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INFLUENCE OF COMPLEX-CREATIVE ADDITIVES ON OXIDATION OF HYDROCARBONS

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Abstract. Article contains results of oxidation of different classes of hydrocarbons (alicyclic, alkylaromatic) in the presence of catalytic systems containing salt of variable valence metal and organic additive of different nature (perfluorooxasulphonates, crown-ethers, polyglycols). It was found that the influence of investigated catalytic systems depends on the nature of the hydrocarbon and the nature of the additive. The main areas of influence of organic additives on the rate and selectivity of oxidation of hydrocarbons were considered and the most probable ones were proved.

Keywords: cyclohexane, ethylbenzene, perfluorooxasulphonate, crown-ether, polyglycol, oxidation.

1. Introduction

Most of the process of liquid hydrocarbon oxidation occurs in the presence of homogeneous catalysts, which are often salts of variable valency metal. Effect of homogeneous catalysts on liquid oxidation of organic matter is associated with selective acceleration (braking) of individual elementary reactions, and with the implementation of new ways of chemical transformations. Variable valence metals (VVM) are involved in all elementary stages of the process – initiation, extension, degenerate branching, and chain breaking [1], which makes their impact on the rate and selectivity of the process of oxidation, or promote flowing of non-chain (inside-sphere) selective catalytic process. Acceleration of the oxidation process by salts of VVM is associated with their participation in the elementary stages of formation of free radicals

It should be emphasized that the presence of organic compounds that can be coordinated at the ion of metal may contribute to the activation of molecular oxygen [2, 3].

The activity of the catalyst at liquid oxidation of organic matter is determined by its ability to maintain

high and stable rate of initiation and continuation of chains, as well as its resistance to complex creation with reaction products and deactivation [5]. It is known that organic ligands, which are used as additives to VVM salt enter the structure of the catalytic complex, modify it, and thus may increase the activity and selectivity of catalysts [4, 6, 7].

The most promising way of intensification of the process of liquid homogeneous oxidation of hydrocarbons (cyclohexane, alkylaromatic hydrocarbons) is creation of complex catalytic systems based on VVM salts and a number of specific additives of different nature. Using such systems in which instead of variable valence metal ions organic ligands are used as co-catalysts is better both from environmental standpoint and from a position of more targeted influence on the process of oxidation [6, 8-10].

The above data indicate a promising application of catalytic systems based on VVM salts containing organic ligands. Therefore, using a variety of ligands (either electron-donor or electron-acceptor) we can selectively accelerate individual elementary stages of radical chain oxidation of organic matter and affect the selectivity and mechanism of oxidative transformations of the original substrate.

2. Experimental

The process of catalytic oxidation of cyclohexane by molecular oxygen was investigated in the temperature range of 403–423 K at the pressure of 1.0 MPa, oxidation of ethylbenzene was carried out in a steel reactor at the temperature of 403 K and the pressure of 0.4 MPa. Oxidation of hydrocarbons was conducted in the autoclave reactor of bubbling type.

Cobalt naphthenate (NC) was used as a basic component of catalytic systems. The organic additives of different nature were investigated:

- crown-ethers: 15-crown-5 (15-CR-5), 18-crown-6 (18-CR-6), dibenzo-18-crown-6 (DBCR) and nitrogen-containing – diaza-18-crown-6 (DACR);

- polyglycols: polyethylene glycol (PEG), polypropylene glycol (PPG425 i PPG1025) and highly molecular ester of polyglycols Tween-80;

- perfluorooxasulphonates:
oxane ($\text{CF}_3\text{CF}_2\text{OCF}_2\text{SO}_3\text{K}$),
chromoxane ($\text{CF}_3\text{CF}_2\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_3\text{K}$),
fluoroxane
($\text{CF}_3\text{CF}_2\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_3\text{K}$),
amineoxane ($\text{CF}_3\text{CF}_2\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{NH}_2$),
aminatoxane
($\text{CF}_3\text{CF}_2\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2[\text{N}(\text{C}_2\text{H}_5)_4]$).

Ingredients of the catalyst were added directly in to the reaction mixture.

The contents of cyclohexyl hydroperoxide (HPCH) and ethylbenzene hydroperoxide (HPEB) were determined by iodometry; adipic acid and esters from oxidation of cyclohexane were determined by known titrimetric methods; the content of cyclohexanol (COL) and cyclohexanone (CON) and acetophenone (APh) and methylphenylcarbinol (MPC) – *via* gas-liquid chromatography. Isopropyl alcohol was used for sample homogenization.

3. Results and Discussion

Oxidation of cyclohexane in the presence of catalytic systems which contain organic additives (perfluorooxasulphonates and crown-ethers) showed that both types of additives affect the rate of oxidation and selectivity of target and by-products; the common feature of both types of additives is change of the value of cyclohexanol/cyclohexanone. However, these effects for additives of different nature are different. Thus, electron-acceptor additives (perfluorooxasulphonates) have deeper influence on the rate of oxidation of cyclohexane than crown-ethers, which are electron-donor compounds. The effect of these additives and selectivity of formation of the target and by-products is different. Analyzing the results obtained in the oxidation of cyclohexane in the presence of catalytic systems containing electron-acceptor additives it can be noted that their presence in the catalytic system leads to a decrease in selectivity for hydroperoxide and increase of cyclohexanol/cyclohexanone ratio. The presence in the catalytic system of crown-ethers, in contrast, leads to some, albeit slight, increase of selectivity for hydroperoxide and decreased cyclohexanol/cyclohexanone ratio (Table 1).

Polyglycols have similar crown-ethers ability to create complexes with metal ions [10], but unlike crown-ethers with metal ions of different, not fixed, sizes. Such feature is connected with high conformational flexibility of the chain. The results of cyclohexane oxidation in the

presence of catalytic systems containing polyglycols of different nature showed that the effect of polyglycols is qualitatively similar to that of crown-ethers, however, quantitative indicators are different. Thus, polyglycols like crown-ethers shift the cyclohexanol/cyclohexanone ratio toward ketones. However, in the case of polyglycols this trend is more clearly expressed. Regarding the impact on selectivity for hydroperoxide of cyclohexyl, the presence of polyglycols has little effect on this rate. A characteristic feature of the use of catalytic systems containing polyglycols is a sharp decrease in selectivity of the formation of esters.

However, it should be noted that for perfluorooxasulphonates and crown-ethers quite clear dependence of the obtained parameters of the process on the structure of crown-ether or salt is observed, while the results obtained in the presence of catalytic systems containing various polyglycols are very close.

Thus, the obtained results showed that the influence of organic additive depends on its nature: it is qualitatively different for the electron-acceptor and electron-donor additives, and effect from additives of the same nature differs quantitatively.

During oxidation of alkylaromatic hydrocarbons (toluene and *p*-xylene) oxidation rate of hydrocarbon remains virtually unchanged in the presence of DACR and increases during usage of the rest of the researched crown-ethers (Table 2). Such close results prove that the influence of catalytic systems that contain crown-ethers on the rate of oxidation of hydrocarbons significantly depends on the structure of the crown-ethers and practically does not depend on the nature of oxidated substrate [11]. This finding is confirmed by results obtained in the oxidation of cyclohexane in the presence of catalytic systems containing crown-ethers [12].

Comparing the effect of organic additives on the selectivity of products formation of alkylaromatic hydrocarbons oxidation it should be noted that in contrast to the oxidation of cyclohexane in the oxidation of alkylaromatic hydrocarbons organic additives exert opposite effects on the selectivity of formation of products: the use of crown-ethers leads to an increase in alcohol content, rather than the aldehyde [13] while using electron-acceptor additives (perfluorooxasulphonates) leads to an increase in the content of aldehyde in the reaction system [14]. The obtained results allow to suggest that the effect of organic additives on the composition of reaction products depends not only on the nature of additives, but also the nature of oxidated substrate.

In the oxidation of ethylbenzene (Table 3) it is revealed that in the presence of catalytic systems NC-polyglycols selectivity of HPEB formation increases. As for the oxidation of cyclohexane in the presence of catalytic systems containing perfluorooxasulphonates, the decrease of HPEB accumulation rate and thus significant increase of the selectivity of its formation are observed.

Table 1

Oxidation of cyclohexane in the presence of organic additives of different nature. Temperature 413 K, pressure 1.0 MPa, catalyst – cobalt naphthenate, catalyst concentration 5×10^{-4} mol/l

Additive	Ratio NC/A, mol/mol	Time, min	Conversion, %	Selectivity, %					Ratio alcohol/ketone	$W \cdot 10^4$, mol/(l·s)
				HPCH	COL	CON	Acids	Esters		
Thermal	–	90	0.8	7.3	48.1	37.7	6.9		1.28	
–	–	40	4.1	9.3	37.6	20.9	13.2	19.0	1.80	
Chromoxane	1/10	30	5.6	2.3	56.7	23.9	17.1		2.37	
15-CR-5	1/5	35	3.7	14.7	37.9	21.4	15.6	10.4	1.77	4.2
18-CR-6	1/5	35	3.3	18.0	34.6	21.2	10.5	15.7	1.63	4.6
DACR	1/5	40	3.2	10.3	38.7	21.6	10.9	18.5	1.79	4.2
DBCR	1/5	40	4.2	10.4	37.4	21.4	10.9	19.9	1.75	3.5
PEG400	1/5	50	4.9	7.5	37.3	34.8	11.3	9.2	1.07	3.8
PPG425	1/5	50	4.5	8.0	39.9	35.8	12.0	4.2	1.11	2.9
PPG1025	1/5	50	4.8	6.9	38.1	33.6	12.8	8.6	1.13	3.1
Tween80	1/5	50	5.3	5.4	39.1	34.4	12.4	8.7	1.14	3.5

Table 2

Composition of products and speed of oxidation of toluene and *p*-xylene in the presence of binary catalysts

Additive (D)	Ratio $C_{Co(OAc)_2}/C_D$	Time, min	Conversion, %	Selectivity, %			$W \cdot 10^4$, mol/l·s	Alcohol/ketone ratio
				Acid	Aldehyde	Alcohol		
Oxidation of toluene. $T = 423$ K, $P = 0.4$ MPa, $[Co(OAc)_2] = 3 \cdot 10^{-3}$ mol/l								
–	–	61	6.5	53.5	28	17.6	4.7	0.63
Oxane	2:1	65	5.9	54.3	29.7	16	3.8	0.54
Chromoxane	2:1	65	5.9	60.7	26.8	12.5	4.2	0.47
Fluoroxane	2:1	71	5.9	51.6	34.1	17.3	4.8	0.51
Aminoxane	5:1	80	5.9	53.9	29.4	16.7	3.1	0.57
Aminateoxane	2:1	50	6.7	66.1	24.2	9.7	5.4	0.40
DACR	5:1	45	6.9	51.5	25.9	22.7	5.4	0.88
DBCR	5:1	65	7	58	24.3	17.7	4.4	0.73
Oxidation of <i>p</i> -xylene. $T = 393$ K, $P = 0.1$ MPa, $[Co(OAc)_2] = 1 \cdot 10^{-3}$ mol/l								
–	–	75	7.9	36.3	37.1	26.6	2.6	0.72
Aminateoxane	1:2	85	7.8	38.5	34.2	27.3	2.6	0.80
DACR	1:2	125	8.3	48.5	30.3	21.2	3	0.70
DBCR	1:2	85	7.9	46.5	65.7	17.8	2.7	0.27

Table 3

Oxidation of ethylbenzene in the presence of catalytic systems that contain organic additives of different nature. Catalyst – naphthenate of cobalt, concentration of catalyst – 0.001 mol/l, molar ratio NC/A – 1/1, temperature – 403 K, pressure – 0.4 MPa

Catalyst	Time, min	Conversion, %	Selectivity, %			Alcohol/ketone ratio
			Aph	MPC	HPEB	
Thermal oxidation						
–	240	0.18	–	–	100	–
Polyglycol	240	0.75	10.3	3.3	86.4	0.31
Chromoxane	240	0.39	33.3	7.5	59.2	0.22
Catalytic oxidation						
NC	240	2.8	58.5	11.6	30.0	0.20
NC – polyglycol	180	2.6	38.3	2.5	59.2	0.06
NC – chromoxane	120	2.8	69.6	2.5	27.9	0.04

The results obtained in the oxidation of ethylbenzene in the presence of catalytic systems containing organic additives such as PG and chromoxan are similar to those obtained in the oxidation of ethylbenzene in the presence of individual compounds. Both for catalytic oxidation and the thermal one the value of alcohol/ketone ratio is bigger in the presence of polyglycols. It should be noted that during the catalytic oxidation of ethylbenzene in all cases the reduction of alcohol content takes place. However, while in the case of NC–chromoxan it is associated with the increase in selectivity for ketone, in the case of NC–polyglycol simultaneous rapid decrease of selectivity for ketone and increase of selectivity of hydroperoxide formation are observed.

Having analyzed the obtained results we can conclude that the effect of organic additives on the process of liquid homogeneous catalytic oxidation of hydrocarbons can be realized in several ways:

- impact on speed of oxidation of hydrocarbons: 1) by facilitating the activation of molecular oxygen, which is used as oxidizer; 2) by interaction of complexes of salts of VVM–organic additive with hydroperoxide or addition of hydroperoxide radicals at the stage of degenerate branching; 3) whereas almost all studied organic additives to greater or lesser degree have surface-active properties, we can assume that their presence in the reaction system leads to increase of dissolved oxygen concentration; 4) due to formation of complexes of salts of VVMS with organic additives there is a significant chance of increase of the concentration of active catalyst, due to decreasing of its share that is deactivated by the interaction of reaction products (such as adipic acid in oxidation of cyclohexane).
- impact on the selectivity of formation of reaction products: 1) by changing the ratio between the valence forms of the catalyst; 2) by passing a moderate form of changes in the coordination sphere of the catalyst.

For example, counting the results of oxidation of cyclohexane in the presence of catalytic systems containing polyglycols and crown-ethers, we can assume that changing the ratio between COL and CON is associated with the occurrence of non-radical changes in the coordination sphere of the catalyst, because simultaneous minimal influence of these organic additives on rate of oxidation of hydrocarbons is observed. At the same time, significant increase in the speed of oxidation of cyclohexane in the presence of catalytic systems containing perfluorooxasulphonates suggests that these organic additives along with the influence on selectivity exert a significant effect on chains initiation stage. In this case we can assume that the impact of chromoxan on oxidation speed, although only partly, can be explained by its surface-active properties (which are higher than those

of the crown-ethers and polyglycols), which may help to increase the concentration of dissolved oxygen in the reaction mixture.

The evidence that the effect of the studied organic additives can not be explained exclusively by their surface activity and effects on mass transition processes (such as increasing the concentration of dissolved oxygen), is that for solutions of cobalt naphthenate and cobalt catalytic system naphthenate-polyglycols in cyclohexanone changes in IR and UV spectra are observed, which clearly show the formation of complexes between the VVM salt and an organic additive [15]. Therefore, we can assume that in the presence of the studied catalytic systems the share of moderate form of transformations that occur in the coordination sphere of the VVM metal ion significantly increases, which leads to a change in selectivity of formation of aimed products and to some deceleration of hydrocarbons oxidation rate in the presence of catalytic systems containing crown-ethers and polyglycols. Thus in view of the increase of the CON/COL ratio in the presence of crown-ethers and polyglycols we can assume that the organic additives entering the catalytic complex increase the proportion of Co^{3+} in the reaction system.

4. Conclusions

Based on the results obtained in liquid-homogeneous catalytic oxidation of various classes of hydrocarbons (cyclohexane, toluene, p-xylene, ethylbenzene) in the presence of catalytic systems containing VVM salt together with organic additives of different nature (polyglycols, crown-ethers, perfluorooxasulphonates) we can conclude that the effect of the above additives depends on the nature of both the substrate and the additives. Besides, the action of the catalytic systems is characterized by a synergistic effect, since the total effect of the catalytic system is not the sum of influences of NC and organic additives. It should be emphasized that the effect of organic additives can not be explained by only one of the factors and it is a combination of additives action on the surface properties of the reaction mixture, on the catalyst interaction with radicals, hydroperoxides *via* coordination on metal ion, and on the ratio of oxidized and reduced forms of the catalyst.

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ВПЛИВ КОМПЛЕКСОУТВОРЮЮЧИХ ДОДАТКІВ НА ОКИСНЕННЯ ВУГЛЕВОДНІВ

Анотація. Наведено результати окиснення різних класів вуглеводнів (аліциклічні, алкілароматичні) у присутності каталітичних систем, які містять сіль металу змінної валентності та органічний додаток різної природи (перфтороксасульфонати, краун-етери, полігілколи). Встановлено, що вплив досліджених каталітичних систем залежить як від природи вуглеводню, так і від природи додатку. Розглянуто основні напрямки впливу органічних додатків на швидкість та селективність окиснення вуглеводнів та обґрунтовано найбільш ймовірні з них.

Ключові слова. циклогексан, етилбензол, перфтороксасульфонат, краун-етер, полігілколь, окиснення.