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RESEARCH INTO KINETIC REGULARITIES OF CATALYTIC LIQUID-PHASE OXIDATION OF n-HEXADECANE IN THE PRESENCE OF METAL COMPLEXES CALALYSTS

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Abstract: Kinetic regularities of catalytic liquid-phase oxidation of n-hexadecane in the presence of metal complexes of variable valence were studied. In the reaction of n-hexadecane oxidation as a catalytic mixture, a complex o-phenanthroline with stearate with variable valence metals (Mn^{2+} , Cu^{2+} , Co^{2+}) was used. It found that o-phenanthroline significantly influences the catalytic activity of metal ions. The introduction of organic ligand into the catalytic system, as well as varying the ligand: metal salt ratio, has effect greatly on the course and character of the process.

Keywords: n-hexadecane, oxidation, liqand, o-phenanthroline, metal complex catalysis, metal, oxygen, liquid phase, complex

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Introduction

It is well-known, that polymers containing functional groups as the bearers are widely used for immobilization the number of complex-making sorbents, catalysts and biologically active substances [1-3]. The catalytic properties of such metal-polymer complexes were studied in the oxidation reactions of some paraffins and cycloparaffins and it was revealed, that they are high-effective catalyst [4, 5].

Side by side with metalpolymer catalysts in the reactions of liquid-phase oxidation of hydrocarbons, there are thoroughly explored metal-complex catalysts where combination and selection of appropriate ligands and donor-acceptor additives make it possible to modify the structure and properties of the catalyst.

It should be noted that the quantitative combination of ligands and metals makes it possible to run the process at a certain stage where one product is mainly formed to thus remove the presence of many parallel and successive reactions as is the case with oxidation process [6-7]. The real raw material as an initial product for the production of synthetic fat acids (SFA) is a complicated

mixture of paraffin hydrocarbons with different molecular weight and some insignificant admixtures of izoalkane, naphthene and aromatic compounds. In the course of oxidation these hydrocarbons behave not identically. Therefore, it is useful to start with analysis of individual hydrocarbons' behavior while studying their kinetic regularities, mechanism and chemism of the process. The obtained data make possible to put and correctly settle the problem of exploring the complicated composition of the initial raw material.

In the industrial production of SFA they very frequently use salts of metals with variable valence and insignificant admixtures of alkali metals as catalysts.

We have studied kinetic regularities of n-decane catalytic oxidation in the sphere of metal complexes with variable valence, and a number of regularities were discovered to be possibly identical with the oxidation of real paraffin mixture [8]. In the reactions of n-decane oxidation, the o-phenanthroline complex with manganese stearate was used as a catalytic mixture. It is well-known that o-

phenanthroline strongly affects the catalytic activity of metal ions. A number of works has been mentioned in references where the course and character of oxidative processes containing o-phenanthroline in the catalytic composition were examined [9-10].

In this connection, the paper studies the catalytic activity of o-phenanthroline complexes with stearates of variable valence metals (Mn^{2+} , Cu^{2+} , Co^{2+}) in the liquid-phase

oxidation of a typical representative of paraffin hydrocarbons - n-hexadecane that is in composition of the fraction C10-C20, which are the initial raw materials for SFA production.

The obtained in this research data of regularities can correctly reflect a real picture of oxidation course for rather complicated paraffin raw material.

Experimental part

The reaction of n-hexadecane oxidation has been carried out in a staging type glass reactor with Scott filter, at atmosphere pressure and a temperature of $140^{\circ}C$, had different ratio of organic ligand and metal compounds with variable valence. Oxygen served as an oxidation agent. The oxidation was carried out by means of catalyzed and non-catalyzed systems. As a catalyst we have chosen o-phenanthroline with stearate of manganese, cobalt and copper. The catalyst was put into a reactor in the stream of inert

gas. Note that n-hexadecane was refined from possible admixtures and distilled at boiling point. In the course of oxidation we selected the samples that had been checked on hydroperoxides, acids and alcohols. The formation of hydroperoxides was established by iodometric method; that of carbonyl compounds – by infrared spectrometry method at a stripe of $1718-1720\text{ cm}^{-1}$. The alcohols were transformed into their corresponding alkyl nitrites and analyzed using the method of ultraviolet spectroscopy [11].

Discussion of results

The experimental results are presented in the figures below. As can be seen from the figures (1,2) when manganese stearate is added to the non-catalyzed system, the decomposition of hydroperoxides sharply increases, which leads to the accumulation of alcohols. The ratio of the catalyst mixture plays a significant role in the direction of the reaction. The addition of o-

phenanthroline promotes the dissolution of manganese salts and the catalyst, while remaining in the homogenized state, does not precipitate. Obviously, this state of the catalyst affects the course of the reaction, which proceeds selectively and with a large yield of alcohols (fig.3, 4).

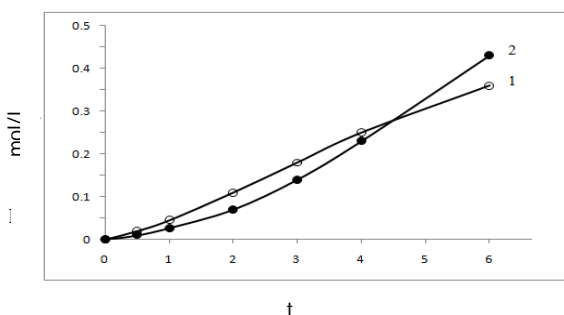


Fig.1. Non-catalyzed oxidation of n-hexadecane. presence. $T=140^{\circ}C$, 1-hydroperoxides, 2-acids.

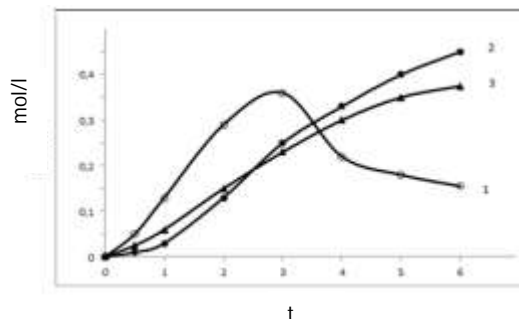


Fig. 2. N-hexadecane oxidation in manganese stearate $T=140^{\circ}C$, 1-hydroperoxides, 2-acids, 3-alcohols

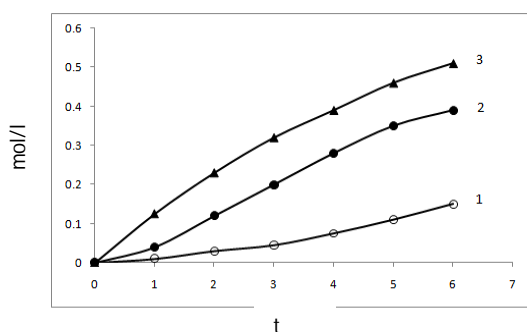


Fig.3. n-Hexadecane oxidation in the presence of complex o-phenanthroline with manganese stearate, $T=140^{\circ}\text{C}$, o-phen.+Mn(St)₂=1:1. 1. hydroperoxides, 2- acids, 3- alcohols.

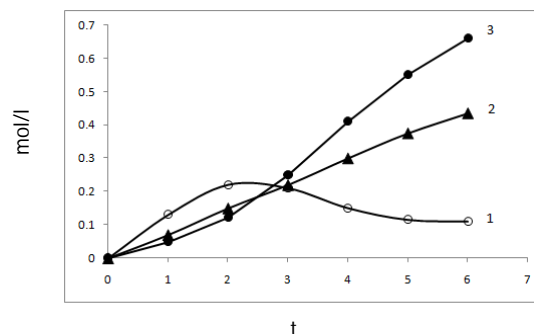


Fig.4. n-Hexadecane oxidation in the presence of complex o-phenanthroline with manganese stearate, $T=140^{\circ}\text{C}$, o-phen.+Mn(St)₂=20:1. 1. hydroperoxides, 2- acids, 3- alcohols.

The liquid phase oxidation of n-hexadecane in the presence of complexes of o-phenanthroline with manganese stearate in the ratio of o-phenanthroline: manganese stearate (0.0450:

0.0153) g showed that the decomposition of hydroperoxides leads to the formation of mainly carbonyl compounds (Fig. 5).

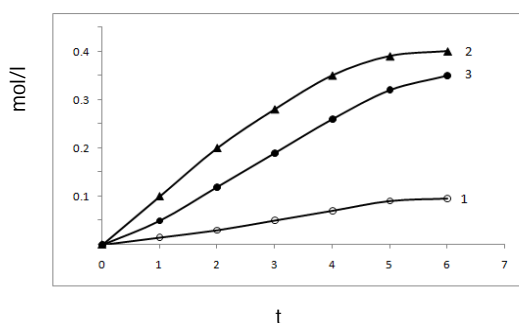


Fig.5. N-hexadecane oxidation in the presence of complex o-phenanthroline with manganese stearate, $T=140^{\circ}\text{C}$, o-phen+Mg(St)₂=(0.0450+0.0153)g. 1. hydroperoxides. 2. carbonyl complexes, 3. acids

Also, an oxidation of n-hexadecane in the presence of o-phenanthroline with copper stearate was carried out. Note that the formation of hydroperoxides is more than 60%. The complexes of o-phenanthroline with copper ions promote accumulation and stabilization of hydroperoxides. The results of experiment were presented in Table below. As is seen, copper salts display high initiative ability. Rates of accumulation in a number of intermediate products are perceptible. However, despite hydrocarbons conversion, selectiveness of each product is insignificant. The variety in catalytic system by the ratio of metal and organic ligands showed that the quantity of the latter influences greatly the nature of hydrocarbons oxidation. Introduction of a small quantity of o-phenanthroline into the catalyst composition slows rates of the formation of reaction products. The same is true of high concentration of organic ligands as well. An optimum concentration of o-

phenanthroline promotes the formation of hydroperoxides and their stabilization. Thermal destruction of the latter leads to the accumulation of carbonyl compounds. Note that changes in metal concentration also influence the character of oxidation.

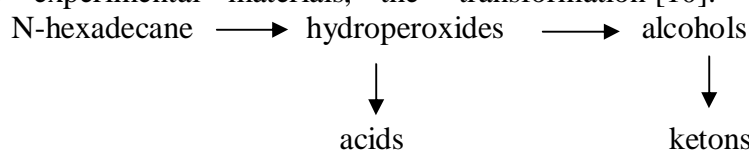
The yield of the products of reaction hydrocarbon oxidation and selectiveness of the process on hydroperoxides are also shown in Table. As follows data presented, there is a stabilization of hydroperoxides at a certain ratio of o-phenanthroline with copper ions.

The results of experiment, which was carried out in the presence of complexes o-phenanthroline with cobalt stearate, testify about the presence on a certain stage of oxidation (2 and 3 hours) the high rate of accumulation hydroperoxides. Their decomposition leads to predominance of carbonyl compounds concentration as well.

Table. n-Hexadecane oxidation in the presence of o-phenanthroline complexes with variable valence metals

No	o-phenanthroline, (g)	Metals stearate, (g)	Duration of reaction, (h)	Hydroperoxides, (mol/l)	Ketones, (mol/l)	Alcohols, (mol/l)	Acids, (mol/l)	Selectiveness on hydroperoxides, (mol/l)
1	0.0450	0.0145 Cu ²⁺	2.0	0.196	0.092	0.060	0.044	50.05
2	0.0450	0.0145 Cu ²⁺	3.0	0.260	0.124	0.092	0.083	50.05
3	0.0900	0.0145 Cu ²⁺	3.0	0.214	0.129	0.075	0.060	44.77
4	0.0452	0.0141 Co ²⁺	2.0	0.196	0.064	0.0102	0.031	49.87
5	0.0452	0.0141 Co ²⁺	3.0	0.256	0.100	0.145	0.069	44.91
6	0.0452	0.0070 Cu ²⁺	3.0	0.270	0.089	0.062	0.045	57.94
7	0.0450	0.0100 Cu ²⁺	3.0	0.240	0.072	0.059	0.066	54.92
8	0.0675	0.0100 Cu ²⁺	3.0	0.170	0.042	0.040	0.029	60.50

According to the scheme repeatedly confirmed by experimental materials, the



alcohols are the products of hydroperoxides transformation [10].

The latter are the primary intermediate compounds and their decomposition leads to

the formation of further products.

Conclusion

The kinetic regularities of the reaction of liquid-phase oxidation of n-hexadecane in the presence of complexes of o-phenanthroline with metals of variable valence were studied. It is established that the presence of o-phenanthroline in the catalytic system opens up new ways of regulating and controlling the oxidation of paraffin hydrocarbons. By varying the ratio of organic ligand to metal,

the process can be directed towards the formation of one of the target products, with suppressing undesirable parallel reactions.

The results obtained make it possible to add o-phenanthralin to the catalytic system as an organic ligand in the reactions of liquid-phase oxidation of aliphatic hydrocarbons in order to obtain mainly one or two oxygen-containing products.

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METALKOMPLEKS KATALİZATORLARIN İŞTİRAKI İLƏ n-HEKSADEKANIN KATALİTİK OKSİDLƏŞMƏ REAKSİYASININ KİNETİK QANUNAUYGÜNLUQLARININ TƏDQIQI

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Dəyişkən valentli metal komplekslər mühitində n-heksadekanın katalitik oksidləşmə reaksiyasının kinetik qanunauyğunluqları öyrənilmişdir. Katalizator qarışığı kimi o-fenantrolinin dəyişkən valentli metalların ştearatları ilə alınan komplekslərindən istifadə olunmuşdur. Müəyyən edilmişdir ki, o-fenantrolin metal ionlarının aktivliyinə nəzərə çarpacaq dərəcədə təsir göstərir. Katalizator qarışığına üzvi liqandı daxil etməklə və həmçinin onun metal duzuna nisbətini dəyişməklə reaksiyanın gedişini və xarakterinin təmzirləmək mümkündür. Metalkompleks katalizatorlarının katalitik aktivliyinin öyrənilməsi maye fazada oksidləşmə reaksiyalarının istifadə olunmasında böyük imkanlar yaradır.

Açar sözlər: n-heksadekan, oksidləşmə, liqand, o-fenantrolin, metalkompleks katalizatorları, metal, oksigen, maye faza, kompleks.

**ИССЛЕДОВАНИЕ КИНЕТИЧЕСКИХ ЗАКОНОМЕРНОСТЕЙ КАТАЛИТИЧЕСКОГО
ЖИДКОФАЗНОГО ОКИСЛЕНИЯ Н-ГЕКСАДЕКАНА В ПРИСУТСТВИИ
МЕТАЛЛОКОМПЛЕКСНЫХ КАТАЛИЗАТОРОВ**

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Изучены кинетические закономерности каталитического окисления н-гексадекана в присутствии комплексов металлов переменной валентности. В качестве каталитической системы были использованы комплексы о-фенантролина со стеаратами металлов переменной валентности (Mn^{2+} , Cu^{2+} , Co^{2+}). Установлено, что о-фенантролин оказывает существенное влияние на каталитическую активность иона металла. Введение в каталитическую систему органического лиганда, а также варьирование соотношения лиганд: соль металла оказывают существенное влияние на ход и характер протекания процесса.

Ключевые слова: *н-гексадекан, окисление, лиганд, о-фенантролин, металлокомплексные катализаторы, метал, кислород, жидкая фаза, комплекс*