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THE EFFECT OF CROWN ETHERS AND POLYGLYCOLS ON THE SUSTAINABILITY INDICATORS OF CYCLOHEXANE OXIDATION PROCESS

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Abstract. The crown ether or polyglycol additives to transition metal catalysts improve both the performance indicators, such as cyclohexane conversion, selectivity of target products, and the sustainability indicators of the oxidation process. It has been shown that the effect of the organic additives on the sustainability indicators is primarily due to a significant (up to 14.3 %) increase in the selectivity of target cyclohexane oxidation products.

Keywords: cyclohexane, catalytic oxidation, crown ethers, polyglycols, sustainability indicators.

1. Introduction

The liquid-phase oxidation of cyclohexane is a significant process of industrial organic chemistry. The target oxidation products (cyclohexanol and cyclohexanone) are used in synthetic fiber manufacture, such as nylon-6 and nylon-6,6[1]. The current industrial process of cyclohexane oxidation involves transition metal salts as homogeneous catalysts and air oxygen as an oxidant. Typically, the conversion of cyclohexane is quite low, ranging from 4 to 6 %. At higher cyclohexane conversion, the higher reactivity of cyclohexanol and cyclohexanone compared to cyclohexane leads to the formation of a significant number of by-products and sharply reduces the alcohol and ketone selectivity. This limitation results in the target product selectivity of approximately 70–85 %. Such indicators are relatively low from both performance and environmental perspectives.

One of the methods for improving the performance of the cyclohexane oxidation process is to enhance the selectivity of target products. To achieve this goal, the development of new catalysts is ongoing. Transition metal salts with oxygen-containing organic additives of various structures, such as cobalt naphthenate and crown ethers or polyglycols, are proposed as catalysts for cyclohexane oxidation[2, 3]. Such catalysts provide higher cyclohexane conversion while maintaining the selectivity of target products corresponding to the industrial process or ensure higher selectivity while maintaining industrial-level cyclohexane conversion. The polyglycol additives to cobalt naphthenate at cyclohexane conversions of 7.0–7.2 % provide industrial-level selectivity of target products, ranging from 78.3 to 80.6 %. An actual feature of the investigated organic additives is their effect on the alcohol-to-ketone ratio. In all cases, the polyglycol additives increase the selectivity of cyclohexanone compared to the selectivity observed in the catalysis of cyclohexane oxidation solely by cobalt naphthenate. The selectivity of cyclohexanol remains unchanged or slightly lower.

The effect of amino acids (glycine, arginine, and serine) on cyclohexane catalytic oxidation at a temperature of 413 K and a pressure of 1.0 MPa has been investigated[4]. Cobalt naphthenate with a concentration of 5×10^{-4} mol/L was used as the catalyst. The authors have established that catalysts containing amino acids increase the selectivity of target products at a cyclohexane conversion of approximately 4 %, corresponding to the industrial-level cyclohexane conversion. The increase in target product selectivity is primarily due to a significant increase in cyclohexanone selectivity. The amino acid additives to cobalt naphthenate catalyst increase the cyclohexanone selectivity to 50.8–59.1 %. The authors have shown that glycine or arginine-containing catalysts have the greatest effect on the selectivity of target products. A significant increase in the cyclohexanol selectivity from 21.9 % to 27.4 % is a feature of cobalt naphthenate and serine additive application as a catalyst. All the investigated catalysts reduce the foremost sharp selectivity of dicyclohexyl adipate. The catalysts containing arginine and serine as additives reduce the ester selectivity of 16.5 % by 2.6–5.0 times. When glycine is used as an additive, the reduction does not exceed 1 %.

Another method for improving the performance of the cyclohexane oxidation process is the use of heterogeneous catalysts[5–7].

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The $Al_{60}Cu_5Co_{35}$ intermetallic substances were used as heterogeneous catalysts of cyclohexane oxidation at a temperature of 413 K and a pressure of 2.0 MPa[5]. The authors established that the catalyst provides cyclohexane conversion of 6.4 % and the cyclohexanol and cyclohexanone selectivity is about 95 % for 8 h reaction time.

The heterogeneous catalyst for cyclohexane oxidation was obtained by applying it to silica sol-gel using the titanium method, which is subsequently used for gold deposition[6]. The catalyst obtained this way allows to achieve at a temperature of 423 K and a pressure of 3 MPa in 3 h a cyclohexane conversion of more than 8 %. The selectivity for oxidation products under such conditions is almost 92 %. A feature of the catalyst is a turnover frequency of up to 40,133 per hour.

It has been demonstrated that the heterogeneous catalysts provide industrial-level cyclohexane conversion, ranging from 4.6 to 5.3 %, in cyclohexane oxidation catalyzed by Ti-Zr-Co at a temperature of 423 K and a pressure of 2.0 MPa[8]. Moreover, under these optimal conditions, the selectivity of oxidation target products reaches nearly 95 %.

The nanocrystal Co_3O_4 catalyst (30–50 nm) of cyclohexane oxidation exhibits higher activity than Co_3O_4 deposited on a carrier or a homogeneous cobalt catalyst[9]. The authors established that the specified catalyst provides a cyclohexane conversion of 7.6 % and a selectivity of target products of 89.1 % for 6 h at a temperature of 393 K and a pressure of 1.0 MPa in the presence of tert-butyl hydroperoxide.

The heterogeneous catalysts of cyclohexane oxidation, such as cobalt, gold, silver, *etc.* require harsh reaction conditions with pressure ranging from 0.5 to 2 MPa and temperatures from 413 K to 448 K[1]. It has been demonstrated that the heterogeneous catalysts containing gold deposited on carriers like ZSM-5, MCM-41, and SBA-15 achieve hydrocarbon conversion of 10–19 %, with target products selectivity ranging from 80 to 95 %.

In addition to using molecular oxygen as an oxidizing agent, the possibility of employing peroxide compounds as oxidants in cyclohexane oxidation is investigated[10, 11]. Catalysts for such a process typically result in significantly higher hydrocarbon conversion while maintaining a high selectivity of target products. The homogeneous catalysts, such as triazolylidene copper (I) complexes, provide the formation of only cyclohexanone and cyclohexanol in various ratios without by-products with a hydrocarbon conversion of almost 40 % by cyclohexane oxidation with hydrogen peroxide in an acetonitrile solution[12].

Carriers such as SiL, NaYL, and MCM-41L were used to prepare heterogeneous catalysts for the cyclohexane and cyclohexene oxidation with hydrogen peroxide[7]. The carriers SiL, NaYL, and MCM-41L were obtained in two steps. The first step was the reaction between 3-glycidoxypropyltrimethoxysilane and (2-hydroxybenzyl)-N-(pyridin-2-yl-methyl) amine in methanol. The second step was the suspending of the inorganic matrix SiO_2, NaY, MCM-41 in this solution. The heterogeneous catalysts obtained by iron (III) precipitation were characterized by elemental analyses such as HR-CS AAS, solid-state MAS NMR (29Si, 13C), IR, UV-vis, TGA, Mossbauer, and textural analyses. The authors established that hydroperoxides are the main oxidation products. The homogeneous iron compounds are more effective in cyclohexane oxidation, whereas the above-mentioned heterogeneous catalysts are more effective in cyclohexene oxidation. The significant drawback of this approach is using peroxide compounds as oxidants along with a solvent, which requires the regeneration of the latter.

The heterogeneous Pt-oxide catalysts with *tert*-butyl hydroperoxide as the oxidant provide mild process conditions by cyclohexane oxidation to cyclohexanol and cyclohexanone at atmospheric pressure and a temperature of 70 °C[13]. The authors have demonstrated that all the employed carriers (Al_2O_3, ZrO_2, TiO_2) exhibit catalytic activity in oxidation but they provide cyclohexane conversion under 15 %. When Pt-oxide catalysts are applied, the hydrocarbon conversion increases to 20–30 %, and Pt content increases from 1 to 5 %. The selectivity of cyclohexanol and cyclohexanone also increases by approximately 2–4 and 1.5–5 times, respectively. Simultaneously acetonitrile as a solvent notably reduces the selectivity of target products.

The use of specific catalysts, oxidants, and solvents in the industrial process of cyclohexane oxidation requires significant industrial changes. It is also evident that increased cyclohexane conversion and target product selectivity, along with improved process performance, will have a significant effect on the cyclohexane oxidation environment, primarily by reducing by-products and waste, but also by reducing the amount of cyclohexane that needs to be recycled[14].

Improving environmental efficiency is currently extremely important for various organic synthesis processes[15, 16].

To assess the environmental effect of chemical production, sustainability indicators are used to quantify aspects of chemical process performance[17–19].

This study is aimed to determine the sustainability indicators of the cyclohexane oxidation catalyzed by transition metal salts and oxygen-containing organic additives and to evaluate the effect of these additives on the environmental effectiveness of the process.

2. Experimental

2.1. Materials

Cyclohexane (reagent grade) was used as the raw material, and molecular oxygen (technical grade) was used as the oxidant. Cobalt naphthenate (CoN) and chromium ethyl hexanoate (CrEH) were used as catalysts. Crown ethers 15-crown-5 (15CR5), 18-crown-6 (18CR6), dibenzo-18-crown-6 (DB18CR6), and diaza-18-crown-6 (DA18CR6), as well as polyglycols polyethylene glycol (PEG), polypropylene glycol with an average molecular weight of 425 (PPG425), polypropylene glycol with an average molecular weight of 1025 (PPG1025), and Tween-80 (all from Merck) were used as the organic additives (OA) to the catalyst.

2.2. Methods

The cyclohexane oxidation was carried out in a steel bubble-type reactor equipped with a jacket for temperature maintenance and a reflux condenser for cyclohexane condensation (Fig. 1). The reaction mixture was stirred with oxygen bubbling and a magnetic stirrer. The cyclohexane oxidation was carried out at a pressure of 1.0 MPa within a temperature range from 403 to 423 K. The concentration of transition metal salts ranged from $(2.5–10)\cdot10^{-4}$ mol/L, and the molar ratio of the salt to organic additive was varied within the range of (1–10): 1.

The peroxide content was determined by iodometric titration in terms of cyclohexyl hydroperoxide (P). The acid content was determined by acid-base titration with adipic acid (Ac), and the ester content was determined by back titration with dicyclohexyl adipate (E). The content of cyclohexanol (A) and cyclohexanone (K) was determined by gas-liquid chromatography using a thermal conductivity detector. Helium was used as the carrier gas at a flow rate of 3 L/min, and the sample volume was 4 μL. The evaporator, column thermostat, and detector temperatures were 453 K, 433 K, and 453 K, respectively. The metal column with a length of 2 m and diameter of 3 mm was filled with 10 % polyethylene glycol sebacate on Chromaton N-AW with a particle size of 60–100 mesh. Isopropyl alcohol (reagent grade) was used for sample homogenization.

The sustainability indicators presented by Heydari *et al.*[15] were used to characterize cyclohexane oxidation in terms of environmental efficiency. To calculate these indicators, the following assumptions were made: the yield of the target products, *ceteris paribus*, corresponds to their selectivity, since unreacted cyclohexane is recycled; the target products are cyclohexyl hydroperoxide, since it decomposes into alcohol and ketone at the subsequent stages of the process, as well as an ester that is hydrolyzed to cyclohexanol at the neutralization stage.

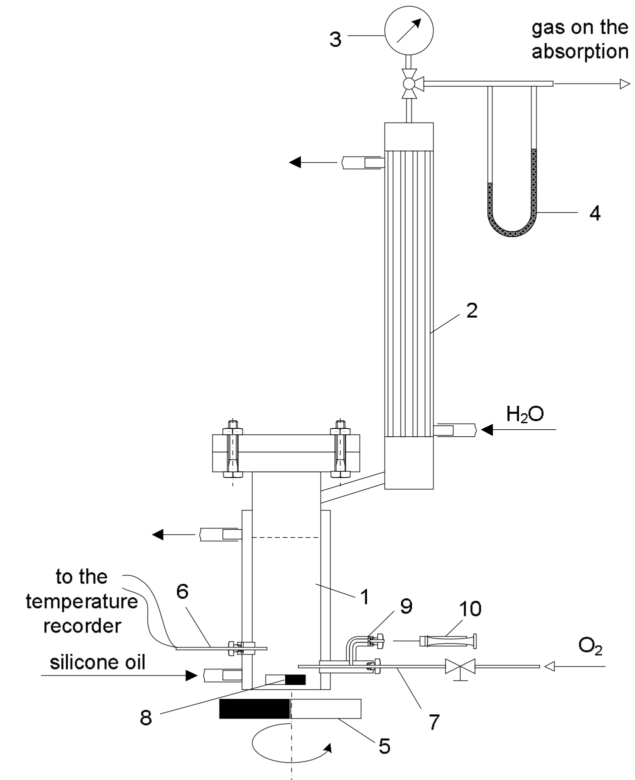


Fig. 1. Reactor scheme for cyclohexane oxidation: 1 – reactor; 2 – condenser; 3 – manometer; 4 – diffmanometer; 5 – magnetic field generator; 6 – temperature sensor; 7 – steel capillary; 8 – magnetic stirrer; 9 – fitting for supplying oxygen and sampling; 10 – syringe for sampling

However, since cyclohexane oxidation can potentially form adipic acid esters and other alcohols as reaction by-products, only one-third of the esters formed is considered to be the target product.

A high value of the cyclohexane oxidation E-factor indicates a significant amount of waste[15]. The value of the E-factor was calculated taking into account the unreacted cyclohexane recirculation according to Eq. (1):

$$E_f = \frac{m_w}{m_p}, \tag{1}$$

where m_w is the mass of the oxidation process waste, g; m_p is the mass of all formed target products of the reaction, g.

Since the atom economy does not consider the yield of the target product, the atom efficiency (AE) was calculated for the cyclohexane oxidation process using Eq. (2)[15]:

$$AE = \sum \frac{\nu_{i,p} M_{i,p}}{\nu_{ch,i} M_{ch} + \nu_{ox,i} M_{ox}} \cdot \eta_{i,p}, \tag{2}$$

where $M_{i,p}$ is the *i*-th product molar mass, g/mol; M_{ch} and M_{ox} is the molar mass of cyclohexane and oxygen, respectively, g/mol; $\nu_{i,p}$ is the stoichiometric coefficient of the *i*-th product; $\nu_{ch,i}$, $\nu_{ox,i}$ is the stoichiometric coefficients of cyclohexane and oxygen in the reaction of the *i*-th product formation; $\eta_{i,p}$ is the yield of the *i*-th product of the cyclohexane oxidation reaction, %.

Mass intensity (MI) and mass productivity (MP) were calculated by the following equations:

$$MI = \frac{\sum m_i}{m_p}, \tag{3}$$

$$MP = \frac{1}{MI} \cdot 100, \tag{4}$$

where Σm_i is the sum of the masses of reagents used in the process, g.

A higher mass intensity value indicates that the process is less environmentally friendly.

Reaction mass efficiency (RME) was determined by Eq. (5):

$$RME = \frac{1}{1+E_f}, \tag{5}$$

and the atom utilization (AU) in the cyclohexane oxidation process was calculated by Eq. (6):

$$AU = \frac{m_p}{\sum m_{p,i}} \tag{6}$$

where $\Sigma m_{p,i}$ is the sum of all product masses, g.

3. Results and Discussion

The results shown in Table 1 were used to assess the effect of organic additives on the sustainability indicators of cyclohexane oxidation.

It has been established that polyglycol additives have a more significant effect on sustainability indicators of cyclohexane oxidation compared to crown ethers (Table 2).

The catalyst containing crown ethers does not affect practically the E-factor. Only when dibenzo-18-crown-6 as an additive to cobalt naphthenate is used, the E-factor value is decreased by approximately 17 %. This result is attributed to a 2.3 % higher selectivity of target products formed using crown ether additives at the identical cyclohexane conversion (Table 1). Consequently, dibenzo-18-crown-6 also affects the reaction mass efficiency, as this sustainability metric is related to the E-factor. The effect of crown ethers on mass intensity and mass productivity is similar. All investigated crown ethers reduce the mass intensity by 1.06–1.19 times and, correspondingly, increase the mass productivity.

Table 1. The organic additives effect on cyclohexane oxidation.
Cobalt naphthenate concentration is $5.0 \cdot 10^{-4}$ mol/L, cobalt naphthenate: organic additive molar ratio is 5: 1, the temperature is 413 K, and the pressure is 1.0 MPa

Organic additive	Time, min	Conversion, %	K: A molar ratio	Selectivity, %				
				P	A	K	Ac	E
–	40	4.1	0.56	9.3	37.6	20.9	13.2	19.0
15CR5	40	4.7	0.65	10.6	36.3	23.5	14.6	15.1
18CR6	40	4.8	0.63	11.5	34.2	21.4	12.6	20.3
DA18CR6	45	4.4	0.65	7.3	37.0	24.0	14.0	17.6
DB18CR6	40	4.2	0.57	10.4	37.4	21.4	10.9	19.8
PEG	45	4.0	0.97	10.4	34.5	33.2	10.6	11.3
PPG425	50	4.5	0.90	8.0	39.9	35.8	12.0	4.2
PPG1025	50	4.8	0.88	6.9	38.1	33.6	12.8	8.6
Tween80	45	4.0	0.87	9.3	39.3	34.1	11.8	5.4

Table 2. The organic additives effect on the sustainability indicators of cyclohexane oxidation

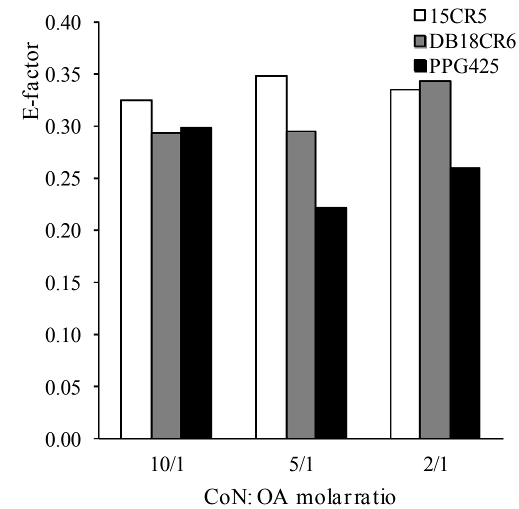
Organic additive	E_f	AE	MI	MP	RME	AU
–	0.35	66.4	3.44	29.1	0.74	53.1
15CR5	0.35	68.9	2.89	34.6	0.74	55.1
18CR6	0.34	65.6	2.93	34.1	0.75	52.9
DA18CR6	0.38	66.7	3.23	30.9	0.73	53.3
DB18CR6	0.29	67.5	3.23	31.0	0.77	55.5
PEG	0.23	74.5	3.09	32.4	0.81	64.3
PPG425	0.22	79.9	2.61	38.3	0.82	69.0
PPG1025	0.26	75.3	2.60	38.4	0.79	63.5
Tween80	0.23	79.2	2.98	33.6	0.81	68.3

All investigated polyglycol additives significantly affect the sustainability indicators of cyclohexane oxidation. The polyglycols reduce the E-factor by 1.32–1.56 times compared to the E-factor value observed in the cyclohexane oxidation catalyzed by cobalt naphthenate only. It indicates the possibility of using these organic additives not only from a technical point of view, but also from an environmental one. The polyglycol additives increase the atom efficiency, reaching almost 80 %. This significantly surpasses the atom efficiency obtained when using cobalt naphthenate as the catalyst. The reaction mass efficiency ranges from 0.79 to 0.82 when using cobalt naphthenate as the catalyst and polyglycol as additives. In catalysis using only cobalt naphthenate, this value is below 0.75. It is obvious that the effect of polyglycols on sustainability indicators is primarily due to a substantial increase in the selectivity of target products (Table 1).

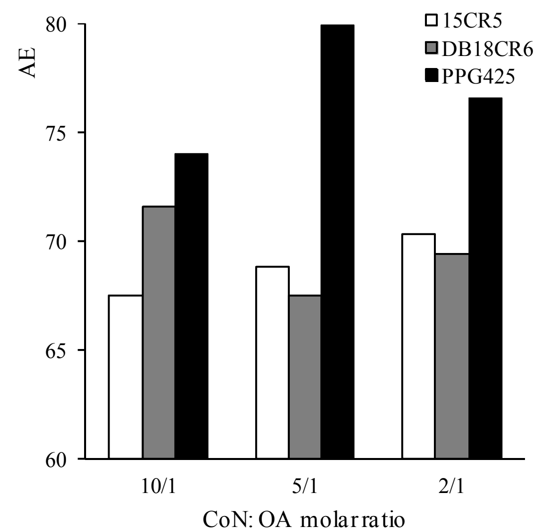
The change in reaction temperature affects the target product selectivity. At a temperature of 423 K, the selectivity remains the same when using organic additives compared to catalysis with cobalt naphthenate only. Both increasing and decreasing the reaction temperature almost neutralize the effect of organic additives on the sustainability indicators of the oxidation process. The dibenzo-18-crown-6 additive decreases the E-factor only by 5 % compared to catalysis with cobalt naphthenate only at a temperature of 403 K. When the reaction temperature increases to 423 K, the E-factor is the same as the E-factor observed in the catalysis with cobalt naphthenate only. In some cases, changing the reaction temperature leads to a decrease in sustainability indicators compared to the process catalyzed by cobalt naphthenate. For instance, the decrease in temperature to 403 K results in nearly a 2 % reduction in atom efficiency in the catalysis with cobalt naphthenate and 15-crown-5 or dibenzo-18-crown-6 additive.

The effect of cobalt naphthenate : organic additive molar ratio was investigated within the range of (1–10): 1 for 15-crown-5 and dibenzo-18-crown-6 and (2–10): 1 for polypropylene glycol (an average molecular mass was 425). It was found that when dibenzo-18-crown-6 and polypropylene glycol are used as additives, there is a range of molar ratio values at which the E-factor is minimal (Fig. 2, *a*). For instance, the lowest E-factor values are observed within the cobalt naphthenate: dibenzo-18-crown-6 molar ratio range (5–10): 1. When using polypropylene glycol (an average molecular mass 425), such a minimum is observed within the molar ratio range of (2–7): 1, and the calculated E-factor is in the range of 0.22–0.26. It is significantly lower than the E-factor value obtained in the catalysis with cobalt naphthenate only.

The extreme dependence of the sustainability indicators on the catalyst concentration is observed at the cobalt naphthenate: organic additive molar ratio of 5: 1 (Table 3).



a



b

Fig. 2. The effect of the cobalt naphthenate: organic additive molar ratio on the sustainability indicators of cyclohexane oxidation

Within the entire molar ratio range of the cobalt naphthenate: organic additive under study, the atom efficiency is higher than the atom efficiency (66.4 %) observed in the cyclohexane oxidation catalyzed only by cobalt naphthenate (Fig. 2, *b*). It was found that an increase in the content of 15-crown-5 and polypropylene glycol (average molecular mass 425) in the molar ratio of cobalt naphthenate: organic additive increases the atom efficiency. In particular, the atom efficiency reaches almost 80 % at a molar ratio of cobalt naphthenate: polypropylene glycol (average molecular weight 425) of 5:1 (Fig. 2, *b*).

It was determined that reducing the cobalt naphthenate concentration improves the sustainability indicators when using crown ether as an additive. For instance, the E-factor values reach 0.25 and 0.21 at a cobalt naphthenate concentration of $2.5 \cdot 10^{-4}$ mol/L in conjunction with 15-crown-5 or—dibenzo-18-crown-6, respectively. Such E-factor values are significantly lower than those observed in cyclohexane oxidation catalyzed by cobalt naphthenate only. The E-factor values are close to the results obtained when using polypropylene glycol (an average molecular mass 425) as an organic additive (Table 3). The decrease in cobalt naphthenate concentration provides atom efficiency and atom utilization values of 80.5 and 69.7 % when using dibenzo-18-crown-6. The use of crown ether surpasses the indicator values obtained when using propylene glycol (an average molecular mass 425) under optimal conditions. It should be noted that the catalyst concentration reduction improves the sustainability indicators despite a slight increase in the duration of cyclohexane oxidation required to achieve a 4–5 % cyclohexane conversion. The catalyst concentration in an industrial oxidation process is approximately $5 \cdot 10^{-5}$ mol/L, but the catalyst is already in the oxidized form. The reaction mixture contains intermediates, primarily hydroperoxide radicals and hydroperoxides. Therefore, it can be assumed that the decrease in the catalyst concentration and, accordingly, the process duration will not have a significant effect on the reaction rate.

Table 3. The effect of cobalt naphthenate concentration on sustainability indicators of cyclohexane oxidation. Cobalt naphthenate: organic additive molar ratio is 5: 1, the temperature is 413 K, and the pressure is 1.0 MPa

Organic additive	CoN concentration $C \cdot 10^4$, mol/L	Conversion, %	Time, min	Selectivity, %					E_f	*AE*	*MI*	*MP*	*RME*	*AU*
				P	A	K	Ac	E						
–	2.5	4.2	60	8.9	40.5	25.4	16.0	9.2	0.34	73.2	3.06	32.7	0.75	58.4
–	5.0	4.1	40	9.3	37.6	20.9	13.2	19.0	0.35	66.4	3.44	29.1	0.74	53.1
–	10.0	4.3	45	7.6	39.0	25.2	17.3	10.8	0.40	70.5	3.19	31.3	0.72	55.1
15CR5	2.5	4.2	50	10.8	44.3	26.0	13.3	5.6	0.25	79.0	2.86	35.0	0.80	65.7
15CR5	5.0	4.7	40	10.6	36.3	23.5	14.6	15.1	0.35	68.9	2.89	34.6	0.74	55.1
15CR5	10.0	4.7	45	6.2	44.0	27.9	14.4	7.5	0.30	75.8	2.68	37.4	0.77	62.0
DB18CR6	2.5	4.4	55	11.6	43.8	27.9	10.6	6.1	0.21	80.5	2.69	37.2	0.83	69.7
DB18CR6	5.0	4.2	40	10.4	37.4	21.4	10.9	19.8	0.29	67.5	3.23	31.0	0.77	55.5
DB18CR6	10.0	5.0	45	6.9	42.6	27.4	11.3	11.8	0.26	74.3	2.53	39.6	0.80	62.6
PPG425	2.0	4.4	55	9.1	39.0	32.4	12.6	7.0	0.25	77.3	2.74	36.5	0.80	65.5
PPG425	4.0	4.8	45	8.0	40.9	33.0	14.0	4.2	0.27	78.8	2.52	39.7	0.79	66.1
PPG425	5.0	4.5	50	8.0	39.9	35.8	12.0	4.2	0.22	79.9	2.61	38.3	0.82	69.0

Table 4. The organic additives effect on cyclohexane oxidation. Chromium ethyl hexanoate concentration is $5.0 \cdot 10^{-4}$ mol/L, chromium ethyl hexanoate: organic additive molar ratio is 5: 1, the temperature is 413 K, and pressure is 1.0 MPa

Organic additive	Time, min	Conversion, %	Selectivity, %					E_f	*AE*	*MI*	*MP*	*RME*	*AU*
			P	A	K	Ac	E						
–	35	4.6	3.3	14.9	53.2	15.5	13.2	0.36	65.3	3.00	33.4	0.73	55.0
15CR5	25	4.4	2.7	14.3	61.6	11.7	9.6	0.25	70.8	2.84	35.2	0.80	63.7
DB18CR6	20	4.3	3.5	11.5	55.4	14.4	15.1	0.35	64.0	3.23	31.0	0.74	54.7
PEG	30	4.7	3.2	19.4	59.1	13.4	4.8	0.26	74.6	2.59	38.5	0.80	66.0
PPG425	35	4.6	3.1	17.1	55.3	11.6	12.9	0.27	68.6	2.82	35.5	0.79	60.7

Chromium salts can be used as a catalyst for cyclohexane oxidation to achieve a higher selectivity of cyclohexanone. Crown ethers as organic additives to chromium ethyl hexanoate allow to increase the cyclohexanone: cyclohexanol molar ratio. When using polyglycol additives, the cyclohexanol: cyclohexanone molar ratio slightly decreases despite an increase in the ketone selectivity. This is due to a significant (15–30 %) increase in selectivity of alcohol. These organic additives reduce the E-factor by 3–44 % compared to the E-factor values obtained in cyclohexane oxidation catalyzed only with chromium ethyl hexanoate. The reaction mass efficiency value when using organic additives such as 15-crown-5, polyethylene glycol, and polypropylene glycol (an average molecular mass 425) ranges from 0.79 to 0.80 and significantly exceeds the reaction mass efficiency obtained when using only chromium ethyl hexanoate as a catalyst (Table 4).

The above additives to chromium ethyl hexanoate catalyst of cyclohexane oxidation increase atom efficiency and atom utilization values by 5–14 % and 10–20 %, respectively (Table 4).

Therefore, the studied organic additives should be considered as a factor in improving the performance parameters of cyclohexane oxidation and its environmental parameters, which is relevantly for modern chemical production.

4. Conclusions

It has been established that the use of crown ethers and polygylcols as an organic additives to the catalysts improves performance indicators, such as the selectivity of target products and cyclohexane conversion, as well as the sustainability indicators of cyclohexane liquid-phase oxidation.

It has been shown that polyglycol additives reduce the E-factor by 1.32–1.56 times compared to the value obtained during cyclohexane oxidation catalyzed with cobalt naphthenate only. It was found that a decrease in cobalt naphthenate concentration while maintaining the optimal cobalt naphthenate: organic additive molar ratio improves sustainability indicators, which is relevant for the industrial process of cyclohexane oxidation.

It has been established that the use of 15-crown-5, polyethylene glycol, or polypropylene glycol (an average molecular weight 425) in cyclohexane oxidation catalyzed by chromium ethyl hexanoate increases atom efficiency and atom utilization values by 14 and 10–20 %, respectively.

It has been shown that the sustainability indicators of cyclohexane liquid-phase oxidation catalyzed by transition metal salt and oxygen-contained organic additives are primarily due to an increase in the selectivity of target products.

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ВПЛИВ КРАУН-ЕТЕРІВ І ПОЛІГЛІКОЛІВ НА ПОКАЗНИКИ СТАЛОСТІ ПРОЦЕСУ ОКИСНЕННЯ ЦИКЛОГЕКСАНУ

Анотація. *Добавки краун-етеру або полігліколю до каталізаторів – солей перехідних металів покращують як показники ефективності, такі як конверсія циклогексану та селективність утворення цільових продуктів, так і показники сталості процесу окиснення. Показано, що вплив органічних добавок на показники сталості зумовлений, насамперед, значним (до 14,3 %) підвищенням селективності утворення цільових продуктів окиснення циклогексану.*

Ключові слова: *циклогексан, каталітичне окиснення, краун-етери, поліглiколі, показники сталості.*