the influence of oligomeric chelates (complexes containing central ion of metals cobalt and copper, which is the part of the industrial catalyst) and the organic ligands coordinated around it was researched.

2. Experimental

2.1. Synthesis of Catalysts

Carbon chain oligoperoxide (CH) (synthesis procedures are given in Table 1) was obtained *via* radical copolymerization of monomers mixture at 333 K in ethyl acetate using azo-*bis-iso*-butyronitrile (AIBN) as the initiator [10]. Vinyl acetate (VA) and butyl acrylate (BA) were purified by vacuum distillation and their characteristics correspond to those given in the literature [11]. Maleic anhydrides (MA) was purified by vacuum sublimation, its melting point after purification was 325 K (lit. 325.9 K) [12]. Monomer 2-(dimethylamino)ethyl methacrylate (99 %, ACROS) (DMAEM) was used without additional purification. The peroxide monomer 5-*tert*-butyl hydroperoxy)-5-methyl-1-hexen-3-in (VEP) $CH_2=CH–C≡C–C(CH_3)_2–O:O–C(CH_3)_3$ synthesized from vinylacetylenic alcohol $CH_2=CH–C≡C–C(CH_3)_2–OH$ and

tert-butyl hydroperoxide was purified by vacuum distillation and characterized by: density $d_4^{20} = 0.867$, refraction index $n_D^{20} = 1.4480$ and active oxygen content 8.79 % [13].

The synthesis of oligoperoxide metalcomplex (OMC) containing transition metal was based on CH as a ligand and carried out as follows: 10 wt % solution of CH_2 and 5 wt % solution of metal salt ($CoCl_2$ or $CuCl_2$), both in ethanol (methanol), were charged into a three-necked

flask equipped with a stirrer. Mixing was carried out for 0.5 h at 298 K.

Metal complexes were purified according to the following method:

1) Alcohol solution of metal complexes containing polymer with carboxylic groups was diluted by water after synthesis. Precipitate of metal complexes was washed by distilled water till negative reaction on metal ions in water and then was dried in vacuum.

Table 1

Receipts of oligoperoxide ligands synthesis

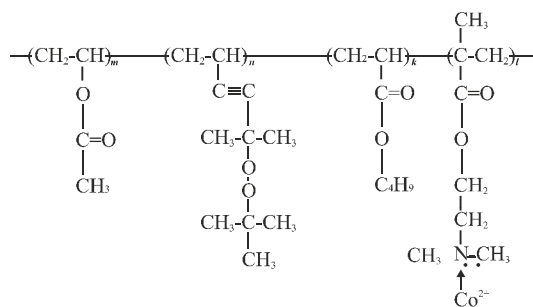| OMC ligand	Monomer mixture, mol %					[AIBN], mol/l	[Monomer], mol/l
	VA	VEP	BA	MA	DMAEM		
CH1	16.7	25.0	41.7	–	16.7	$5 \cdot 10^{-2}$	3.8
CH2	50.0	30.0	–	–	20.0	$5 \cdot 10^{-2}$	4.0
CH3	45.5	9.1	18.2	–	27.3	$5 \cdot 10^{-2}$	3.8
CH4	33.3	33.3	–	33.3	–	$5 \cdot 10^{-2}$	4.0
CH5	33.3	33.3	–	33.3	–	$5 \cdot 10^{-2}$	4.0
CH6	16.7	25.0	16.7	–	41.7	$5 \cdot 10^{-2}$	3.8
CH7	18.2	9.1	27.3	–	45.5	$5 \cdot 10^{-2}$	3.8
CopH1	25.0	16.7	41.7	–	16.7	$5 \cdot 10^{-2}$	3.8

Fig. 1. Cobalt oligoperoxide complex (CH1). Ligand: copolymer vinyl acetate (VA), 5-*tert*-butyl hydroperoxy)-5-methyl-1-hexen-3-in (VEP), butyl acrylate (BA), 2-(dimethylamino)ethyl methacrylate (99 %, ACROS) (DMAEM) (ligand: VA-VEP-BA-DMAEM (2:3:5:2)).
m = 10 %, n = 33 %, k = 38 %, l = 19 %, $[Co^{2+}]$ = 1.2 %, M = 3000

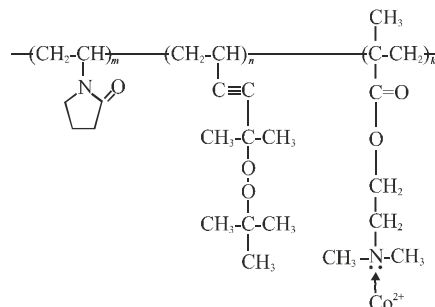**Fig. 2.** Cobalt oligoperoxide complex (CH2). OMC with ligand-based copolymer of N-vinylpyrrolidone (NVP), VEP, DMAEM.
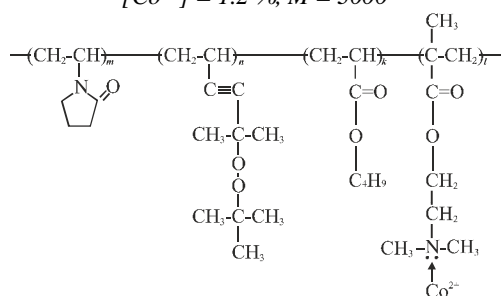*m = 48 %, n = 25 %, k = 27 %, $[Co^{2+}]$ = 9.5 %, M = 1800–2000*

Fig. 3. Cobalt oligoperoxide complex (CH3). OMC with ligand-based copolymer of NVP, VEP, BA, DMAEM.
m = 32 %, n = 14 %, k = 19 %, l = 35 %, $[Co^{2+}]$ = 1.6 %, M = 3000

Fig. 4. Cobalt oligoperoxide complex (CH4). OMC with ligand-based copolymer of VEP, VA, MA.
m = 22 %, n = 33 %, k = 43 %, l = 1 %, $[Co^{2+}]$ = 0.5 %, M = 2000

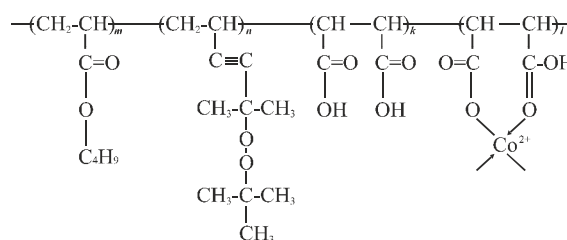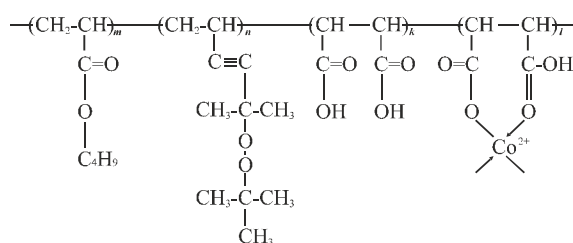**Fig. 5.** Cobalt oligoperoxide complex (CH5). OMC with ligand-based copolymer of VEP, VA, MA.
$m = 22$ %, $n = 33$ %, $k = 43$ %, $l = 1$ %, $[Co^{2+}] = 0.1$–0.15 %, $M = 2000$
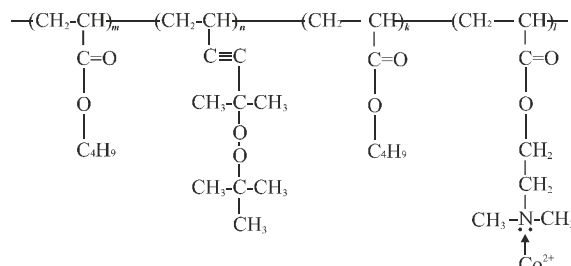

Fig. 6. Cobalt oligoperoxide complex (CH6). OMC with ligand-based copolymer of VA, VEP, BA, DMAEM (ligand: VA-VEP-BA-DMAEM (2:3:2:5)).
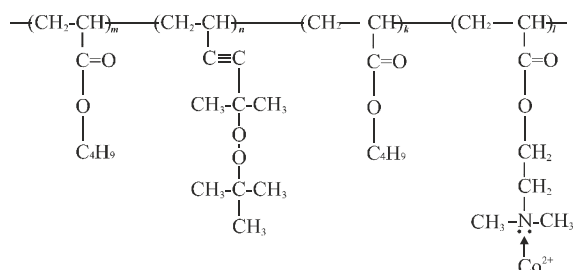$m = 9$ %, $n = 32$ %, $k = 15$ %, $l = 44$ %, $[Co^{2+}] = 1.7$ %, $M = 3000$

Fig. 7. Cobalt oligoperoxide complex (CH7). OMC with ligand-based copolymer of VA, VEP, BA, DMAEM (ligand: VA-VEP-BA-DMAEM (2:1:3:5)).
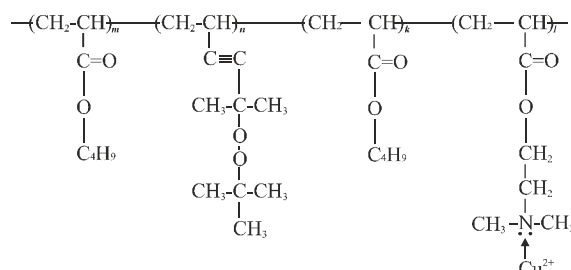$m = 11$ %, $n = 12$ %, $k = 25$ %, $l = 52$ %, $[Co^{2+}] = 2.1$ %, $M = 3000$

Fig. 8. Copper oligoperoxide complex (CopH1). OMC with ligand-based copolymer of VA, VEP, BA, DMAEM.
$m = 15$ %, $n = 25$ %, $k = 33$ %, $l = 25$ %, $[Cu^{2+}] = 1.5$ %, $M = 3000$

2) Metal complexes based on polymers with tertiary amino groups are insoluble in alcohol and they form precipitates during synthesis. Precipitates were washed by alcohol till negative reaction on metal ion in alcohol.

The content of metal cations in the oligoperoxide complex was determined using elemental analysis and controlled by atom-adsorption spectroscopy. Structure of obtained metal complexes was investigated by IR-, UV- and NMR spectroscopy (Figs. 1–8).

2.2. Experimental conditions

Cyclohexane oxidation in the presence of cobalt chelates at temperature of 418K and pressure of 1.0 MPa was studied. These conditions are similar to the industrial process of cyclohexane oxidation. The technical oxygen was used as the oxidant.

Research of cyclohexane oxidation at the pilot autoclave plant with electric heating jacket reactor was conducted. The stable temperature was maintained by the silicon oil in the reactor shell (Fig. 9).

The samples in the capacity with the isopropyl alcohol were chosen. It was done for sample homogenization and dissolution of adipic acid formed in large quantity at cyclohexane conversion increasing.

Products composition was determined by titrimetric and chromatographic analyses.
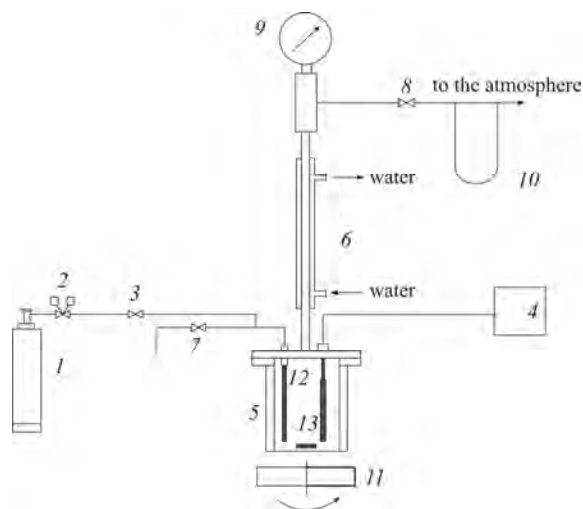

Fig. 9. Autoclave plant for cyclohexane oxidation: oxygen cylinder (1), reducer (2), valves (3, 7, 8), control equipment (4), reactor for cyclohexane oxidation (5), shell-and-tube heat exchanger (6), pressure gauge (9), differential pressure gauge for the oxygen consumption measuring (10), magnetic mixer (11), capillary for oxygen (12) and thermocouple (13)

3. Results and Discussion

Analyzing experimental data, first of all we were interested in the results obtained at cyclohexane conversion close to 2 and 4 %. Cyclohexane conversion value $X = 2$ % is the critical point to observe the practical effect of using the catalyst; $X = 4$ % is close to the parameters of the production process (Table 2).

Table 2

Cyclohexane oxidation parameters at conversion values $X = 2$ %, $X = 4$ %
($T = 148$ К, $P = 1.0$ MPa, $C_{cat.} = 5.0 \times 10^{-4}$ mol/l)

Catalyst	S(CHP[1]), %	S(A[2]), %	S(ET[3]),%	S(COL), %	S(CON), %	S(AP[4]), %	C(COL)/C(CON)
Conversion $X \sim 2$ %							
CoNph[*]	18.53	12.48	11.58	40.72	16.69	79.80	2.44
CH1	2.13	4.85	3.28	62.48	27.26	91.50	2.29
CH2	16.79	1.87	24.85	23.95	32.55	81.57	0.74
CH3	62.39	37.61	0.00	0.00	0.00	62.39	–
CH4	54.01	8.10	5.23	11.96	20.70	88.41	0.58
CH5	40.88	8.11	51.01	0.00	0.00	57.88	–
Conversion $X \sim 4$ %							
Catalyst	S(CHP), %	S(A), %	S(ET),%	S(COL), %	S(CON), %	S(AP), %	C(COL)/C(CON)
CoNph	5.11	18.58	22.08	36.91	17.32	73.30	2.13
CH1	1.54	4.58	4.68	53.60	35.60	92.30	1.51
CH2	–	–	–	–	–	–	–
CH3	10.43	20.33	1.01	42.04	26.19	78.99	1.61
CH4	5.68	29.43	8.22	27.90	28.77	65.09	0.97
CH5	–	–	–	–	–	–	–

Notes: [1]cyclohexyl hydroperoxide; [2]acids, [3]ethers, [4]aim (base) products, [*]cobalt naphthenate, industrial catalyst of cyclohexane oxidation

Table 3

Cyclohexane oxidation parameters at conversion values $X = 2$ %, $X = 4$ %
($T = 148$ К, $P = 1.0$ MPa, $C_{cat.} = 5.0 \times 10^{-4}$ mol/l)

Catalyst	S(CHP), %	S(A), %	S(ET),%	S(COL), %	S(CON), %	S(AP), %	C(COL)/C(CON)
Conversion $X \sim 2$ %							
CoNph	18.53	12.48	11.58	40.72	16.69	79.80	2.44
CH1	2.13	4.85	3.28	62.48	27.26	91.50	2.29
CH6	20.32	7.35	54.85	9.30	8.18	56.08	1.14
CH7	27.82	19.16	3.71	24.53	24.78	78.36	0.99
CopH1	42.30	9.37	48.34	0.00	0.00	58.41	–
Conversion $X \sim 4$ %							
Catalyst	S(CHP), %	S(A), %	S(ET),%	S(COL), %	S(CON), %	S(AP), %	C(COL)/C(CON)
CoNph	5.11	18.58	22.08	36.91	17.32	73.30	2.13
CH1	1.54	4.58	4.68	53.60	35.60	92.30	1.51
CH6	8.52	16.09	28.23	28.79	18.38	65.09	1.57
CH7	20.05	15.88	16.04	27.39	20.64	73.43	1.33
CopH1	–	–	–	–	–	–	–

Results of experimental research indicate that the use of metal complexes as catalysts for CYH oxidation process leads to CON accumulation of the reaction mixture, and accordingly reduces the ratio of COL/CON in the reaction medium (Table 2). At the initial stages of oxidation ($X = 2$ %) CH3 and CH5 oligomers don't lead to the formation of main products; CYH conversion values ($X = 4$ %) are not achieved by using catalysts CH2 and CH5. Using catalyst CH3 at $X = 4$ % allows to obtain main products – COL and CON, although their selectivity is much higher than using the industrial catalyst cobalt naphthenate (CoNph).

CH4 shifts the ratio COL/CON to the maximum, but the total selectivity relative to the main products is lower than using CoNph. As for the by-products of cyclohexane oxidation – it is an interesting ability of CH4 to contribute a significant accumulation of dicarboxylic acids (including prevailing adipic acid) in the reaction medium. The presence of ligand MA in the oligomer may contribute notable acids accumulation (Fig. 4). This catalyst property can be used for further industrial obtaining of adipic acid.

In contrast to other oligomers, the usage of which has drawbacks, the catalyst CH1 increases selectivity S_{AP} and shifts the ratio of main products towards the accumulation of ketone. At value $X = 4$ % the catalyst CH1 increases the selectivity relative to the main products to 92.3 % and shifts the ratio COL/CON to 1.51 (Table 2).

it is necessary to determine the dependence, observed in the experimental results, while changing the concentration of $[Co^{2+}]$ in oligomeric complexes. Under the conditions close to industrial ones, optimal values of the main products selectivity were achieved using CH1 and CH3 oligomers, where the content of $[Co^{2+}]$ was 1.2 % and 1.6 %, respectively (Table 2, Figs. 1 and 3). Reduction of cobalt content (oligomers CH4, CH5) and its excessive increase (CH2) does not allow to get the satisfactory parameters of CYH oxidation process. The optimum concentration of $[Co^{2+}]$ in the oligomers was found to be within 1.0–1.5 %.

It was reasonable to investigate cobalt oligomers, similar to CH1, with other ligand ratios (CH6, CH7) and the oligomer with the same composition and other central metal ion – copper (CopH1). The results were compared with the data, obtained using industrial catalyst CoNph and oligomer CH1 as the catalysts (Table 3).

The results show that the qualitative effect of using oligomer catalysts CH1, CH6 and CH7 remains, however, quantitative indexes become worse.

Using of copper oligomer does not allow to reach the industrial values of CYH conversion. CopH1 does not contribute to the formation of the main products (COL, CON) at the early stages of oxidation process (Table 3).

The experimental data confirms conclusion about the irrationality of using copper in a complex (oligomer CopH1) and increasing content of $[Co^{2+}]$ in the oligomers above 1.5% (CH6 and CH7 oligomers, containing $[Co^{2+}]$ 1.7 % and 2.1 %, respectively) (Table 3, Figs. 6-8).

4. Conclusions

The results show a common mechanism of action of cobalt oligomers and complicated catalytic systems in the cyclohexane oxidation process – the use of cobalt oligomers as the individual catalyst increases the selectivity of the main products (COL, CON) and contributes to ketone accumulation in the reaction medium. But not all OMC can be used as efficient industrial catalysts – among the studied catalysts only CH1 showed satisfactory results. Its use increases the selectivity of the main products to 25.9 rel. % and shifts the ratio of COL/CON to 29.9 rel %.

The experimental results showed the necessity of individual oligomers research as oxidation catalysts for liquid-phase CYH oxidation and perspective of further studies and search of optimum individual catalyst.

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**ОКИСНЕННЯ ЦИКЛОГЕКСАНУ
В ПРИСУТНОСТІ ХЕЛАТІВ МЕТАЛІВ ЗМІННОЇ
ВАЛЕНТНОСТІ**

Анотація. *Розглянуто рідиннофазне окиснення циклогексану у присутності індивідуальних каталізаторів – хелатних олігомерних комплексів кобальту та міді. Наведено методику синтезу металокомплексних каталізаторів. Проаналізовано вплив комплексоутворювача та лігандів олігомерів на показники процесу окиснення циклогексану.*

Ключові слова: *циклогексан, окиснення, каталіз, хелати, комплексні сполуки.*