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ВПЛИВ ПОВЕРХНЕВО-АКТИВНИХ СПОЛУК НА ГОМОГЕННО-КАТАЛІТИЧНІ ПРОЦЕСИ ОКИСНЕННЯ АЛКІЛАРОМАТИЧНИХ ВУГЛЕВОДНІВ

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Досліджено вплив поверхнево-активних речовин різної природи (йонно- та нейонногенних) на процес рідиннофазного окиснення алкілароматичних сполук. Одержані результати дають змогу стверджувати, що вплив застосування поверхнево-активних сполук як каталітичних добавок пов'язаний не тільки і не стільки з їх природою, скільки зі здатністю формувати активні каталітичні комплекси [добавка – каталізатор – субстрат]. Створенні каталітичні системи не лише збільшують продуктивність реакційного обладнання за цільовими продуктами, але й здатні змінювати селективність процесу в бік утворення необхідного продукту.

Ключові слова: окиснення, етилбензол, поверхнево-активні сполуки, каталітичні системи, гідропероксид етилбензолу, ацетофенон.

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IMPACT OF SURFACE-ACTIVE COMPOUNDS ON HOMOGENEOUS CATALYTIC PROCESS OF OXIDATION OF ALKYLAROMATIC COMPOUNDS

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Article is devoted to research of impact of surface-active compounds of different nature (ion- and non-ionogenic) at alkylaromatic compounds liquid-phase oxidation process. Obtained results showed that impact of surface-active compounds, used as catalytic additives, depends not only from their nature but more from ability to create active catalytic complexes [additive – catalyst – substrate]. Created catalytic systems not only increase productivity of reaction volume (for aim products), but also allow to shift process selectivity towards creation of desired product.

Key words: Oxidation, ethylbenzene, surface active compounds, catalytic systems, hydroperoxide of ethylbenzene, acetophenone.

Introduction. The practical significance of oxidation processes in the production of basic organic and petrochemical synthesis is overemphasized. Their primary role is based on following reasons:

1. Great value of compounds derived by oxidation (alcohols, aldehydes, ketones, carboxylic acids and their anhydride, a-oxides, nitrils, etc.) and intermediates, solvents, monomers and precursors for the production of polymers, plasticizers, etc.

2. Wide variety of oxidation reactions, which are possible for many organic compounds, including hydrocarbons of all classes. This allows to use oxidation processes for primary processing of hydrocarbons and to receive large number of substances on their basis.

3. Accessibility and low cost of most oxidative agents, among which most dominant is air oxygen. This defines a higher efficiency of synthesis methods of oxidation of certain products over other possible methods of their preparation.

Oxidation processes are widely used in organic synthesis, often replacing less economical ways to produce many products.

Analysis of published data and problem definition. Most processes of hydrocarbons liquid-phase oxidation occurs in the presence of homogeneous catalysts, which often are salts of variable valence metal (VVM). Impact of homogeneous catalysts on liquid-phase oxidation of organic substances is associated either with selective acceleration (braking) of the individual elementary reactions, or with the implementation of new ways for chemical transformations. VVM participation in all the elementary stages of the process – origin, continuing, degenerate branching and chain termination determines their effect on the rate and selectivity of oxidation process. Acceleration of oxidation process by salts of VVM is associated with their participation in the elementary stages of the formation of free radicals [1–5, 7, 9].

Origin and branching of chains in the presence of VVM salts is going thru formation of an intermediate complex with charge transfer between the catalyst and hydroperoxide molecule or oxygen, leading to activation of molecules that react. During chain initiating activity of catalyst primarily depends on the redox potential of the metal cation and the ability to give and receive electrons. Chain initiating (involving catalyst) may occur thru direct interaction between substrate molecules and VVM cation in higher oxidative form. Such scheme of oxygen and hydrocarbon phased activation in some cases allows satisfactorily explain patterns of catalytic initiation of oxidation reaction, but majority of theoretical and experimental data indicates simultaneous activation of molecular oxygen and hydrocarbon at one reaction center – VVM cation [1, 2, 9, 10].

It should be emphasized that presence of organic compounds that are able to be coordinated on a metal ion, may contribute to the activation of molecular oxygen.

Despite possibility of free radicals generation by direct reaction between hydrocarbons and VVM salts initiating action of mentioned catalysts is primarily associated with their participation in acceleration of peroxide compounds decomposition, as well as the interaction of VVM ion in a higher valence state with oxygen-containing products.

Process of liquid-phase ethylbenzene oxidation is a classic version of the liquid-phase, radical-chain process [3]. Meaning: low conversion of raw materials and complexity of formed products selectivity managing. Industrial versions of this process can reach values of conversion – up to 10–15 %. Such conversion value can be reached due to fact that the process is carried out in multiple (up to 6) consecutive reactors with intermediate removal of ethylbenzene hydroperoxide (HPEB), etc. Conversion in one reactor is 3–4 %. It should also be noted that in the literature you can find data on achieving ethylbenzene conversion up to 80 % and selectivity for HPEB up to 90 % [8–10], but in these studies received hydroperoxide immediately binds and thus eliminated from the oxidation reaction. Further processing of binded HPEB is very difficult and, in some processes, impossible. Also it is worth noting that the average length of such processes is about 30 hours, which significantly reduces the productivity of the reaction equipment.

In the literature there is data on the use of bi-component catalytic systems, which along with VVM salt contain inorganic salts of sodium, potassium and calcium[5–7]. Usage of these salts enhanced the conversion process of oxidation and also increases selectivity for HPEB.

Purpose and objectives of the work. Previous work showed the influence of surface-active compounds (SAC) on the processes of liquid-phase oxidation of hydrocarbons, that is why it was appropriate to study the impact of the SAC use as catalytic additives in the process of liquid-phase

oxidation of ethylbenzene, and try to create a new selective binary catalytic systems based on common industrial catalysts of ethylbenzene oxidation (naphthenate and acetate of cobalt).

Methods of experiments. Patterns of liquid phase oxidation of ethylbenzene in the presence of industrial catalysts [NC and ACK] were studied at 403 K and a pressure 0.4–0.45 MPa. The concentration of VVM salt was $1,0 \cdot 10^{-3}$ mol/L.

Patterns of liquid phase oxidation of ethylbenzene in the presence of catalytic systems [VVM salt – SAC] were studied at 403K and a pressure 0.4–0.45 MPa. The concentration of VVM salt was $1,0 \cdot 10^{-3}$ mol / L. The mass ratio of VVM salt / SAC was 1/1. As VVM salts were used industrial catalysts – cobalt naphthenate (NC) and cobalt acetate (AC).

The results obtained in the oxidation of ethylbenzene in the presence of catalytic systems [NC – SAC; AK – SAC] were compared with those indicators that have been achieved in the oxidation of ethylbenzene in the presence of individual industrial catalyst under the same conditions.

As SAC were used: polyethylene glycol (PG), chromoxane (Ch) and cyanethyl ether (CEE).

HPEB concentration was determined tytremetrycly, concentration of acetophenone (AP) and methylphenylcarbinol (MPC) – by gas-liquid chromatography.

Results and Discussion. At beginning it was logical to determine the impact of industrial catalysts (NC and AC) at course of liquid-phase oxidation of ethylbenzene [4].

Table 1

Influence of catalysts at liquid-phase ethylbenzene oxidation.

P = 0.4-0.45 MPa, T = 403 K

Cat	t, min	C(HPEB) mol/l	C(AP) mol/l	C(MPC) mol/l	Conversion EB	S (AP)	S (MPC)	S (HPEB)
Thermal	10	0.0065	traces	Traces	0.08	-	-	-
	60	0.007	traces	Traces	0.09	-	-	-
	180	0.014	traces	Traces	0.17	-	-	-
	240	0.015	traces	Traces	0.18	-	-	-
NC	10	0,0055	0,0107	0,00328	0,24	54,93	16,84	28,23
	60	0,028	0,0299	0,01144	0,85	43,12	16,50	40,38
	180	0,0675	0,0887	0,01816	2,15	50,87	10,42	38,71
	240	0,067	0,1307	0,02584	2,75	58,47	11,56	29,971
AC	10	0,007	0,0146	0,00184	0,29	62,29	7,85	29,86
	60	0,009	0,6025	0,1908	9,87	75,10	23,78	1,12
	180	0,017	0,8745	0,1236	12,49	86,15	12,18	1,67
	240	0,019	1,2745	0,1492	17,75	88,34	10,34	1,32

As it can be seen from Table 1, both industrial catalysts significantly accelerate oxidation of EB. However, it is worth noting the difference in the mechanisms of influence of catalysts. Most energetically favorable route of EB oxidation is oxidation to ketone (AP). Thus the use of AC can significantly accelerate the direct reaction of oxidation. AC forms the active catalytic complex with organic substrate, meaning reaction with HPEB instead of EB (concentration of HPEB – commensurate with the concentration of HPEB during thermal oxidation).

Mechanism of NC influence favors to formation of the active catalytic complex [NC – organic substrate] that promotes HPEB formation shifting selectivity and directing its energy on less favorable route.

HPEB and AP are valuable intermediate products of organic synthesis, so it would be logical to examine impact of SAC of different nature as catalytic additives for both catalysts.

**Oxidation of ethylbenzene in the presence of binary catalytic systems
[VVM salt – SAC]. P=0.4-0.45 MPa, T=403 K. VVM salt –NC**

Cat	t, min	C (HPEB) mol/l	C (AP) mol/l	C (MPC) mol/l	Conversion EB	S (AP)	S (MPC)	S (HPEB)
NC	10	0,006	0,011	0,003	0,24	54,93	16,84	28,23
	60	0,028	0,03	0,011	0,85	43,12	16,50	40,38
	180	0,068	0,089	0,018	2,15	50,87	10,42	38,71
	240	0,067	0,131	0,026	2,75	58,47	11,56	29,97
NC+PG	10	0,012	0,012	0,0009	0,3	49,50	2,66	47,84
	60	0,055	0,036	0,0013	1,13	39,12	1,48	59,39
	180	0,124	0,08	0,0052	2,58	38,33	2,48	59,19
	240	0,157	0,227	0,051	5,35	52,16	11,76	36,08
NC+Ch	10	0,012	0,013	0,004	0,35	44,44	13,89	41,67
	60	0,042	0,032	0,005	0,98	40,28	6,85	52,87
	180	0,069	0,207	0,006	3,46	73,44	2,02	24,54
	240	0,087	0,259	0,006	4,31	73,71	1,62	24,67
NC+CEE	10	traces	0,013	0,004	0,19	76,19	23,81	traces
	60	Traces	0,022	0,006	0,33	79,77	20,23	traces
	180	Traces	0,039	0,009	0,9	80,07	9,93	traces
	240	Traces	0,047	0,012	0,72	79,23	20,77	traces

Obtained data (Tab. 2) showed that in the presence of the catalytic system [NC-PG] increases rate of HPEB reduction, indicating that the presence of PG increases the amount of dissolved oxygen in the system. However, given that the impact of the catalytic system on oxidation is less than combined impacts of NC and PG usages we can assume that in the reaction mixture there is reaction of complexation involving NC and PG and a catalyst for oxidation in this case is not an individual compound but complex between VVM salt and organic additive. Another characteristic of PG as catalytic additive usage is that the maximum of HPEB concentration in the reaction mixture is achieved earlier comparing to individual NC and/or thermal oxidation of EB.

Application of PG as catalytic additive shifts the ratio of alcohol (MPC) / ketone (AP) to formation of alcohol (compared with NC). Also in the presence of a binary catalytic system [PG – NC] there is an increase of HPEB concentration in reaction products and also increase of selectivity for HPEB (compared with other studied systems) that allows to recommend the use of the mentioned catalytic system for the process of HPEB obtaining followed by its usage in Halkon – process.

Usage of Ch as catalytic additive to NC increases average rate of accumulation of reaction products. Ch affects the ratio of an oxidizing and reducing catalyst forms shifting the balance toward the formation of Co^{3+} , which in its own turn increases the molecular component in the process of oxidation. In this case, during comparison of catalytic additives impacts we should noted that unlike PG main product of oxidation in this case is Ap, and the number of formed HPEB approximately corresponds to the number of HPEB formed in NC catalyzed process. Ch as catalytic additive shifts the equilibrium toward the formation of ketone, and it allows to recommend usage of catalytic systems [NC – Ch] in the process of AP obtaining.

The results obtained in the application of the system [NC – CEE] also correspond to the literature data as CEE contains a triple bond, and its structure inhibits oxidation.

According to the data presented in Tables 1 and 3 application of AC as a catalyst increases the rate of EB oxidation and allows to achieve conversion above 15 %. At the same time, increase of oxidation speed is achieved due to the growth of secondary oxidation products (AP and MPC) formation rate. HPEB formation rate thus is reduced compared with the use of NC.

During usage of [AC – PG] catalytic system, despite the fact that a relative constant of accumulation of reaction products is almost unchanged, the relative speed of accumulation is reduced, compared to the oxidation of ethylbenzene in presence of individual AC. This can be explained by formation of inactive complex [PG – AC – substrate] that subsequently hardly participates in the oxidation reaction.

**Oxidation of ethylbenzene in the presence of binary catalytic systems
[VVM salt – SAC]. P=0.4-0.45 MPa, T=403 K. VVM salt –AC**

Cat	t, min	C (HPEB) mol/l	C (AP) mol/l	C (MPC) mol/l	Conversion EB	S (AP)	S (MPC)	S (HPEB)
AC	10	0,007	0,015	0,0018	0,29	62,29	7,85	29,86
	60	0,009	0,603	0,191	9,87	75,10	23,78	1,12
	180	0,017	0,875	0,124	12,49	86,15	12,18	1,67
	240	0,019	1,275	0,149	17,75	88,34	10,34	1,32
AC+PG	10	0,006	0,012	0,0006	0,22	65,39	3,61	31,00
	60	0,013	0,021	0,005	0,47	53,42	12,86	33,71
	180	0,017	0,05	0,008	0,91	66,89	10,23	22,88
	240	0,017	0,191	0,041	3,05	76,85	16,30	6,86
AC+Ch	10	0,007	0,014	0,0014	0,28	62,50	6,25	31,25
	60	0,01	0,625	0,201	10,28	74,76	24,04	1,20
	180	0,022	0,953	0,196	14,40	81,38	16,74	1,88
	240	0,022	1,374	0,211	19,77	85,50	13,13	1,37

Comparing the data obtained in the presence of an individual AC and [AC – PG] system shows that the speed and the number of formed HPEB almost doesn't change. This fact can be put forward to confirm the assumption that the AC affects the oxidation at stage of HPEB oxidation and not reacting thus with ethylbenzene. At the same time, data obtained during the study of the effect of the system [AC – PG] in demonstrates impact of ligand surrounding not only at catalyst activity, but at mechanism of its participation in the reactions in general.

The use of catalytic system [AC – Ch] achieves 19 % EB conversion. Comparing the behavior of catalytic systems [NC – Ch] and [AC – Ch] we can see that the impact of Ch as catalytic additive remains unchanged, namely – creation of active catalytic complex, which accelerates the reaction of ethylbenzene oxidation by the main route.

Conclusions. On the basis of the research the following conclusions and assumptions can be made:

1. New experimental results which allow to solve specific scientific and applied problems – to develop highly effective catalytic systems for ethylbenzene oxidation process – were obtain.
2. A new binary selective catalytic systems for liquid-phase ethylbenzene oxidation process based on NC, AC and organic modifiers of different nature – PG and Ch (allowing to improve technical and economic performance compared to commercially by increasing process performance, selectivity the targeted products and adjusting their composition) were created. In the case of a binary system [NC – PG] reaction volume performance by HPEB increased by 90 % compared with individual NC.
3. New data on the impact of modifier nature, its quantitative characteristics and value components in binary catalytic systems was obtained. It is shown that the use of catalytic systems leads to increased of accumulation of oxidation products rates compared to industrial catalysts oxidation.

1. Melnyk Y. R., Reutskyy V. V., Mokryj E. M. *The influence of crown ethers by catalytic oxidation of cyclohexane // Reports of NAS of Ukraine, 1(2001), 154–157.* 2. Melnyk Y. R., Reutskyy V. V., Mokryj E. M. *Influence of polyglycols on catalytic oxidation of cyclohexane // Bulletin of NU “Lvivska politechnika”. Chemistry, technology of materials and their applications. – 2001. – 426, – P. 91–94.* 3. Emanuel N. M., Gal D. *Oxidation of ethylbenzene. (Model Reaction). – M.: Nauka, 1984. – 376 p.* 4. Reutskyy V. V., Melnyk Yu. R., Starchevskyy V. L. *Influence of surface-active matters on ethylbenzene oxidation // Book of abstracts of 17 th International Symposium on Homogeneous Catalysis. Poznan, Poland, 2010, p. 201.* 5. Haifeng Xiong, Yuhua Zhang, Kongyong Liew, Jinlin Li *Ruthenium promotion of Co/SBA catalysts with high cobalt loading for Fisher-Tropsh synthesis // Fuel Processing Technology, 90, Issue 2(2009). – P. 237–246.* 6. Shanghong Zeng, Dongping Du, Fenghua Bai, Haiquan Su *Bridging complexes of rare earth and cobalt cluster as catalyst precursor for Fisher-Tropsh synthesis. // Journal of Rare Earths, 29, Issue 4(2011), 349-353* 7. Cancheng Guo, Quingjing Peng, Qiang Liu *Selective oxidation of ethylbenzene with air catalyzed by simple μ -oxo dimeric metalloporphyrins under mild conditions in the absence of additives. // Journal of Molecular Catalysis A: Chemical, 192, Issues 1-2(2003), 295-302.*

8. M. Arshadi, M. Ghiaci, A. Rahmadian, H. Ghaziaskar, A. Gil Oxidation of ethylbenzene to acetophenone by a Mn catalyst supported on a modified nanosized $\text{SiO}_2/\text{Al}_2\text{O}_3$ mixed-oxide in supercritical carbon dioxide. // *Applied Catalysis B: Environmental*, 119–120 (2012), 81–90 9. Xiao Gang Li, Jing Wang, Ren He Selective oxidation of ethylbenzene catalyzed by fluorinated metalloporphyrins with molecular oxygen // *Chinese Chemical Letters*, 18, Issue 9 (2007), 1053–1056 10. Ahmadreza Esmaeilbeig, Hamidreza Samouei, Sedigheh Abedanzadeh, Zahra Amirghofran Synthesis, characterization and antitumor activity study of some cyclometalated organoplatinum(II) complexes containing aromatic N-donor ligands. // *Journal of Organometallic Chemistry*, 696, Issue 20 (2011), 3135–3142.

УДК 539.232

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ГІДРОХІМІЧНИЙ СИНТЕЗ ТОНКИХ ПЛІВОК ЦИНКУ СЕЛЕНІДУ (ZnSe) В ПРИСУТНОСТІ НАТРІЮ ГІДРОКСИДУ ТА ЇХНІ ВЛАСТИВОСТІ

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Тонкі плівки цинку селеніду (ZnSe) синтезовано з водного розчину натрію гідроксиду на скляних підкладках. Методом інверсійної вольтамперометрії встановлено вплив концентрації вихідної цинк-вмісної солі, комплексуючого реагенту натрію гідроксиду, іонів Селену та гідразину гідрату на масу Цинку в плівках ZnSe за різної тривалості і температури осадження. На основі отриманих даних оптимізовано умови синтезу тонких плівок цинку селеніду. Досліджено структуру, оптичні властивості, морфологію поверхні, атомний склад, товщину отриманих плівок ZnSe.

Ключові слова: цинку селенід, плівка, хімічне осадження, морфологія поверхні, інверсійна вольтамперометрія.

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HYDROCHEMICAL SYNTHESIS OF ZINC SELENIDE (ZnSe) THIN FILMS AT THE PRESENCE OF SODIUM HYDROXIDE AND THEIR PROPERTIES

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Zinc selenide (ZnSe) thin films were synthesized on glass substrates from an aqueous solution of sodium hydroxide. The concentration effect of zinc-containing salt, complexing agent of sodium hydroxide, selenium and hydrazine hydrate on the zinc mass in ZnSe films was set at various deposition time and temperature by the stripping voltammetry method. The synthesis conditions of zinc selenide thin films were optimised. The crystal structure, optical properties, surface morphology, atomic composition, thickness of obtained ZnSe films were studied.

Key words: zinc selenide, film, chemical deposition, surface morphology, stripping voltammetry.

Постановка проблеми. Цинку селенід (ZnSe) є важливим II–IV напівпровідником з шириною забороненої зони 2,68 eV. Він має перспективи застосування у виготовленні світловипромінюючих лазерних діодів, оптичних детекторів, недорогих сонячних батарей та інших оптоелектронних