

Ludmila Matienko, Larisa Mosolova, Vladimir Binyukov and Gennady Zaikov

CATALYTIC ACTIVITY OF BINARY AND TRIPLE SYSTEMS BASED ON REDOX INACTIVE METAL COMPOUND, LiSt AND ADDITIVES OF MONODENTATE LIGANDS-MODIFIERS: DMF, HMPA AND PhOH, IN SELECTIVE ETHYLBENZENE OXIDATION WITH DIOXYGEN

Emanuel Institute of Biochemical Physics, Russian Academy of Sciences,
4, Kosygin St., 119334 Moscow, Russia; matienko@sky.chph.ras.ru

Received: December 01, 2014 / Revised: December 09, 2014 / Accepted: June 01, 2015

© Matienko L., Mosolova L., Binyukov V., Zaikov G., 2016

Abstract. Mechanism of catalysis with binary and triple catalytic systems based on redox inactive metal (lithium) compound $\{\text{LiSt}+\text{L}^2\}$ and $\{\text{LiSt}+\text{L}^2+\text{PhOH}\}$ ($\text{L}^2=\text{DMF}$ or HMPA), in the selective ethylbenzene oxidation by dioxygen into α -phenylethyl hydroperoxide is researched. The results are compared with catalysis by nickel-lithium triple system $\{\text{Ni}^{\text{II}}(\text{acac})_2+\text{LiSt}+\text{PhOH}\}$ in selective ethylbenzene oxidation to PEH. The role of H-bonding in mechanism of catalysis is discussed. The possibility of the stable supramolecular nanostructures formation on the basis of triple systems, $\{\text{LiSt}+\text{L}^2+\text{PhOH}\}$, due to intermolecular H-bonds, is researched with the AFM method.

Keywords: nanostructure, binary and triple catalytic systems, H-bonds, catalysis, ethylbenzene, oxidation, dioxygen, α -phenylethyl hydroperoxide.

1. Introduction

The problem of selective oxidation of alkylarenes to hydroperoxides is economically sound. Hydroperoxides are used as intermediates in the large-scale production of important monomers. For instance, propylene oxide and styrene are synthesized from α -phenylethyl hydroperoxide, and cumyl hydroperoxide is the precursor in the synthesis of phenol and acetone [1]. The method of modifying the Ni^{II} and $\text{Fe}^{\text{II,III}}$ complexes used in the selective oxidation of alkylarenes (ethylbenzene and cumene) with molecular oxygen to afford the corresponding hydroperoxides aimed at increasing their selectivity has been first proposed by L. Matienko [2, 3]. This method consists of introducing additional mono- or multidentate modifying ligands into catalytic metal complexes. The mechanism of action of such modifying

ligands was elucidated. New efficient catalysts of selective oxidation of ethylbenzene to α -phenylethyl hydroperoxide were developed [2, 3].

The phenomenon of a substantial increase in the selectivity (S) and conversion (C) of the ethylbenzene oxidation to the α -phenylethyl hydroperoxide upon addition of PhOH together with alkali metal stearate MSt ($M = \text{Li}, \text{Na}$) as ligands to metal complexes $\text{Ni}^{\text{II}}(\text{acac})_2$ was discovered in our works (Fig. 1) [3, 4].

In this case the observed values of C [$C > 35\%$ at $(S_{\text{PEH}})_{\text{max}} = 85\text{--}87\%$], $[\text{ROOH}]_{\text{max}}$ (1.6–1.8 mol/l) far exceeded those obtained with the other triple catalytic systems $\{\text{Ni}^{\text{II}}(\text{acac})_2 + \text{L}^2 + \text{PhOH}\}$ (L^2 is N-methyl-2-pyrrolidone (MP), hexamethylphosphorotriamide (HMPA),) and the majority of active binary systems. These results are protected by the Russian Federation patent №2237050, 2004 (Priority from 2002).

The advantage of these triple systems is the long-term activity of the *in situ* formed complexes $\text{Ni}^{\text{II}}(\text{acac})_2 \cdot \text{L}^2 \cdot \text{PhOH}$. The high efficiency of three-component systems that introduced compound of redox inactive metal, $\{\text{Ni}^{\text{II}}(\text{acac})_2 + \text{MSt} + \text{PhOH}\}$ ($M = \text{Na}, \text{Li}$), in the reaction of selective oxidation of ethylbenzene to α -phenylethyl hydroperoxide was associated with the formation of extremely stable binuclear heteroligand complexes $\text{Ni}(\text{acac})_2 \cdot \text{MSt} \cdot \text{PhOH}$ due to intermolecular H-bonds [4, 5].

We have proposed a new approach to research the possibility of supramolecular structures formation based on catalytic active nickel complexes [6], including $\text{Ni}^{\text{II}}(\text{acac})_2 \cdot \text{MSt} \cdot \text{PhOH}$ ($M = \text{Na}, \text{Li}$) due to H-bonds, and at first with the AFM method we have received the evidence in favor of this hypothesis [6, 7]. In the present work we examined catalysis with triple system $\{\text{LiSt}+\text{L}^2+\text{PhOH}\}$ ($\text{L}^2=\text{DMF}$), based on compound of

redox inactive metal only, in ethylbenzene oxidation to PEH. We researched the possibility of supramolecular structures formation based on triple system including Li-contained compounds, in comparison with action of analogical systems based on Ni-complex – $\{\text{Ni}^{\text{II}}(\text{acac})_2 + \text{L}^2 + \text{PhOH}\}$ ($\text{L}^2 = \text{MSt}$ ($\text{M} = \text{Na}, \text{Li}$), DMF, HMPA) [4, 5].

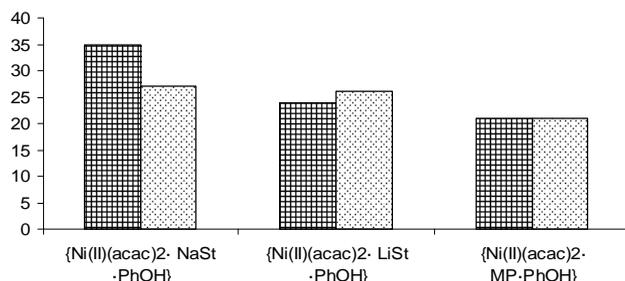


Fig. 1. Values of conversion C (%) (I row), maximum values of hydroperoxide concentrations $[\text{PEH}]_{\text{max}}$ (mas %) (II row) in reactions of ethylbenzene oxidation in the presence of triple catalytic systems $\{\text{Ni}^{\text{II}}(\text{acac})_2 + \text{L}^2 + \text{PhOH}\}$ ($\text{L}^2 = \text{NaSt}, \text{LiSt}, \text{MP}$. $[\text{Ni}^{\text{II}}(\text{acac})_2] = [\text{NaSt}] = [\text{LiSt}] = [\text{PhOH}] = 3.0 \cdot 10^{-3}$ mol/l, $[\text{MP}] = 7 \cdot 10^{-2}$ mol/l, 393 K

Often metals of constant valency compounds are used in combination with redox-active transition-metal complexes to promote a variety of reactions involving the transfer of electrons. It was reported that rates of O_2 reduction by Mn^{II} complex are accelerated in the presence of group 2 metal ions [8]. This effect is typified in metalloproteins such as the copper zinc superoxide dismutase, in which both metal ions have been proposed to be functionally active [8].

It is known also [9] that compounds of redox inactive metals are used in many cases as catalysts for oxidation of hydrocarbons. Earlier we have researched the possibility of activating alkali metals compounds with additions of modifying ligands [10]. We established the positive effects of monodentate electron donating ligands HMPA and DMF on the rate, selectivity, max concentration PEH, and conversion of ethylbenzene oxidation to PEH, catalyzed with LiSt [10]. In the present article we will examine our new data on catalysis with triple systems $\{\text{LiSt} + \text{L}^2 + \text{PhOH}\}$ ($\text{L}^2 = \text{DMF}$) and will generalize these data with results received by us earlier and in the present article, on mechanism of catalysis with binary systems $\{\text{LiSt} + \text{L}^2\}$ ($\text{L}^2 = \text{DMF}, \text{HMPA}$), and also triple system, based on nickel complex $\{\text{Ni}^{\text{II}}(\text{acac})_2 + \text{LiSt} + \text{PhOH}\}$, in reactions of selective ethylbenzene oxidation to PEH.

2. Experimental

Ethylbenzene (RH) was oxidized with dioxygen at 393 K in glass bubbling-type reactor [5] in the presence of

LiSt and also binary $\{\text{LiSt} + \text{DMF}\}$ or triple $\{\text{LiSt} + \text{DMF} + \text{PhOH}\}$ systems.

HMPA and DMF were cleared with vacuum distillation above the CaO .

LiSt was got by adding of hot water solution of LiOH (brands of Ch.Cl.) to the heated spirit solution of HSt (brands of Ch.Cl.). The got LiSt solution was filtered, washed with hot water and dried in a vacuum at 293 K to permanent weight.

Analysis of oxidation products. *a*-Phenylethyl hydroperoxide (PEH) was analyzed by iodometry. By-products, including methylphenyl carbinol (MPC), acetophenone (AP), and phenol (PhOH) as well as the RH content in the oxidation process were examined by GLC [5].

An order in which PEH, AP, and MPC formed was determined from the time dependence of product accumulation rate ratios at $t \rightarrow 0$. The variation of these ratios with time was evaluated by graphic differentiation ([4], see Figs. 2 and 3). Experimental data processing was done using special computer programs Mathcad and Graph2Digit.

AFM SOLVER P47/SMENA/ with Silicon Cantilevers NSG11S (NT MDT) with curvature radius of 10 nm, tip height: 10–15 μm and cone angle $\leq 22^\circ$ in tapping mode on resonant frequency 150 KHz was used [6].

The polished silicone surface special chemically modified was used as substrate.

Waterproof modified silicone surface was exploit for the self-assembly-driven growth due to H-bonding of complexes $\text{LiSt} \cdot \text{HMPA} \cdot \text{PhOH}$ (1:1:1) with silicone surface. The saturated chloroform (CHCl_3) solution of complex $\text{LiSt} \cdot \text{HMPA} \cdot \text{PhOH}$ was put on a surface, maintained for some time, and then solvent was deleted from a surface by means of special method – spin-coating process.

In the course of scanning of investigated samples it has been found that the structures are fixed on a surface strongly enough due to H-bonding. The self-assembly-driven growth of the supramolecular structures on modified silicone surface on the basis of complexes $\text{LiSt} \cdot \text{HMPA} \cdot \text{PhOH}$ (1:1:1), and also $\text{LiSt} \cdot \text{HMPA}$, or $\text{LiSt} \cdot \text{PhOH}$, due to H-bonds and perhaps the other non-covalent interactions, was researched.

3. Results and Discussion

3.1. Catalysis with LiSt and with Binary System $\{\text{LiSt} + \text{L}^2\}$ ($\text{L}^2 = \text{DMF}, \text{HMPA}$) in Ethylbenzene oxidation by Dioxygen

Earlier we have researched the effect of DMF and HMPA on the kinetics of ethylbenzene oxidation with dioxygen in the presence of LiSt at 393 K [10]. The

concentration of LiSt has varied within the interval $(0.1-1.0) \cdot 10^{-2}$ mol/l. It was not possible to raise the concentration of LiSt above $1.0 \cdot 10^{-2}$ mol/l due to difficult solubility of LiSt in ethylbenzene.

First of all in the presence of the LiSt catalyst increasing in initial rate of accumulation of PEH was observed, similar to the influence of metal compounds of constant valency [11]. The rates of the accumulation of other oxidation products of AP and MPC were falling compared with no catalyzed ethylbenzene oxidation. This is possibly due to the decreasing in the chain decomposition of PEH in the presence of constant valence metal salts. Unlike no catalyzed ethylbenzene oxidation, in reactions of ethylbenzene oxidation in the presence of the LiSt the phenol was formed in relatively small concentrations $\cong 1.0 \cdot 10^{-2}$ mol/l at deep stages of ethylbenzene oxidation. Other oxidation products in concentrations compared with PEH, AP, MPC, and PhOH, were not found. $\sum[P] = \Delta[RH]$ ($\sum[P] = [PEH] + [AP] + [MPC] + [PhOH]$).

The initial rate of oxidation of ethylbenzene, w_0 , in the presence of the LiSt is increased slightly from $(2.0 \pm 0.2) \cdot 10^{-6}$ mol \cdot l $^{-1}$ s $^{-1}$ (without Cat) to $(3.5 \pm 0.3) \cdot 10^{-2}$ mol \cdot l $^{-1}$ s $^{-1}$ ([LiSt] = $1.0 \cdot 10^{-3}$ mol/l) and to $(6.8 \pm 0.3) \cdot 10^{-6}$ mol \cdot l $^{-1}$ s $^{-1}$ ([LiSt] = $1.0 \cdot 10^{-2}$ mol/l). Selectivity of oxidation of ethylbenzene into PEH takes about $S_{PEH} \approx 90-92\%$ at the conversion of oxidation $C \approx 5\%$ (Fig. 2c), that is substantially higher than in no catalyzed oxidation ($S_{PEH} \approx 80-75\%$) at the same conversion.

This is the first time we have shown that the use of additives of electron donating ligands L^2 allows under certain conditions to considerably improve the properties of LiSt (and also NaSt, and KSt) as catalysts for ethylbenzene oxidation into PEH [10]. For example, in the presence of additions of HMPA or DMF we observed the synergetic increasing in initial w_0 (Fig. 3) and growth of conversion of ethylbenzene oxidation into PEH ($C \sim 16-20\%$ at the conservation of selectivity not less than $S_{PEH} \sim 90-93\%$, catalyzed with LiSt [10]).

Later activities of the donor additives were confirmed in [12] on example of ethylbenzene oxidations in the presence of the other catalytic systems {cadmium or zinc compounds with *o*-phenantroline}.

Dependence of initial rates w_0 on $[L^2]$ ([LiSt] = = const) at catalysis with system {LiSt + L^2 } has extreme character (Table 1 [10]), as at catalysis with systems including transition metal compounds $\{M(\text{acac})_n + L^2\}$ ($M = Ni^{II}, Co^{II}, Fe^{III}$) [3, 4]. This, apparently, can also be explained by the influence of degree of saturation of the coordination sphere with electron donating ligands L^2 on the catalytic activity of metal complexes.

One can see from Table 1 that the maximum rate of ethylbenzene oxidation, w_0 , in the presence of catalytic system {LiSt+HMPA} far surpasses (14 times and in the case of {LiSt+DMF} – ~ 5 times) the rate of oxidation catalyzed by the LiSt.

As in the case of catalysis with $Ni^{II}(\text{acac})_2$, additives of HMPA increase the activity (w_0) of LiSt to a greater extent than additives of DMF, which is consistent with the values of the donor numbers of these ligands HMPA(DN = 155.2 kJ/mol) > DMF(DN = 106.4 kJ/mol) [4].

Increase in activity of LiSt (growth of w_0) in ethylbenzene oxidation in the presence of additives of HMPA or DMF can be associated with the destruction of the associates [13, 14], for example, $(LiSt)_n$ ($n \geq 2$). Associates are able to be less active in the oxidation reactions compared with the monomer form of catalyst [13]. However, the synergetic growth of w_0 (14 times in the presence of HMPA or ~ 5 times in the case of DMF additives) suggest that the role of these ligands at initial stages of catalytic oxidation is not only in the destruction of the associates [15]. In all probability, the primary function of donor ligands HMPA or DMF is to control activity of formed complexes $LiSt \cdot L^2$ in reactions of chain initiation (O_2 activation), homolytic decomposition of PEH and, perhaps, chain propagation $Cat + RO_2^{\bullet} \rightarrow$.

Table 1

The initial rates of ethylbenzene oxidation in the presence of LiSt ($1.0 \cdot 10^{-2}$ M) and various additives of HMPA and DMF [10]

$L^2, \text{mol/l} \cdot 10^3$	HMPA, $w_0 \cdot 10^5, \text{mol} \cdot \text{l}^{-1} \text{s}^{-1}$	DMF, $w_0 \cdot 10^5, \text{mol} \cdot \text{l}^{-1} \text{s}^{-1}$
–	0.68 ± 0.3	
0.5	2.8 ± 0.3	
1.0	4.9 ± 0.2	1.9 ± 0.1
2.0	5.4 ± 0.1	
3.0		2.4 ± 0.2
4/0	9.4 ± 0.7	
5.0		3.3 ± 0.1
10.0	4.4 ± 0.2	2.6 ± 0.1

3.2. Mechanism of Catalysis with Triple $\{\text{LiSt}+\text{L}^2+\text{PhOH}\}$ ($\text{L}^2 = \text{DMF}$) and Binary $\{\text{LiSt}+\text{L}^2\}$ ($\text{L}^2 = \text{DMF}, \text{HMPA}$) Systems in Ethylbenzene Oxidation with Dioxygen

As mentioned before, the phenomenon of a substantial increase in the selectivity (S) and conversion (C) of the ethylbenzene oxidation to the α -phenylethyl hydroperoxide upon addition of PhOH together with monodantate ligands *N*-methylpyrrolidone-2, HMPA, or alkali metal stearates MSt ($M = \text{Li}, \text{Na}$) as metalloligands to metal complexes $\text{Ni}^{\text{II}}(\text{acac})_2$ was discovered in our works [3, 4].

There are characteristic features for triple systems including metalloligand-modifiers $\text{L}^2 = \text{NaSt}, \text{LiSt}$ (and *N*-methylpyrrolidone-2 (MP), HMPA also) compared with the most active binary systems. The advantage of these triple systems is long-term activity of the *in situ* formed complexes $\text{Ni}^{\text{II}}(\text{acac})_2 \cdot \text{L}^2 \cdot \text{PhOH}$. Unlike binary systems, the acac^- ligand in nickel complex does not undergo transformations in the course of ethylbenzene oxidation in this case. (The formation of triple complexes $\text{Ni}^{\text{II}}(\text{acac})_2 \cdot \text{L}^2 \cdot \text{PhOH}$ at very early stages of oxidation was established with kinetic methods [3-5]). Therefore, the reaction rate remains practically the same during the oxidation process. In the course of oxidation the rates of products accumulation remain unchanged during a long period $t \leq 30\text{--}40$ h (see Fig. 2).

The additives of PhOH to binary system $\{\text{LiSt}+\text{DMF}\}$ change kinetics of products formation in

ethylbenzene oxidation, catalyzed with $\{\text{LiSt}+\text{DMF}\}$, by analogy with catalysis by $\{\text{Ni}^{\text{II}}(\text{acac})_2+\text{MSt}+\text{PhOH}\}$. That is, in the presence of $\{\text{LiSt}+\text{DMF}+\text{PhOH}\}$ (Fig. 3b) the rates of accommodation of oxidation products PEH, AP, MPC remain practically the same during the oxidation process ($\leq 20\text{--}30(40)$ h) unlike the catalysis with binary system $\{\text{LiSt}+\text{DMF}\}$ (Fig. 3a). Interestingly, at catalysis with $\{\text{LiSt}+\text{DMF}+\text{PhOH}\}$ (and $\{\text{LiSt}+\text{DMF}(\text{HMPA})\}$) the oxidation products PEH, AP and MPC are formed with maximum initial rate without the auto acceleration period by analogy with the catalysis with the triple system $\{\text{Ni}^{\text{II}}(\text{acac})_2+\text{LiSt}(\text{NaSt})+\text{PhOH}\}$ (see Fig. 2). At the same time the products PEH, AP, MPC, and PhOH are formed with auto acceleration periods in the case of catalysis with LiSt, or $\{\text{Ni}^{\text{II}}(\text{acac})_2+\text{MP}+\text{PhOH}\}$ (Fig. 2a, curve 2).

At catalysis with triple system $\{\text{LiSt}+\text{DMF}+\text{PhOH}\}$ the parallel formation of α -phenylethyl hydroperoxide (PEH), acetophenone (AP) and methylphenylcarbinol (MPC) was observed ($w_{\text{AP}(\text{MPC})}/w_{\text{PEH}} \neq 0$ at $t \rightarrow 0$, $w_{\text{AP}}/w_{\text{MPC}} \neq 0$ at $t \rightarrow 0$) throughout the reaction of ethylbenzene oxidation at $t \leq 20\text{--}30(40)$ h (see, for example, Figs. 4 a, b and Fig. 5).

Similar kinetics were observed earlier in the case of the catalysis with triple complexes $\text{Ni}(\text{acac})_2 \cdot \text{L}^2 \cdot \text{PhOH}$ ($\text{L}^2 = \text{NaSt}, \text{LiSt}$). α -Phenylethyl hydroperoxide (PEH), acetophenone (AP) and methylphenylcarbinol (MPC) were formed also in parallel during ethylbenzene oxidation ($w_{\text{AP}(\text{MPC})}/w_{\text{PEH}} \neq 0$ at $t \rightarrow 0$, $w_{\text{AP}}/w_{\text{MPC}} \neq 0$ at $t \rightarrow 0$) (see, for example, Fig. 6).

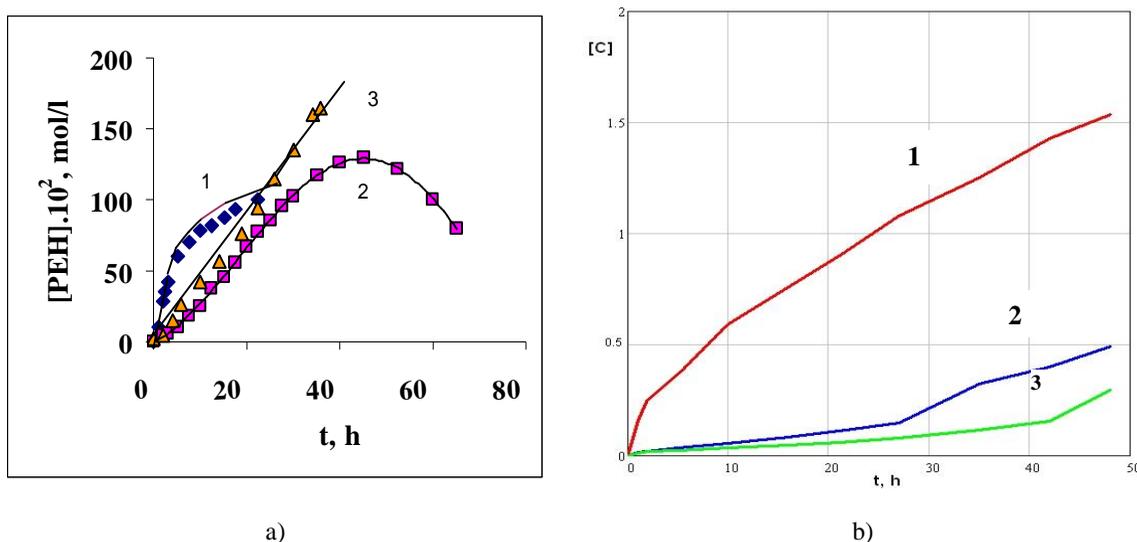


Fig. 2. Kinetics of accumulation of: a) PEH in reactions of ethylbenzene oxidation, catalyzed by binary system $\{\text{Ni}^{\text{II}}(\text{acac})_2+\text{MP}\}$ (1) and two triple systems $\{\text{Ni}^{\text{II}}(\text{acac})_2+\text{L}^2+\text{PhOH}\}$ with $\text{L}^2 = \text{MP}$ (2) and $\text{L}^2 = \text{NaSt}$ (3). $[\text{Ni}^{\text{II}}(\text{acac})_2] = 3 \cdot 10^{-3}$ mol/l, and $[\text{MP}] = 7 \cdot 10^{-2}$ mol/l, $[\text{NaSt}] = 3 \cdot 10^{-3}$ mol/l, $[\text{PhOH}] = 3 \cdot 10^{-3}$ mol/l, 393 K
b) PEH (1), AP (2), MPC (3) in ethylbenzene oxidation, catalyzed by triple system $\{\text{Ni}^{\text{II}}(\text{acac})_2+\text{LiSt}+\text{PhOH}\}$. $[\text{Ni}^{\text{II}}(\text{acac})_2] = 3 \cdot 10^{-3}$ mol/l, $[\text{LiSt}] = 3 \cdot 10^{-3}$ mol/l, $[\text{PhOH}] = 3 \cdot 10^{-3}$ mol/l, 393 K [29]

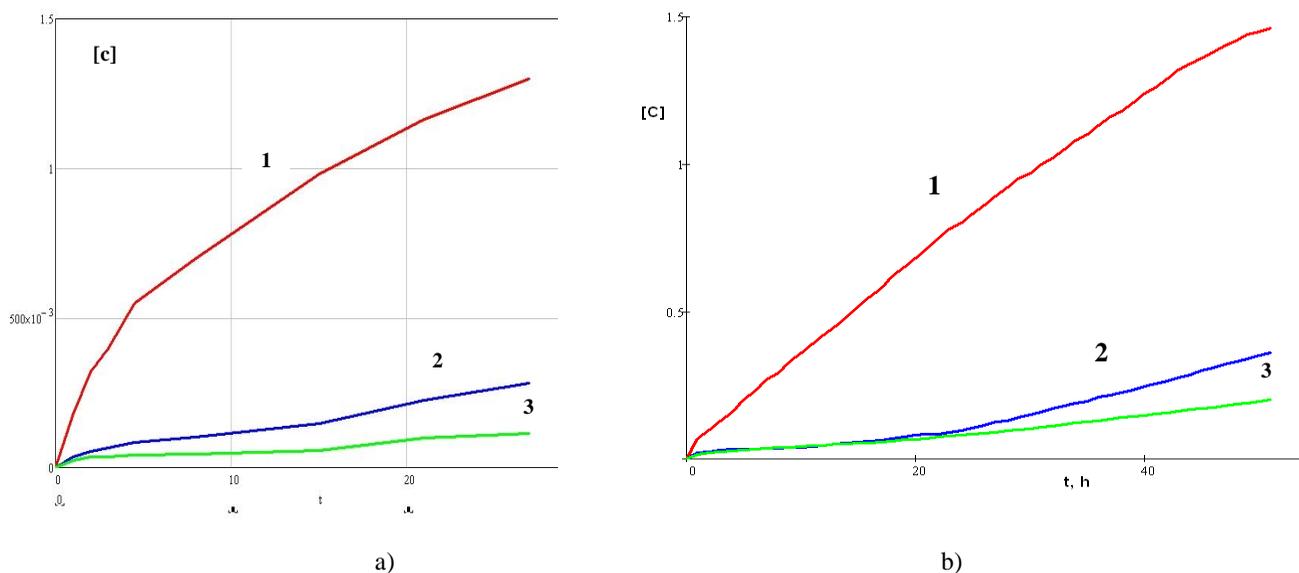


Fig. 3. Kinetics of accumulation of PEH (1), AP (2), MPC (3) in ethylbenzene oxidation, catalyzed by binary {LiSt+DMF} (a) and triple system {LiSt+DMF+PhOH} (b). [LiSt] = $1 \cdot 10^{-2}$ mol/l, [DMF] = $1 \cdot 10^{-2}$ mol/l, [PhOH] = $1.2 \cdot 10^{-2}$ mol/l, 393 K

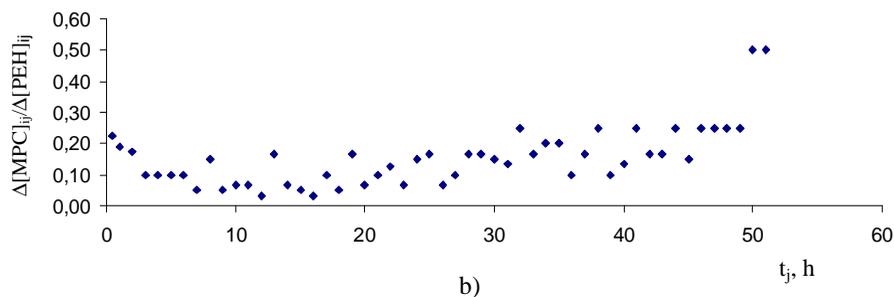
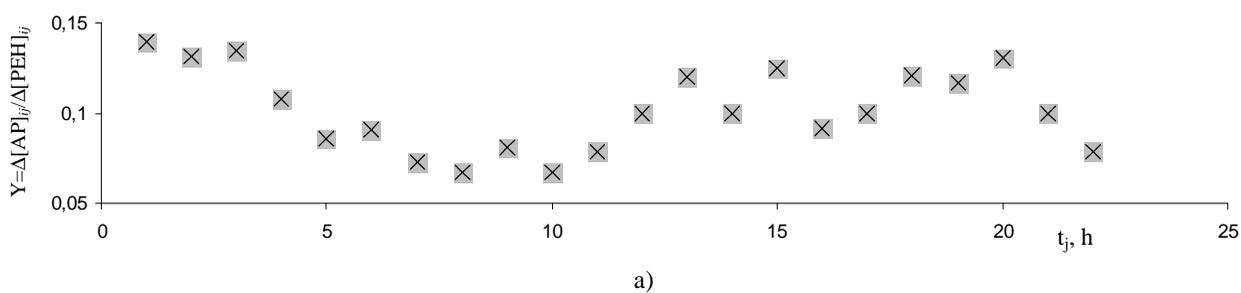


Fig. 4. Dependences $\Delta[AP]_{ij} / \Delta[PEH]_{ij} \cdot 10^2$ (a) and $\Delta[MPC]_{ij} / \Delta[PEH]_{ij} \cdot 10^2$ (b) on time t_j in the course of ethylbenzene oxidation, catalyzed with triple system {LiSt+DMF+PhOH}. [LiSt] = $1 \cdot 10^{-2}$ mol/l, [DMF] = $1 \cdot 10^{-2}$ mol/l, [PhOH] = $1.2 \cdot 10^{-2}$ mol/l, 393 K

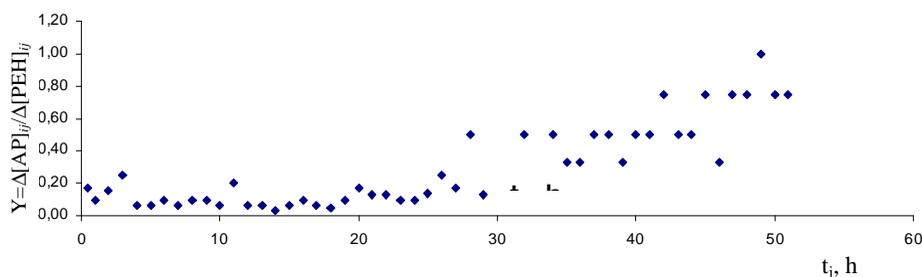


Fig. 5. Dependences $\Delta[AP]_{ij} / \Delta[PEH]_{ij}$ on time t_j in the course of ethylbenzene oxidation catalyzed with triple system {LiSt+DMF+PhOH}. [LiSt] = $1 \cdot 10^{-2}$ mol/l, [DMF] = $1 \cdot 10^{-2}$ mol/l, [PhOH] = $0.8 \cdot 10^{-2}$ mol/l, 393 K

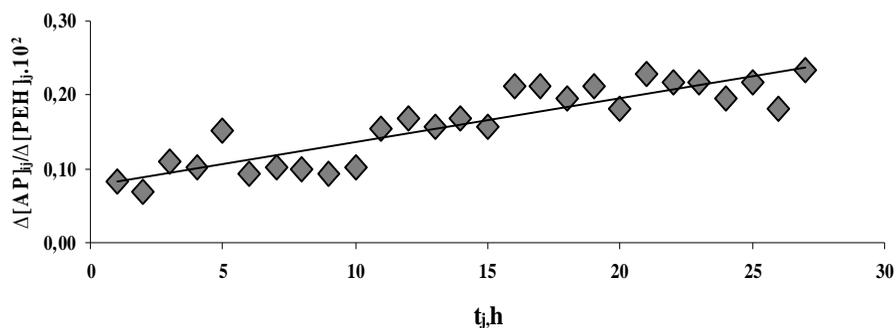


Fig. 6. Dependence $\Delta[AP]_{ij}/\Delta[PEH]_{ij} \cdot 10^2$ on time t_j in the course of ethylbenzene oxidation, catalyzed with complexes $Ni^{II}(acac)_2 \cdot LiSt \cdot PhOH$, 393 K

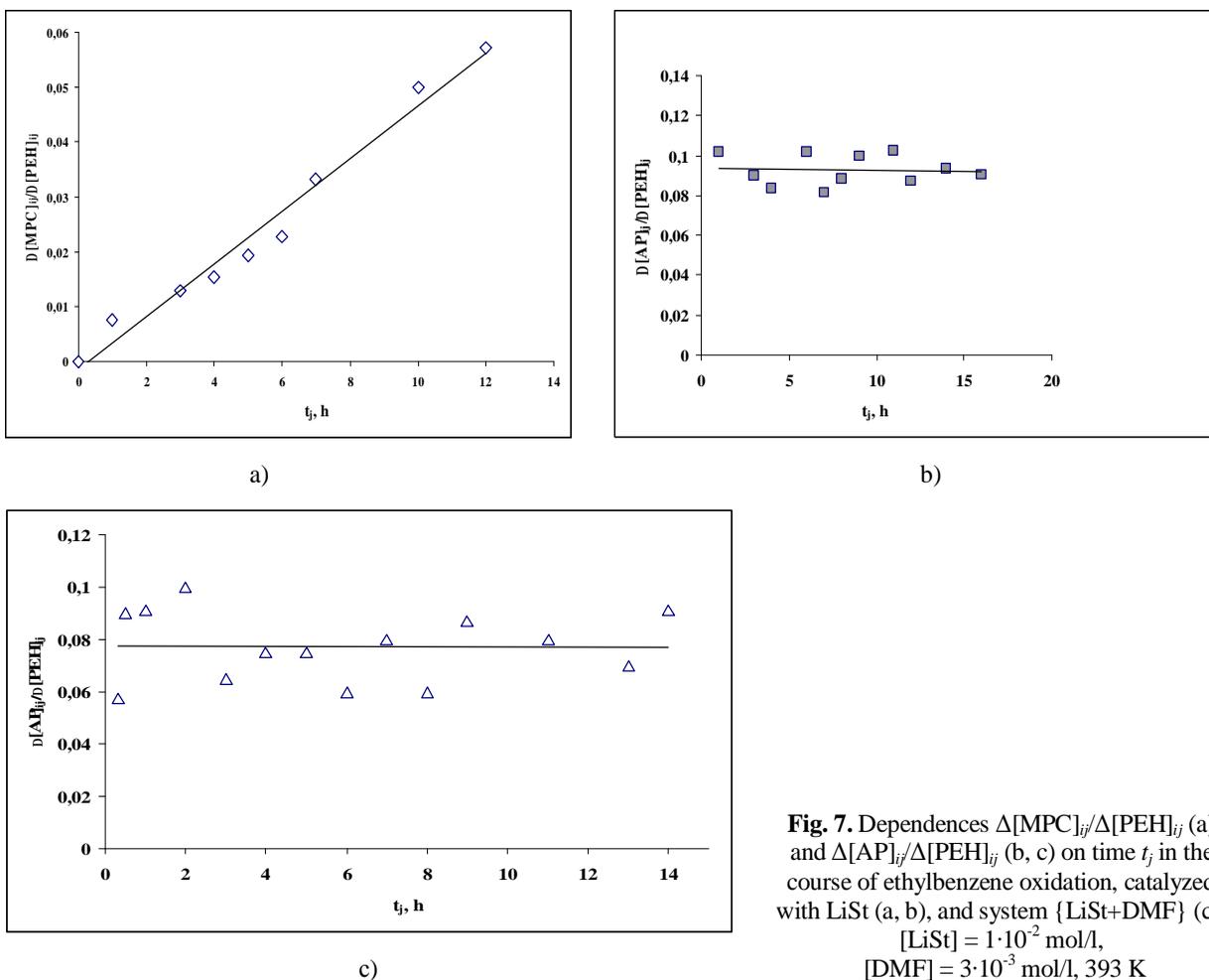


Fig. 7. Dependences $\Delta[MPC]_{ij}/\Delta[PEH]_{ij}$ (a) and $\Delta[AP]_{ij}/\Delta[PEH]_{ij}$ (b, c) on time t_j in the course of ethylbenzene oxidation, catalyzed with LiSt (a, b), and system {LiSt+DMF} (c).
 $[LiSt] = 1 \cdot 10^{-2}$ mol/l,
 $[DMF] = 3 \cdot 10^{-3}$ mol/l, 393 K

The data (Figs. 4-5) point to the next mechanism of acetophenone and methylphenylcarbinol formation in ethylbenzene oxidation in the presence of {LiSt+DMF+PhOH} system: AP and MPC form in parallel with PEH rather than as a result of PEH decomposition by analogy with the catalysis by triple system $Ni^{II}(acac)_2 \cdot L^2 \cdot PhOH$ ($L^2 = LiSt$ (NaSt)) (Fig. 6), and binary system {LiSt+DMF} at the absence PhOH (Fig. 7c) – in the chain propagation at participation of Cat

($Cat + RO_2 \bullet \rightarrow$) and quadratic chain termination ($2RO_2 \bullet \rightarrow$). This is unlike non-catalytic oxidation and catalysis of ethylbenzene oxidation by LiSt (see, for example, Fig. 7a) and binary system $\{Ni^{II}(acac)_2 + MSt\}$. In these reactions AP and MPC are the results of PEH decomposition and quadratic chain termination ($2RO_2 \bullet \rightarrow$) (catalysis by LiSt), and also the chain propagation at participation of Cat ($Cat + RO_2 \bullet \rightarrow$) (catalysis by $\{Ni^{II}(acac)_2 + MSt\}$) [4].

An interesting result was received in the case of ethylbenzene oxidation, catalyzed with LiSt without additives (Fig. 7a, b). Acetophenone AP and hydroperoxide PEH are formed in parallel ($w_{AP}/w_{PEH} \neq 0$ at $t \rightarrow 0$) (Fig. 7b), but MPC is a product of PEH decomposition ($w_{MPC}/w_{PEH} \rightarrow 0$ at $t \rightarrow 0$) during all reaction of oxidation (Fig. 7a). At that AP and MPC are formed in parallel with each other ($w_{AP}/w_{MPC} \neq 0$ at $t \rightarrow 0$). Analogous kinetics of oxidation products: AP formed in parallel with ROOH, but dimethylphenylcarbinol (DMPC) – from ROOH, – we observed in the cumene oxidation, catalyzed with $Ni^{II}(\text{acac})_2$ and system $\{Ni^{II}(\text{acac})_2 + MP\}$ [4].

Additions of ligand-modifier of DMF ($[DMF] = (3-10) \cdot 10^{-3}$ mol/l) in the reaction of ethylbenzene oxidation, catalyzed with LiSt, change the mechanism of formation of MPC. In this case at catalysis with complex LiSt·DMF both products, AP and MPC, appear in parallel

with PEH. At this parallelism of formation of AP and MPC also takes place. The analogical mechanism was established for catalysis with the system $\{LiSt + HMPA\}$: $w_{AP(MPC)}/w_{PEH} \neq 0$ at $t \rightarrow 0$, $w_{AP}/w_{MPC} \neq 0$ at $t \rightarrow 0$.

Earlier we have established that concentration of PhOH at catalysis with system $\{Ni^{II}(\text{acac})_2 (3.0 \cdot 10^{-3}$ mol/l) + LiSt (NaSt) ($3.0 \cdot 10^{-3}$ mol/l) + PhOH ($3.0 \cdot 10^{-3}$ mol/l) $\}$, as well as at catalysis with similar system $\{Ni^{II}(\text{acac})_2 (3.0 \cdot 10^{-3}$ mol/l) + MP ($7.0 \cdot 10^{-2}$ mol/l) + PhOH ($3.0 \cdot 10^{-3}$ mol/l) $\}$ including MP as donor exo ligand L^2 , decreases during the first hours of oxidation (see, for example, Fig. 8a) [3-5, 7]. Similar results were obtained in the case of ethylbenzene oxidation with molecular oxygen at catalysis with triple system $\{LiSt + DMF + PhOH\}$ (Fig. 8b). These changes in PhOH concentrations seem to be due to the triple complexes $Ni^{II}(\text{acac})_2 \cdot L^2 \cdot PhOH$ formation [3-5, 7] and point to triple complexes LiSt·DMF·PhOH formation also.

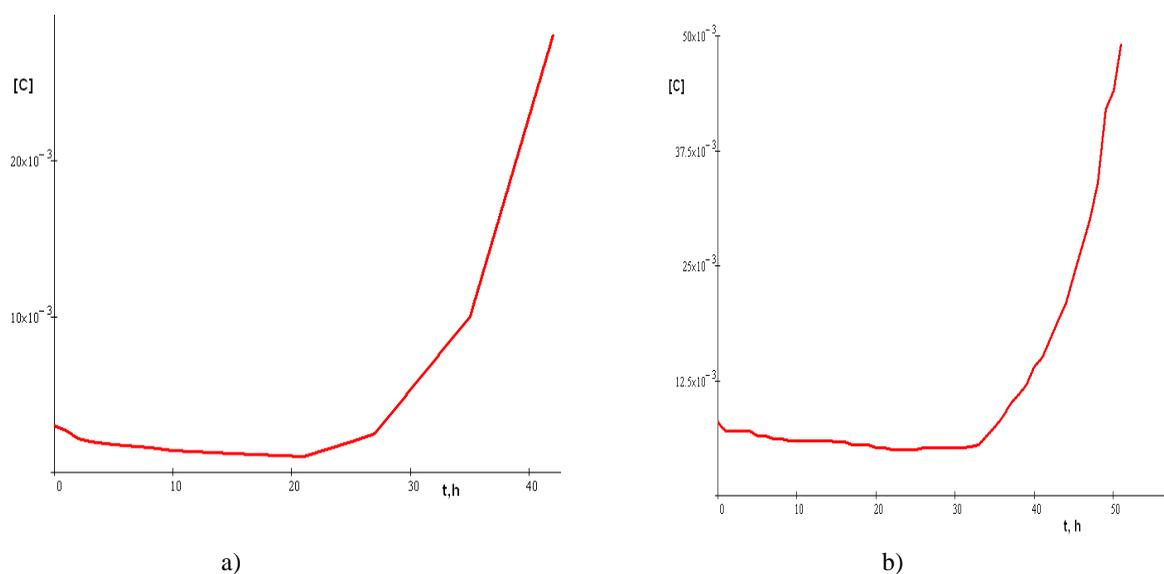
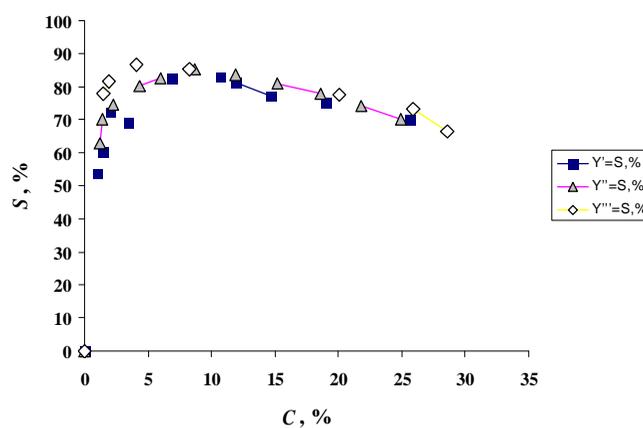


Fig. 8. PhOH kinetics in reactions of ethylbenzene oxidation catalyzed by triple systems: $\{Ni^{II}(\text{acac})_2 (3.0 \cdot 10^{-3}$ mol/l) + LiSt ($3.0 \cdot 10^{-3}$ mol/l) + PhOH ($3 \cdot 10^{-3}$ mol/l) $\}$ [29] (a) and $\{LiSt (1.0 \cdot 10^{-2}$ mol/l) + DMF ($1.0 \cdot 10^{-2}$ mol/l) + PhOH ($0.8 \cdot 10^{-2}$ mol/l) $\}$ (b), 393 K. Our data on the catalysis with LiSt·DMF·PhOH complexes are presented for the first time

Fig. 9. Dependences S_{PEH} on C in ethylbenzene oxidation in PEH, catalyzed with triple systems $\{LiSt + DMF + PhOH\}$:

- – $[LiSt] = 1 \cdot 10^{-2}$ mol/l, $[DMF] = 1 \cdot 10^{-2}$ mol/l, $[PhOH] = 1.2 \cdot 10^{-2}$ mol/l; Δ – $[LiSt] = 1 \cdot 10^{-2}$ mol/l, $[DMF] = 1 \cdot 10^{-2}$ mol/l, $[PhOH] = 0.8 \cdot 10^{-2}$ mol/l;
- \diamond – $[LiSt] = 1 \cdot 10^{-2}$ mol/l, $[DMF] = 3 \cdot 10^{-3}$ mol/l, $[PhOH] = 1 \cdot 10^{-3}$ mol/l, 393 K



Dependences S_{PEH} on C in ethylbenzene oxidation in PEH, catalyzed with triple systems $\{\text{LiSt} + \text{DMF} + \text{PhOH}\}$ at $[\text{LiSt}] = 1 \cdot 10^{-2}$ mol/l = const and different concentrations $[\text{PhOH}]$ and $[\text{DMF}]$ (Fig. 9), also show in favor of triple complexes $\text{LiSt} \cdot \text{DMF} \cdot \text{PhOH}$ formation.

3.3. Mechanism of Catalysis with Li-compound Catalytic Systems in the Hydrocarbons Oxidation by Dioxygen. Role of Chain Initial Stage (O_2 Activation) and Chain Propagation Stage ($\text{Cat} + \text{RO}_2 \cdot \rightarrow$)

The mechanism of action of compounds of redox inactive metals in liquid-phase reactions of hydrocarbons oxidation is researched insufficiently because of their relatively small activity and poor solubility in hydrocarbon media. The limited data suggest that lithium salts accelerate the hydrocarbons oxidation by increasing the chain initial rates (activation of molecular O_2) [16, 17] and chain branching [17, 18]. Accelerating of decomposition of the PEH to the free radicals at the catalysis with the LiSt may be due to the lower energy barrier in consequence of complex $\text{LiSt} \cdot \text{ROOH}$ formation by analogy with [19].

Based on quantum chemical calculations [16] prominent activity of lithium salts in comparison with other alkaline metals (Na, K, Rb) is connected with partial filling in of vacant Li^+ s -orbital with electrons from opposite charged anion, and this can explain the weak covalent character of Li-X bond and greater solubility of lithium salts in organic solvents. It was shown that the interaction of Li^+ with O_2 is the most strong in the case of bent end-on configuration ($2s$) $\text{Li}^+ \cdot \text{O}_2(1pg)$. The assessing catalytic activity of Li^+ ion in the "radical" reactions [20-22], including those featuring $^3\text{O}_2$ and radical $\cdot\text{OOH}$ was filled with quantum-chemical methods of calculation. In complex $\text{Li}^+ \cdot \text{O} \cdot \text{O}$ with enhanced electronic density on distance atom of oxygen, O-O bond is less stable compared to O-O bond in the complexes of transition metal with dioxygen [22].

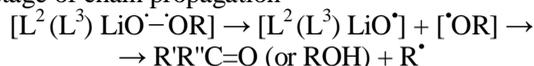
As was shown, the systems based on lithium ion – triple $\{\text{LiSt} + \text{DMF} + \text{PhOH}\}$ and binary $\{\text{LiSt} + \text{DMF}(\text{HMPA})\}$ systems, obviously were inactive in the reaction of hydroperoxide decomposition. However the ability of redox-inactive lithium ions to facilitate free radical formation in chain initiation (activation of O_2), possibly, takes place in the case of the catalysis with Li-systems, $\{\text{LiSt} + \text{DMF} + \text{PhOH}\}$ and $\{\text{LiSt} + \text{DMF}(\text{HMPA})\}$.

In these systems dioxygen activation may be promoted through the formation of intramolecular H-bonds [4]. The role of intramolecular H-bonds in catalysis was established by us in the case of formation of triple

catalytic complexes $\{\text{Ni}^{\text{II}}(\text{acac})_2 \cdot \text{L}^2 \cdot \text{PhOH}\}$ ($\text{L}^2 = N$ -methylpyrrolidone-2 (MP)) in the process of ethylbenzene oxidation with molecular oxygen [4].

The schemes of radical chain hydrocarbons oxidation including intermediate formation peroxy complexes $[\text{LMOOR}]$ with their further homolytic decomposition at the O-O bond [4] may explain parallel formation of alcohol and ketone under catalytic ethylbenzene oxidation in the presence of $\text{LiSt} \cdot \text{DMF}(\text{HMPA})$ or $\text{LiSt} \cdot \text{DMF} \cdot \text{PhOH}$.

Presumably, the additional coordination of LiSt with DMF or HMPA (L^2) (and PhOH (L^3)) favors the stabilization of oxo-species $[\text{L}^2(\text{L}^3)\text{LiO}^*]$ formed in the homolytic decomposition of peroxy complexes $[\text{L}^2(\text{L}^3)\text{LiOOR}]$ at the O-O bond, and AP and MPC formation in the stage of chain propagation



Thus, catalysis with $\{\text{LiSt} + \text{DMF} + \text{PhOH}\}$ and $\{\text{LiSt} + \text{DMF}(\text{HMPA})\}$ is largely associated with involvement of these systems in the steps of chain initiation (activation of O_2) and also chain propagation ($\text{Cat} + \text{RO}_2 \cdot \rightarrow$).

As one can see in Fig. 9, in the case of catalysis with triple system on the basis of Li compound the degree of conversion C and selectivity S_{PEH} of ethylbenzene oxidation in PEH are reduced compared to nickel-containing triple systems (Fig. 1). Because the triple system $\{\text{LiSt} + \text{DMF} + \text{PhOH}\}$ is not active in PEH decomposition, falling S_{PEH} appears to be associated with the increasing role of chain propagation stage ($\text{Cat} + \text{RO}_2 \cdot \rightarrow$) in mechanism of catalysis with triple systems based on lithium complex $\{\text{LiSt} \cdot \text{DMF} \cdot \text{PhOH}\}$.

The reduction in conversion of ethylbenzene oxidation (Fig. 9) compared with catalysis by complexes $\{\text{Ni}^{\text{II}}(\text{acac})_2 \cdot \text{NaSt}(\text{LiSt}) \cdot \text{PhOH}\}$ can be associated with less stability of triple complexes $\{\text{LiSt} \cdot \text{DMF} \cdot \text{PhOH}\}$ in the course of ethylbenzene oxidation.

3.4. Role of Intermolecular H-bonding in Stabilization of Triple Catalytic Complexes $\{\text{LiSt} \cdot \text{L}^2 \cdot \text{PhOH}\}$

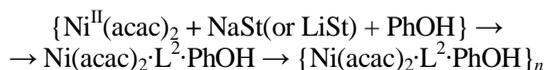
Nanostructure science and supramolecular chemistry are fast evolving fields that are concerned with manipulation of materials that have important structural features of nanometer size (1 nm to 1 μm) [23]. Nature has been exploiting no covalent interactions for the construction of various cell components. For instance, microtubules, ribosomes, mitochondria, and chromosomes use mostly hydrogen bonding in conjunction with covalently formed peptide bonds to form specific structures.

H-bonds are commonly used for the fabrication of supramolecular assemblies because they are directional

and have a wide range of interactions energies that are tunable by adjusting the number of H-bonds, their relative orientation, and their position in the overall structure. H-bonds in the center of protein helices can be 83.7 kJ/mol due to cooperative dipolar interactions [24, 25].

The porphyrin linkage through H-bonds is the binding type generally observed in nature. One of the simplest artificial self-assembling supramolecular porphyrin systems is the formation of a dimer based on carboxylic acid functionality [26].

The high efficiency of three-component systems $\{\text{Ni}^{\text{II}}(\text{acac})_2 + \text{L}^2 + \text{PhOH}\}$ ($\text{L}^2 = \text{MSt}$ ($\text{M} = \text{Na}, \text{Li}$), HMPA) in the reaction of selective oxidation of ethylbenzene to *a*-phenylethyl hydroperoxide on parameters S , C , $w = \text{const}$ is associated with the formation of extremely stable heterobimetallic heteroligand complexes $\text{Ni}(\text{acac})_2 \cdot \text{L}^2 \cdot \text{PhOH}$. We assumed that the stability of complexes $\text{Ni}(\text{acac})_2 \cdot \text{L}^2 \cdot \text{PhOH}$ during ethylbenzene oxidation can be associated, as one of reasons, with the supramolecular structures formation due to intermolecular H-bonds (phenol-carboxylate) [26-28] and, possibly, with the other non-covalent interactions:



Data of AFM-microscopy, which we received at first [7, 30] ($\text{L}^2 = \text{NaSt}, \text{LiSt}, \text{HMPA}$, Fig. 10) testify to formation of supramolecular macrostructures due to intermolecular (phenol-carboxylate) H-bonds and, possibly, other non-covalent interactions [27-29], based on the triple complexes $\{\text{Ni}(\text{acac})_2 \cdot \text{L}^2 \cdot \text{PhOH}\}$ in the real catalytic ethylbenzene oxidation. Spontaneous organization process, *i.e.*, self-organization, of triple complexes on surfaces of modified silicon are driven by the balance between intermolecular and molecule-surface interactions, which may be the consequence of hydrogen bonds and other non-covalent interactions [31].

As mentioned above, complexes of lithium with DMF or HMPA as catalysts practically do not differ relative to the parameters of $S_{\text{PEH}} \sim 90\text{--}93\%$ and $C = 20\%$, and the mechanism of products formation. Therefore, possibility of forming stable self-organized supramolecular nanostructures in the course of ethylbenzene oxidation due to hydrogen bonding, as one of possible reasons of stabilizing the three-component systems $\text{LiSt} \cdot \text{L}^2 \cdot \text{PhOH}$ (on parameters S_{PEH} , C , $w = \text{const}$) we researched on the example of complexes of LiSt with HMPA.

The association of triple complexes $\text{LiSt} \cdot \text{L}^2 \cdot \text{PhOH}$ ($\text{L}^2 = \text{HMPA}$) in supramolecular structures due to intermolecular H-bonding may be followed from analysis of data which we received with AFM-microscopy. Data of structures on the basis of complexes $\text{LiSt} \cdot \text{HMPA} \cdot \text{PhOH}$ (and also $\text{LiSt} \cdot \text{HMPA}$) (Figs. 11-12) which are self-organized on the surface of the modified silicon at the apartment of a uterine solution on a surface were got for the first time.

As one can see (Fig. 11), nanoparticles on the basis of triple complexes $\{\text{LiSt} \cdot \text{HMPA} \cdot \text{PhOH}\}$ (image of $4.0 \times 4.0 \mu\text{m}$) have clear cell-type structure and are characterized in height from 2 to 3.5 nm (Figs. 11a, b) and have the width of $\sim 100\text{--}120$ nm (Fig. 11c).

Results presented in Fig. 12, relate to nanostructures based on binary complexes $\{\text{LiSt} \cdot \text{HMPA}\}$. As one can see in this case nanostructures differ in heterogeneity in form and height changing from ≤ 2 to 35–40 nm (Figs. 12 a-c) as compared with more clear cell-type nanostructures on the basis of triple complexes $\{\text{LiSt} \cdot \text{HMPA} \cdot \text{PhOH}\}$ (Fig. 11). The greater number of particles based on binary complexes has a height less than 2 nm and the width of $\sim 50\text{--}60$ nm (see, for example, profile in Fig. 12c). Nanostructures based on $\{\text{LiSt} \cdot \text{PhOH}\}$ have height $< 1\text{--}2$ nm.

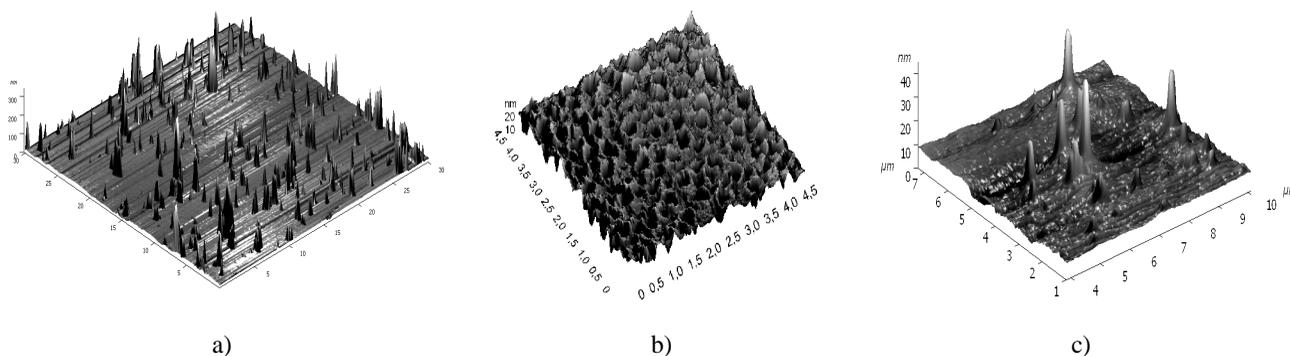


Fig. 10. AFM three-dimensional images: a) ($30 \times 30 \mu\text{m}$) of the structures formed on a surface of modified silicon on the basis of triple complexes $\text{Ni}^{\text{II}}(\text{acac})_2 \cdot \text{NaSt} \cdot \text{PhOH}$; b) ($4.5 \times 4.5 \mu\text{m}$) of the structures ($h \sim 10$ nm) formed on a surface of modified silicon on the basis of triple complexes $\text{Ni}^{\text{II}}(\text{acac})_2 \cdot \text{LiSt} \cdot \text{PhOH}$; c) ($6.0 \times 6.0 \mu\text{m}$) of the structures ($h \sim 40$ nm) formed on a surface of modified silicon on the basis of triple complexes $\{\text{Ni}^{\text{II}}(\text{acac})_2 \cdot \text{HMPA} \cdot \text{PhOH}\}$ (Data in Fig. 10c are presented for the first time)

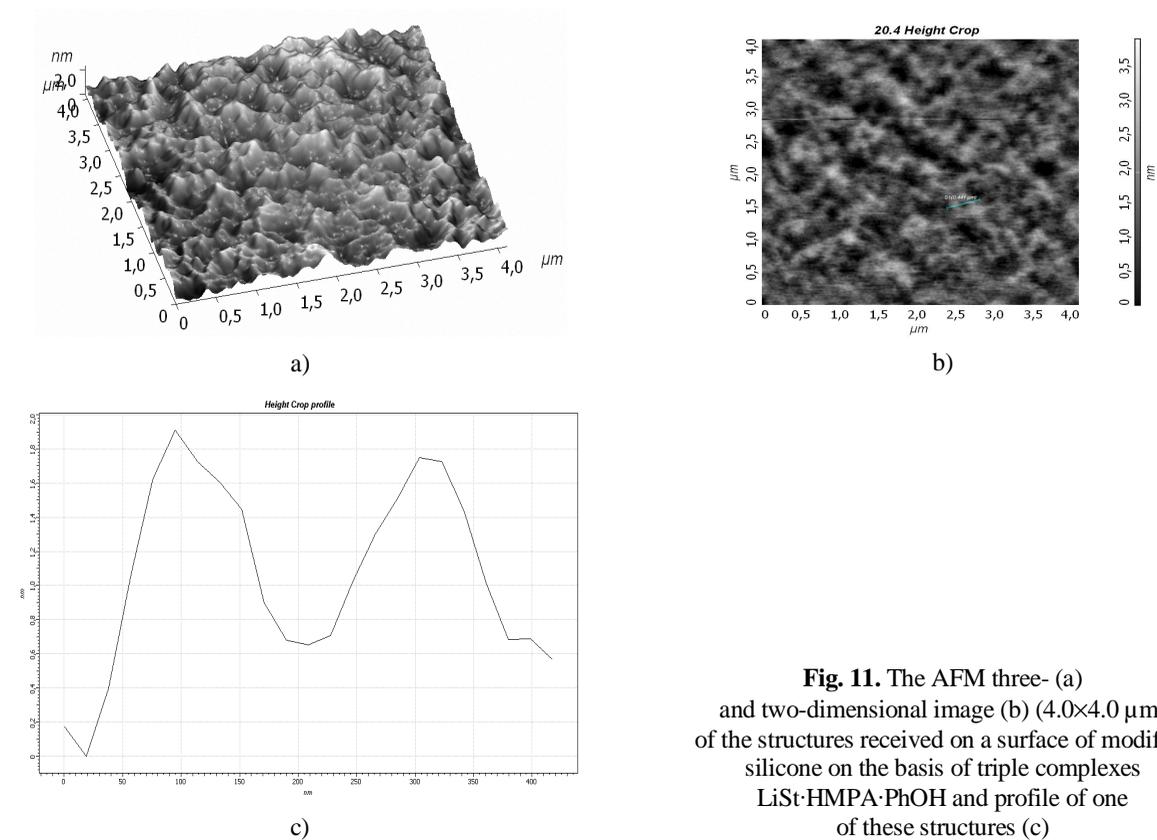


Fig. 11. The AFM three- (a) and two-dimensional image (b) ($4.0 \times 4.0 \mu\text{m}$) of the structures received on a surface of modified silicone on the basis of triple complexes $\text{LiSt} \cdot \text{HMPA} \cdot \text{PhOH}$ and profile of one of these structures (c)

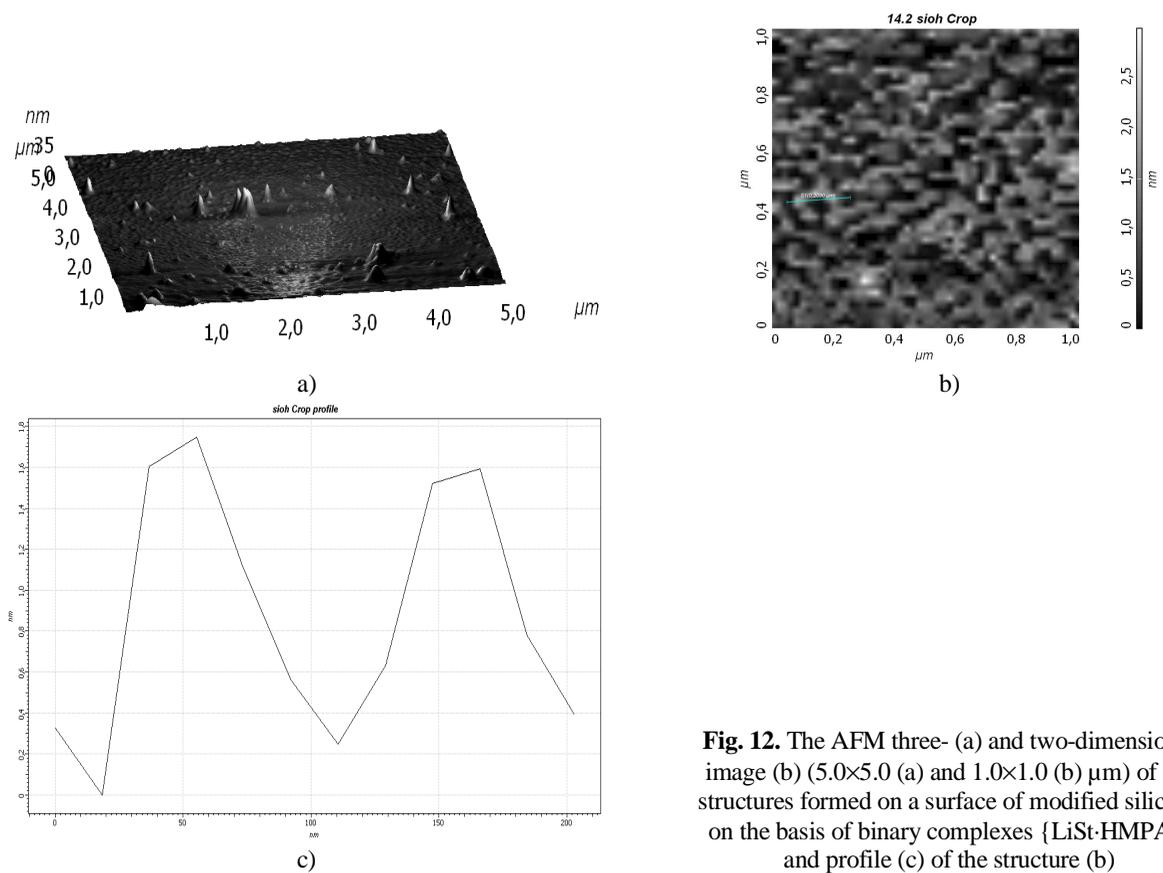


Fig. 12. The AFM three- (a) and two-dimensional image (b) (5.0×5.0 (a) and 1.0×1.0 (b) μm) of the structures formed on a surface of modified silicone on the basis of binary complexes $\{\text{LiSt} \cdot \text{HMPA}\}$, and profile (c) of the structure (b)

The received AFM data (Figs. 11-12) point to the very probable stable supramolecular nanostructures appearance on the basis of heteroligand triple complexes $\{\text{LiSt}\cdot\text{L}^2\cdot\text{PhOH}\}_n$ at the expense of intermolecular (phenol-carboxylate) H-bonds [27-31] and, possibly, other non-covalent interactions [27-31] also in the real catalytic ethylbenzene oxidation with dioxygen, catalyzed by triple complexes $\text{LiSt}\cdot\text{L}^2\cdot\text{PhOH}$.

4. Conclusions

1. Inclusion of phenol in coordination sphere of a complex $\{\text{LiSt}\cdot\text{L}^2\}$ ($\text{L}^2 = \text{DMF}$) leads to formation of a triple complex $\{\text{LiSt}\cdot\text{L}^2\cdot\text{PhOH}\}$ with different catalytic activity. In the presence of $\{\text{LiSt}+\text{DMF}+\text{PhOH}\}$ the rates of accommodation of oxidation products PEH, AP and MPC remain practically the same during the oxidation process ($\leq 20-30$ h) unlike the catalysis with binary system $\{\text{LiSt}+\text{DMF}\}$. At catalysis with $\{\text{LiSt}+\text{DMF}+\text{PhOH}\}$ (and $\{\text{LiSt}+\text{DMF}\}$) the oxidation products PEH, AP and MPC are formed with maximum initial rate without the auto acceleration period by analogy with the catalysis with the triple nickel-lithium (sodium) catalytic systems, $\{\text{Ni}^{\text{II}}(\text{acac})_2+\text{LiSt}(\text{NaSt})+\text{PhOH}\}$.

The mechanism of acetophenone and methylphenylcarbinol formation in ethylbenzene oxidation in the presence of triple $\{\text{LiSt}+\text{DMF}+\text{PhOH}\}$ and binary $\{\text{LiSt}+\text{DMF}\}$ systems was identical: unlike non-catalytic oxidation and catalysis by LiSt, AP and MPC form in parallel with PEH rather than as a result of PEH decomposition. The increase in selectivity $S_{\text{PEH,max}} \sim 90\%$ at catalysis with $\{\text{LiSt}\cdot\text{HMPA}\cdot\text{PhOH}\}$ in comparison with no catalyzed oxidation ($S_{\text{PEH,max}} \leq 80\%$) is due to change in an order, in which products PEH, AP, and MPC form. Catalysis with $\{\text{LiSt}+\text{DMF}+\text{PhOH}\}$ and $\{\text{LiSt}+\text{DMF}\}$ is largely associated with involvement of these systems in the stages of chain initiation (activation of O_2) and also chain propagation ($\text{Cat}+\text{RO}_2^\bullet \rightarrow$).

2. We applied at first AFM method with the analytical purposes to research the possibility of the formation of supramolecular structures on the basis of heteroligand triple complexes $\{\text{LiSt}\cdot\text{L}^2\cdot\text{PhOH}\}$ ($\text{L}^2 = \text{HMPA}$) with the assistance of intermolecular H-bonds.

We have shown that the self-assembly-driven growth of structures on the basis of $\{\text{LiSt}\cdot\text{L}^2\cdot\text{PhOH}\}$ ($\text{L}^2 = \text{HMPA}$) seems to be due to the connection of complexes with a surface of modified silicone, and further formation of supramolecular nanostructures $\{\text{LiSt}\cdot\text{L}^2\cdot\text{PhOH}\}_n$ at the expense of directional intermolecular (phenol-carboxylate) H-bonds, and, possibly, other non-covalent interactions (van Der Waals-attractive and p -bonding). The nanostructures based on triple

complexes $\text{LiSt}\cdot\text{L}^2\cdot\text{PhOH}$ are characterized by clear cell-type structure.

It is possible to suppose formation of stable supramolecular structures in the course of the ethylbenzene oxidation with dioxygen, catalyzed by catalytic system $\{\text{LiSt}+\text{L}^2+\text{PhOH}\}$ and this can be one of the explanations of the stability of triple systems ($w \equiv \text{const}$) during the selective oxidation process of the ethylbenzene oxidation into α -phenylethyl hydroperoxide.

Abbreviations:

AFM method – Atomic-Force Microscopy method

(Acac)⁻ – Acetylacetonate ion

PhOH - phenol

DMF – dimethylformamide

HMPA – hexamethylphosphorotriamide

MP – N-methylpyrrolidone-2

MSt – stearates of alkaline metals (M = Li)

DN – donor number

References

- [1] Suresh A., Sharma M. and Sridhar T.: Ind. Eng. Chem. Res., 2000, **39**, 3958.
- [2] Weissmerl K. and Arpe H.-J.: Industrial Organic Chemistry, 3rd edn., VCH, New York 1997.
- [3] Matienko L.: Solution of the problem of selective oxidation of alkylarenes by molecular oxygen to corresponding hydroperoxides. Catalysis initiated by Ni(II), Co(II), and Fe(III) complexes activated by additives of electron-donor mono- or multidentate extra-ligands [in:] D'Amore A. and Zaikov G. (Eds.), Reactions and Properties of Monomers and Polymers.: Nova Science Publ. Inc., New York 2007, 21-41.
- [4] Matienko L., Mosolova L. and Zaikov G.: Selective Catalytic Hydrocarbons Oxidation. New Perspectives. Nova Science Publ. Inc., New York 2010.
- [5] Matienko L., Binyukov V. and Mosolova L.: Oxid. Commun., 2014, **37**, 20.
- [6] Matienko L., Mosolova L., Binyukov V. *et al.*: The New Approach to Research of Mechanism Catalysis with Nickel Complexes in Alkylarene Oxidation [in:] Zaikov G., Sirghie C. and Kozlowski R. (Eds.), Polymer Yearbook 2011. Nova Science Publ. Inc., New York 2012, 221-230.
- [7] Matienko L., Binyukov V., Mosolova L. and Zaikov G.: Polym. Res. J., 2011, **5**, 423.
- [8] Park Y., Ziller J. and Borovik A.: J. Am. Chem. Soc., 2011, **133**, 9258.
- [9] Siroegko A.: Doct. thesis, LenSovet Technical Institute, Leningrad 1985.
- [10] Mosolova L. and Matienko L.: Kinetika i Cataliz, 1984, **25**, 1262.
- [11] Ciskovski V. and Moskovich Yu.: Kinetika i Cataliz, 1974, **15**, 1466.
- [12] Kozlov S., Tovstokhatko Ph. and Potekhin V.: Zh. Prikl. Khim., 1986, **59**, 217.
- [13] Monakov M., Kudryashov V. and Kastalskaya-Borozdinskaya N.: Kinetika i Cataliz, 1981, **22**, 183.
- [14] Fenton D. and Nave C.: J. Chem. Soc. Chem. Comm., 1971, 662.

- [15] Reich H.: Chem. Rev., 2013, **113**, 7130.
- [16] Ohkubo K., Shimata H., Shiotani Y. and Okada M.: Bull. Chem. Soc. Jap., 1971, **44**, 1188.
- [17] Ivanov S. and Boneva M.: Oxid. Commun., 1984, **7**, 305.
- [18] Ckarlampidi Ch., Batyrshin N. and Ivanov V.: Neftekhimiya, 1980, **20**, 708.
- [19] Petrov L., Solyanikov V. and Petrova Z.: Dokl. Acad. Nauk SSSR, 1976, **230**, 366.
- [20] Von Onciul A. and Crark T.: J. Chem. Soc. Chem. Comm. 1989, 1082.
- [21] Hofman H. and Crark T.: J. Am. Chem. Soc., 1991, **113**, 2422.
- [22] Hofman H. and Crark T.: Angew. Chem. Int. Ed. Engl., 1990, **29**, 648.
- [23] Leninger St., Olenyuk B. and Stang P.: Chem. Rev., 2000, **100**, 853.
- [24] Stang P. and Olenyuk B.: Acc. Chem. Res., 1997, **30**, 502.
- [25] Drain C. and Varotto Radivojevic A.: Chem. Rev., 2009, **109**, 1630.
- [26] Beletskaya I., Tyurin V., Tsivadze A. et al.: Chem. Rev., 2009, **109**, 1659.
- [27] Dubey M., Koner R. and Ray M.: Inorg. Chem., 2009, **48**, 9294.
- [28] Basiuk E., Basiuk V., Gomez-Lara J. and Toscano R.: J. Incl. Phenom. Macrocycl. Chem., 2000, **38**, 45.
- [29] Mukherjee P., Drew M., Gómez-García C. and Ghosh A.: Inorg. Chem., 2009, **48**, 4817.
- [30] Matienko L., Mosolova L., Binyukov V. et al.: Polymers Res. J., 2014, **8**, 91.
- [31] Gentili D., Valle F., Albonetti C. et al.: Acc. Chem. Res., 2014, **47**, 2692.

**КАТАЛИТИЧНА АКТИВНІСТЬ ПОДВІЙНИХ
ТА ПОТРІЙНИХ СИСТЕМ НА ОСНОВІ СПОЛУК
МЕТАЛУ ПОСТІЙНОЇ ВАЛЕНТНОСТІ, LiSt
ТА ДОДАТКІВ МОНОДЕНТАТНИХ ЛІГАНДІВ-
МОДИФІКАТОРІВ: ДМФ, ГМФТА, ФЕНОЛУ ПРИ
СЕЛЕКТИВНОМУ ОКИСНЕННІ ЕТИЛБЕНЗОЛУ
МОЛЕКУЛЯРНИМ КИСНЕМ**

Анотація. Вивчено механізм каталізу подвійними та потрійними каталітичними системами на основі сполук металу постійної валентності, LiSt та додатків монодентатних лігандів-модифікаторів: диметилформаміду, гексаметилфосфоротриаміду, фенолу в селективному окисненні етилбензолу молекулярним киснем. За допомогою атомно-силової мікроскопії досліджено можливість формування стабільних супрамолекулярних структур наноструктур на основі потрійних систем $\{LiSt+L^2+PhOH\}$ за рахунок міжмолекулярних H-зв'язків.

Ключові слова: наноструктура, подвійні і потрійні каталітичні системи, H-зв'язки, каталіз, етилбензол, окиснення, молекулярний кисень, *o*-феніл етилгідропероксид.