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EFFECT OF CROWN ETHERS AND POLYGLYCOLS ON THE CATALYTIC OXIDATION OF CYCLOHEXANE AND ALKYLARENES

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The effect of crown ethers and polyglycols on the liquid-phase oxidation of cyclohexane and alkylaromatic hydrocarbons (toluene and p-xylene) with molecular oxygen catalyzed by transition metal salts has been investigated. It has been determined that crown ethers increase the reaction rate at both low and high conversion levels of cyclohexane and alkylaromatic hydrocarbons. The additives under study primarily affect the selectivity of the oxidation products. Crown ether and polyglycol additives to cobalt naphthenate increase the cyclohexanone to cyclohexanol molar ratio in cyclohexane oxidation. The crown ether additives to cobalt acetate increase the selectivity for alcohol in the initial stage of toluene and p-xylene oxidation. At higher alkylarene conversion, the additives enhance the selectivity for carboxylic acids. We assume that crown ethers and polyglycols form complexes with transition metal ions, changing the redox potential of the ions. This change in redox potential affects both the reaction rate and the selectivity of the oxidation products. The study concludes that crown ether and polyglycol additives influence the stages of the catalytic liquid-phase oxidation of hydrocarbons.

Keywords: oxidation, cyclohexane, toluene, p-xylene, cobalt salt, crown ether, polyglycol.

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Introduction

The oxidation processes are essential for industrial organic chemistry. Cyclohexanol, cyclohexanone, carboxylic and dicarboxylic acids, hydroperoxides, etc. are the main products of oxidation of cyclohexane, toluene, xylene, ethylbenzene and isopropylbenzene [1–3].

Polyamide fiber manufacture is the next stage of cyclohexane industrial oxidation catalyzed by cobalt salts. The achieved cyclohexane conversion is small (4–5%), and selectivity for the main reaction products (cyclohexanol and cyclohexanone) is up to 80% [4,5].

Designing the new catalyst enhances cyclohexane conversion and selectivity for the main reaction products. When homogeneous catalysts are used for cyclohexane oxidation, the hydrocarbon conversion can be increased by adding organic substances formed complexes with industrial catalysts (cobalt naphthenate) [6]. In addition, complex catalysts containing ligands of naphthene acids, such as porphyrins, are used [4].

In particular, complexes of cobalt and metalloporphyrins provide 15% cyclohexane conversion at a temperature of 155°C and pressure of 0.8 MPa in 3 hours. The total selectivity for cyclohexanol and cyclohexanone is up to 60.8%. Metalloporphyrins containing iron ions provide 13.8% cyclohexane conversion and 80.0% selectivity for the main product [4].

The use of heterogeneous catalysts is the alternative direction of cyclohexane oxidation with molecular oxygen. In particular, Co₃O₄ heterogeneous catalyst in the form of nanocrystals with dimensions of 30–50 nm, obtained from cobalt nitrate, provides cyclohexane conversion of 7.6% and selectivity for main products of 89.1% at a temperature of 393 K in 6 hours of reaction [7].

An alloy containing aluminum, cobalt, and copper ensures the cyclohexane conversion of 6.4% at an industrial temperature of 413 K and pressure of 2MPa [8]. However, achieving such a conversion rate



requires a process duration of 8 hours. Simultaneously, the selectivity for the main target products exceeds 95%.

Heterogeneous catalysts containing cobalt, zirconium, and titanium provide the selectivity for cyclohexanol and cyclohexanone over 90% without cyclohexyl hydroperoxide among the reaction products [9]. The cyclohexane conversion is up to 6.8% at a temperature of 413 K and pressure of 2MPa in 6 hours of reaction. However, heterogeneous catalysts provide a significantly lower reaction rate of cyclohexane oxidation due to their lower activity [8,9].

Homogeneous catalysts also allow changing cyclohexanol: cyclohexanone molar ratios of reaction products in cyclohexane oxidation. In particular, cyclohexanol is the main reaction product when cobalt naphthenate is used as a catalyst [4,5]. The additives to cobalt naphthenate change the reaction products' ratio. The cyclohexanone content slightly increases when hydrocarbon oxidation is catalyzed by cobalt naphthenate and crown ether additive, and the cyclohexanol content increases by catalysis of cobalt naphthenate and perfluoroxasulphoacid salt additive [6]. A heterogeneous catalyst also affects the cyclohexanol:cyclohexanone molar ratio [7–9].

The main products of alkylarene oxidation are correspondent carboxylic (benzoic, p-toluic) or dicarboxylic (terephthalic) acids, unlike cyclohexane oxidation, while reaction intermediates are the main products. Transition metal salts are used as catalysts of oxidation of alkylaromatic hydrocarbons. In particular, 0.0044 wt.% Co(acac)₂ as a catalyst provides a toluene conversion of 19% and benzoic acid yield of 80% in 4 hours of reaction [10].

Organic additives to catalysts of alkylarenes oxidation affect the ligand spheres of transition metal ions and improve technical indicators of the process. In particular, alkylarene conversion depends on the metalloporphyrin structure and concentration of a catalyst for p-xylene oxidation in the acetic acid medium [11]. In p-xylene oxidation catalyzed by tetrakis(p-chlorophenylporphinato)manganese chloride, hydrocarbon conversion is 44% and selectivity of p-toluic acid is 84% at a temperature of 180°C and pressure of 2MPa in 3.5 hours of reaction. This salt is the most active catalyst among other salts.

Among heterogeneous oxidation catalysts, Co and Mn polysiloxanes are more active than cobalt naphthenate [12]. This is associated with the high activity of heterogeneous catalysts due to the polysiloxane hydrophobic surface and the impact of the catalyst on the reaction involving peroxides.

Thus, additives affect the catalytic activity of transition metal ions or change the ligand spheres of

the catalyst, therefore they can enhance hydrocarbon conversion and selectivity for main oxidation products. The additives also can change the molar ratio of oxidation products. Crown ethers and polyglycols, because of their structure, are promising additives for liquid-phase oxidation catalysts. The research of cyclohexane [2] and aromatic hydrocarbons [13] oxidation indicates the effectiveness of crown ethers as organic additives for hydrocarbon oxidation catalysts. The study of the effect of polyglycols on hydrocarbon oxidation is promising because of the correlation between the properties and structure of crown ethers and polyglycols [14].

The research goal was an investigation of the effect of crown ethers and polyglycols on the catalytic liquid-phase oxidation of cyclohexane and alkylarenes.

Experimental

Cyclohexane, toluene, and p-xylene (all reagent grades) were used as reagents. Toluene and p-xylene were purified by treatment with concentrated sulfur acid to eliminate thiophene impurities. The processed alkylarene was sequentially washed with distilled water, 10% solution of sodium hydroxide, then again distilled water, and dried over anhydrous magnesium sulfate. The dried hydrocarbon was distilled.

Molecular oxygen (technical grade) was used as another reagent. Cobalt (II) naphthenate (industrial) and cobalt (II) acetate (reagent grade) were used as catalysts. 15-Crown-5 (15CR5), 18-crown-6 (18CR6), dibenzo-18-crown-6 (DBCR) and diaza-18-crown-6 (DACR), polyethylene glycol (PEG), polypropylene glycol (PPG425 and PPG1025), and Tween-80 (all Merck) were used as catalyst additives.

The hydrocarbon oxidation was carried out in a steel (toluene and cyclohexane) or glass (p-xylene) bubble-type reactor equipped with a jacket for temperature providing and a reverse refrigerator for the vapor hydrocarbon condensation (Fig. 1). The glass equipment has a similar design but without manometer. The reaction mixture was stirred by oxygen bubbling and with a magnetic stirrer. The conditions of the oxidation reaction are given in Table 1.

The molar ratio of catalyst to organic additive was chosen from the results of preliminary studies. The optimal molar ratio of catalyst to organic additive was 5:1 for the cyclohexane and toluene oxidation, whereas it was 1:2 for the p-xylene oxidation.

The content of peroxides was determined by iodometric titration. The content of acids was determined by titration, while the ester content was determined by back acid-base titration. The content of alcohols (cyclohexanol, benzyl alcohol, and p-tolyl alcohol), aldehydes (benzyl and p-tolyl aldehyde), and cyclohexanone was determined by gas-

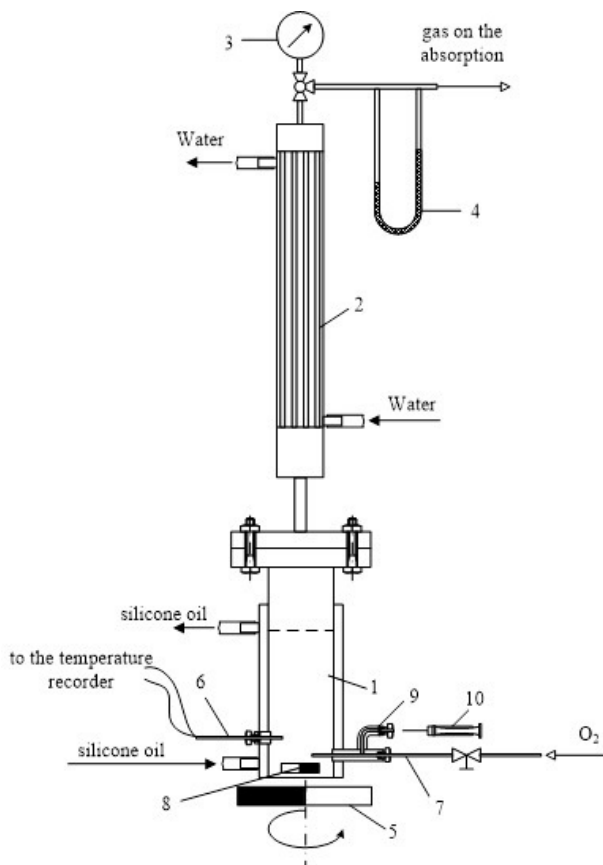


Fig. 1. Steel reactor for hydrocarbon oxidation: 1 – reactor; 2 – refrigerator; 3 – manometer; 4 – differential manometer; 5 – magnetic field generator; 6 – temperature sensor; 7 – steel capillary; 8 – magnetic stirrer; 9 – fitting for supplying oxygen and sampling; 10 – syringe for sampling

liquid chromatography. Chromatograph «VEB Chromatron» type GTO1.6 was used to determine the content of cyclohexane oxidation products, and chromatograph LKhM-80 was used to determine the content of alkylarene oxidation products. All chromatographs were equipped with a thermal conductivity detector. Isopropyl alcohol (reagent grade) was used for sample homogenization. The chromatographic analysis conditions are summarized in Table 2.

The oxidation reaction rate was calculated according to the following equation:

$$r = \frac{\Delta C}{\Delta \tau}, \quad (1)$$

where ΔC is the change of hydrocarbon concentration for a $\Delta \tau$ time interval, mol/L; $\Delta \tau$ is the time interval, s.

The selectivity for the *i*-substance (%) was calculated as the ratio of the *i*-substance molar concentration to the sum of the concentrations of hydrocarbon oxidation products:

$$S_i = \frac{C_i}{\frac{v_i}{v_{HC(i)}} \cdot \sum C_i} \cdot 100\% \quad (2)$$

The selectivity for main reaction products in cyclohexane oxidation was calculated according to the following equation:

$$S_p = S_{HP} + S_{OL} + S_{ON} + \frac{1}{3} S_E, \quad (3)$$

Table 1

Conditions of reaction of hydrocarbons oxidation

Hydrocarbon	Temperature, K	Pressure, MPa	Catalyst	Catalyst concentration, mol/L
cyclohexane	430–423	1.0	cobalt naphthenate	0.0005
toluene	413–438	0.3–0.8	cobalt acetate	0.001–0.008
p-xylene	383–403	0.1	cobalt acetate	0.001–0.008

Table 2

Conditions for chromatographic analysis of oxidation products of hydrocarbons. Sample volume is 2 μ L (toluene and p-xylene) or 4 μ L (cyclohexane)

Hydrocarbon	Column length and diameter, mm	Chromatographic phase	Carrier gas (He) flow rate, L/min	Temperature, K		
				evaporator	column thermostat	detector
cyclohexane	2000×3	10% polyethylene glycol sebacate on Chromaton N-AW (60–100 mesh)	2	453	433	453
Toluene and p-xylene	1000×3	10% polyethylene glycol sebacate on Celite 545 (60–100 mesh)	3	533	353	513

where S_p is the selectivity for main reaction products, %; S_{HP} is the selectivity for cyclohexyl peroxide, %; S_{OL} is the selectivity for cyclohexanol, %; S_{ON} is the selectivity for cyclohexanone, %; and S_E is the selectivity for esters, % (we assumed that 1/3 of the formed esters are hydrolyzed with the cyclohexanol formation at an acids neutralization and esters saponification stage).

Carboxylic acids were the main oxidation products of alkylaromatic hydrocarbons. The content of esters in the reaction mixture was not determined.

Results and discussion

The results of cyclohexane oxidation catalyzed by cobalt naphthenate (CoNaph₂) and crown ether or polyglycol additive show the change in reaction rate and composition of reaction products compared to oxidation catalysis solely by cobalt naphthenate. In particular, the additives of crown ether or polyglycols, with the exception of 15-crown-5 and 18-crown-6, increase the reaction rate by 1.52–2.81 times at the initial stage of the cyclohexane oxidation process (Fig. 2a). The reaction rate of cyclohexane oxidation catalyzed by cobalt naphthenate and 15CR5 and 18CR6 additives at hydrocarbon conversion of up to 1% is 19–23% less than the cyclohexane oxidation rate of reaction catalyzed solely by cobalt naphthenate. Simultaneously, crown-5 and 18-crown-6 additives decrease the reaction rate by 9–38% at a cyclohexane conversion of about 4% (Fig. 2a).

The crown ether or polyglycol additive to cobalt naphthenate also affects the selectivity for cyclohexyl peroxide (a primary molecular product) and the main products of the oxidation reaction. All investigated additives increase the selectivity for cyclohexyl peroxide at a cyclohexane conversion of up to 1%. In particular, the PPG425 additive enhances the cyclohexyl peroxide selectivity by 1.21 times, and the 15CR6 additive increases it by 1.82 times. The additives of 15-crown-5, 18-crown-6, and polyethylene glycol to the catalyst provide the higher selectivity for cyclohexyl peroxide, but the lower (15CR5, 18CR6) or slightly higher (PEG) reaction rate at the initial stage compared to cyclohexane oxidation solely by cobalt naphthenate. Additives having a different structure, in particular propylene glycol PPG425 and PPG 1025, Tween 80, macroheterocycle DBCR or nitrogen-containing DACR provide less selectivity for cyclohexyl peroxide compared to 15CR5, 18CR6, and PEG, but higher selectivity for cyclohexyl peroxide in cyclohexane oxidation solely by cobalt naphthenate at the initial reaction stage. We assume that the 15CR5, 18CR6, and PEG additives stabilize peroxides or radical ROO^{\bullet} at the initial stage of cyclohexane oxidation. Other additives providing lesser cyclohexyl peroxide selectivity

stabilize peroxides to a lesser extent and have the highest effect on the hydroperoxide radical transformation.

The 15CR5 and 18CR6 additives also provide a higher selectivity for cyclohexyl peroxide at a cyclohexane conversion of about 4%. Such a high content of cyclohexyl peroxide obviously causes a higher oxidation reaction rate (Fig. 2a,b). The values of the oxidation reaction rate at a cyclohexane conversion of about 4% correlate with lower or commensurate values of selectivity for cyclohexyl hydroperoxide when using other additives, as well as only cobalt naphthenate catalyst (Fig. 2a,b).

Peroxides decay involving metal ions of an oxidation catalyst. The formation of complexes between an organic additive and a metal ion changes the ion redox potential and increases the hydroperoxide decay rate and cyclohexane oxidation rate, accordingly. Therefore, the obtained results correlate well with the literature data [15].

All investigated additives also increase selectivity for main products at the initial stage of cyclohexane oxidation. Foremost, it is due to the increase of selectivity for cyclohexyl hydroperoxide (Fig. 2b,c). The most increase of main products' selectivity is conditioned in cyclohexane oxidation catalyzed by cobalt naphthenate and polyglycol additives (Fig. 2c). At high cyclohexane conversion, the polyglycol additives provide the selectivity for main products of 85.2–86.5% compared to the selectivity of 80.4% in hydrocarbon oxidation catalyzed solely by cobalt naphthenate.

The 15CR5 and 18CR6 additives to cobalt naphthenate increase the outcyclohexanone: cyclohexanol molar ratio from 0.55:1 to 0.63:1 and to 1:1 for the use of 18CR5 and 18CR6, respectively. The polyglycol additives also contribute to cyclohexanol accumulation and cyclohexanone:cyclohexanol molar ratio is about (1.23–1.72):1 (Fig. 2d).

The high ketone content among reaction products is also achieved at a cyclohexane conversion of about 4%. The polyglycol additives significantly enhance the cyclohexanone:cyclohexanol molar ratio up to (0.87–0.97):1 compared to the molar ratio of 0.56:1 by catalysis of cyclohexane oxidation reaction solely by cobalt naphthenate (Fig. 2d).

Crown ethers slightly decrease selectivity for esters except for 15-crown-5, which reduces it by 1.83 times. The polyglycol additives decrease selectivity for esters from 1.68 (PEG) to 4.52 times (PPG425). Since esters are a product of the alcohol transformation, the decrease in selectivity for esters by cyclohexane oxidation is caused by a sharp reduction in selectivity for cyclohexanol with a simultaneous increase in

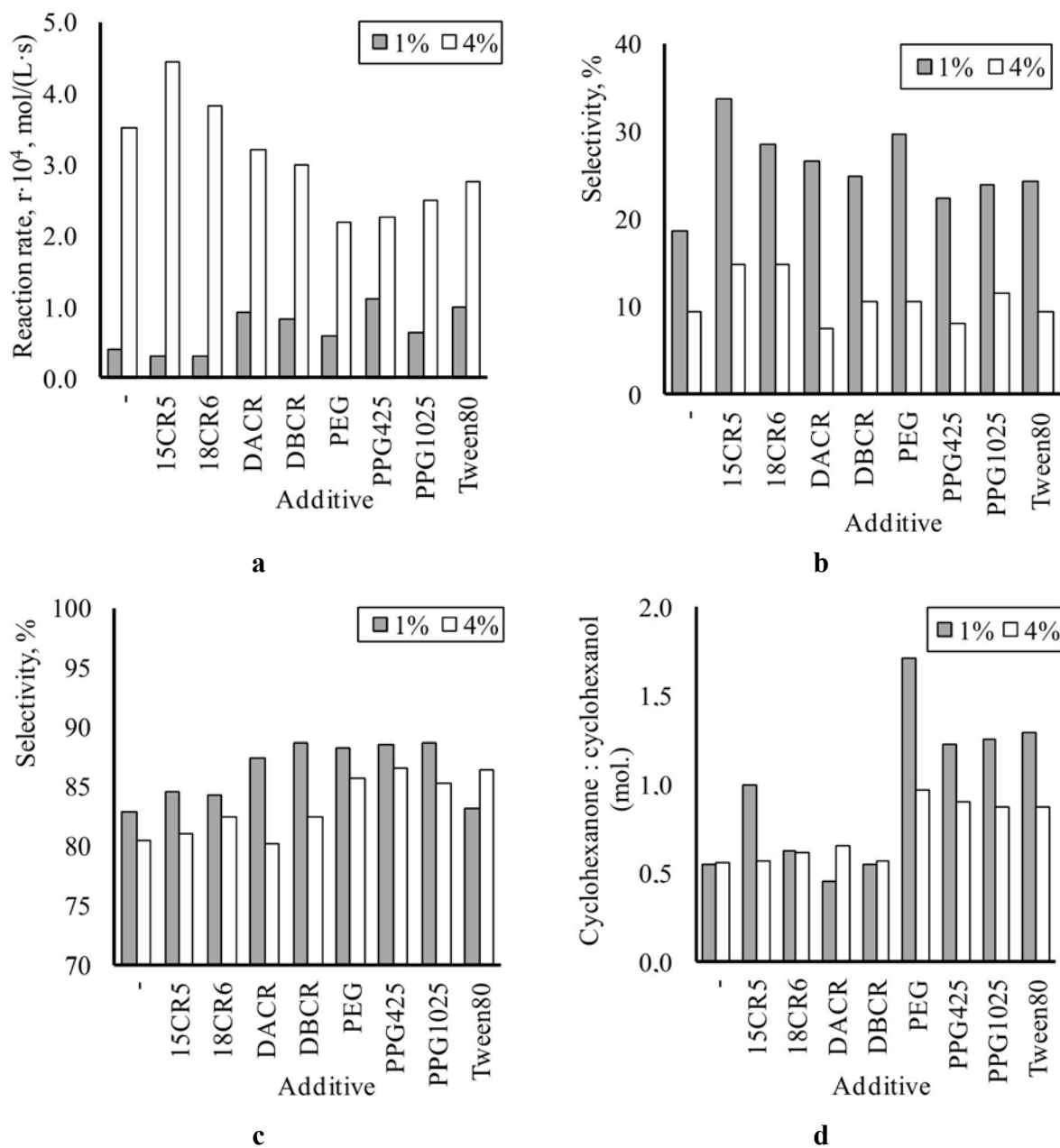


Fig. 2. Effects of organic additives on the rate of cyclohexane oxidation reaction (a), selectivity for cyclohexyl peroxide (b), selectivity for main reaction products (c), and cyclohexanone:cyclohexanol molar ratio. The cyclohexane conversion is about 1% and ~4% (shown in figure). Temperature is 413 K; pressure is 1.0 MPa; cobalt naphthenate concentration is $5 \cdot 10^{-4}$ mol/L; and CoNaph_2 :additive molar ratio is 5:1

selectivity for ketone.

Carboxylic acids are the main oxidation products of alkylaromatic hydrocarbons (toluene and p-xylene). Peroxides concentration does not exceed $5 \cdot 10^{-3}$ mol/L within all catalytic toluene and p-xylene oxidation times. In contrast, peroxides concentration is several times higher and reaches $5.5 \cdot 10^{-2}$ mol/L in cyclohexane oxidation catalyzed by cobalt naphthenate and crown ether additives.

As by cyclohexane oxidation, crown ether additives to the catalyst affect the reaction rate of toluene and p-xylene oxidation (Table 3). In particular, at the cobalt acetate:additive molar ratio of 5:1, the toluene oxidation rate is 2 times higher than the rate of reaction catalyzed solely by cobalt acetate. The effect of crown ether additive is also observed at higher conversion of hydrocarbons. For instance, the DACR additive increases the reaction rate of toluene oxidation

by 15% (Table 3).

When toluene conversion is about 1%, crown ether additives affect the selectivity for benzyl alcohol and benzyl aldehyde and their molar ratio. In contrast to the cyclohexane oxidation, when using crown ether additives to the catalyst, the selectivity for benzyl alcohol increases from 25.7% by catalysis solely of cobalt acetate to 30.7% when using the DBCR additive and even to 53.4% when using the DACR additive. This trend is less expressed at a higher hydrocarbon conversion, and the DBCR additive to cobalt acetate increases the selectivity for benzoic acid (Table 3).

At the initial stage of p-xylene oxidation, crown ether additives also increase selectivity for p-tolyl alcohol. The selectivity for p-tolyl aldehyde remains the same as by cobalt acetate catalysis, and the selectivity for p-toluic acid sharply decreases (Table 3). At a higher p-xylene conversion, the selectivity for alcohol and aldehyde sharply decreases, and the selectivity for p-toluic acid increases by 1.28–1.34 times.

Crown ether additives to cobalt acetate also change the composition of alkylarenes oxidation products.

The obtained results indicate the effect of crown ether on the reaction rates ratio of the alkylarene oxidation stages. Considering the scheme of toluene oxidation product transformations [10], it can be stated that at the oxidation initial stage, the reaction rate of alcohol formation increases. Perhaps, along with the decrease in the reaction rate of p-xylene to aldehyde conversion, the reaction rate of alcohol to aldehyde conversion also decreases. At higher hydrocarbon conversion, the ratio between the reaction rates of alcohol and aldehyde formation from hydrocarbons

is preserved, but the rate of transformation of alcohol to aldehyde, which can be easily oxidized to p-toluic acid, is increased.

Conclusions

Research results indicate that crown ethers or polyglycols effectively influence the catalyst activity and selectivity for main products of oxidation of alicyclic and alkylaromatic hydrocarbons catalyzed by cobalt salts. The studied organic additives, primarily polyglycols, to the catalyst of cyclohexane oxidation increase the reaction rate and hydrocarbon conversion and affect the selectivity for the main reaction products and the cyclohexanone:cyclohexanol molar ratio. The last factor is significant when cyclohexane oxidation is the first stage of the caprolactam production involving cyclohexanone as raw material. The additives of crown ethers or polyglycols increase the conversion of cyclohexane or alkylbenzenes while maintaining the selectivity for the main products or additives increase the selectivity for the main products while providing sufficiently higher hydrocarbon conversion.

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Table 3

Effect of crown ether on the indicators of toluene and p-xylene oxidation

Additive	Co(OAc) ₂ :additive (mol.)	Time, min	Conversion, %	Selectivity, %			Reaction rate, r·10 ⁴ , mol/(L·s)
				acid	aldehyde	alcohol	
toluene, the temperature is 423 K, the pressure is 0.4 MPa, C(Co(OAc) ₂) is 3.0·10 ⁻³ mol/L							
–	–	30	0.9	23.3	51.0	25.7	0.5
DACR	5:1	25	1.5	7.5	39.0	53.4	1.0
DBCR	5:1	35	1.2	27.0	42.3	30.7	0.6
–	–	61	6.4	53.5	28.9	17.6	4.7
DACR	5:1	45	6.9	51.5	25.9	22.7	5.4
DBCR	5:1	65	7.0	58.0	24.3	17.7	4.4
p-xylene, the temperature is 393 K, the pressure is 0.1 MPa, C(Co(OAc) ₂) is 3.0·10 ⁻³ mol/L							
–	–	30	1.2	15.2	46.1	38.7	0.5
DACR	1:2	75	1.0	0.2	46.7	53.1	0.2
DBCR	1:2	30	0.9	7.7	47.3	45.0	0.4
–	–	75	7.9	36.3	37.1	26.6	2.6
DACR	1:2	125	8.3	48.5	30.3	21.2	3.0
DBCR	1:2	85	7.9	46.5	35.7	17.8	2.7

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ВПЛИВ КРАУН-ЕТЕРІВ І ПОЛІГЛІКОЛІВ НА КАТАЛІТИЧНЕ ОКИСНЕННЯ ЦИКЛОГЕКСАНУ І АЛКІЛАРЕНІВ

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Досліджено вплив краун-етерів і полігліколів на рідиннофазне окиснення молекулярним киснем циклогексану і алкілароматичних вуглеводнів (толуену та *n*-ксилену) в присутності солей металів змінного ступеня окиснення. Встановлено, що краун-етери збільшують швидкість реакції як на початковій стадії окиснення, так і за вищої конверсії циклогексану і алкіларенів. Показано, що вищевказані добавки, насамперед, максимально впливають на селективності продуктів окиснення. Зокрема, застосування краун-етерів і полігліколів з кобальт нафтенатом збільшує мольне співвідношення циклогексанон:циклогексанол в процесі окиснення циклогексану, а використання добавок краун-етерів до ацетату кобальту при окисненні толуену та *n*-ксилену збільшує на початковій стадії реакції селективність за спиртом, а за вищої конверсії алкіларенів – селективність за карбоною кислотою. Зроблено припущення, що вплив добавок краун-етерів і полігліколів на швидкість та селективності утворення продуктів реакції зумовлений утворенням комплексів між іоном металу змінного ступеня окиснення та добавкою, та зміною внаслідок цього окисно-відновлювального потенціалу іону металу. Зроблено висновок про вплив краун-етерів і полігліколів на окремі стадії рідиннофазного каталітичного окиснення вуглеводнів.

Ключові слова: окиснення, циклогексан, толуен, *n*-ксилен, солі кобальту, краун-етер, полігліколь.

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Keywords: oxidation; cyclohexane; toluene; p-xylene; cobalt salt; crown ether; polyglycol.

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