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THE SELECTIVE ETHYLBENZENE OXIDATION BY DIOXYGEN INTO a-PHENYL ETHYL HYDROPEROXIDE, CATALYZED WITH TRIPLE CATALYTIC SYSTEM {$Ni^{II}(acac)_2$+NaSt(LiSt)+PhOH}. FORMATION OF NANOSTRUCTURES {$Ni^{II}(acac)_2$·NaSt·(PhOH)}$_n$ WITH ASSISTANCE OF INTERMOLECULAR H-BONDS

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Abstract. The role of intra- and intermolecular H-bonds in mechanisms of catalysis with triple heterobinuclear hetero ligand complexes $Ni^{II}(acac)_2\cdot NaSt(LiSt)\cdot PhOH$, including nickel and redox-inactive metal Na(Li), in the ethylbenzene oxidation by dioxygen into α-phenyl ethyl hydroperoxide is discussed. The AFM method has been used for research of the stable supramolecular nanostructures formation possibility on the basis of triple complex $Ni^{II}(acac)_2\cdot NaSt\cdot PhOH$, with the assistance of intermolecular H-bonds.

Keywords: nanostructures, triple complexes $Ni^{II}(acac)_2\cdot NaSt\cdot PhOH$, H-bonds, catalysis, ethylbenzene, oxidation, dioxygen, *a*-phenyl ethyl 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 *a*-phenyl ethyl hydroperoxide, and cumyl hydroperoxide is the precursor in the synthesis of phenol and acetone [1]. The method of modifying the Ni^{II} and $Fe^{II,III}$ complexes used in the selective oxidation of alkylarenes (ethylbenzene and cumene) with a molecular oxygen to afford the corresponding hydroperoxides aimed at increasing their selectivities 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 such modifying ligands action was elucidated. New efficient catalysts of ethylbenzene selective oxidation to *a*-phenyl ethyl hydroperoxide were developed [2, 3].

The phenomenon of a substantial increase in the selectivity (*S*) and conversion (*C*) of the ethylbenzene oxidation to *a*-phenyl ethyl hydroperoxide upon addition of PhOH together with an alkali metal stearate M'St (M' = Li, Na) as ligands to metal complexes $Ni^{II}(acac)_2$ was discovered in our works [1, 2, 4].

The observed values of *C* [$C > 35$ % at $(S_{PEH})_{max}$ = = 85–87 %], $[ROOH]_{max}$ (1.6–1.8 $mol\cdot l^{-1}$ and $\tilde{S}\cdot C$ (~$30.1\cdot 10^2$ %%) far exceeded those obtained with other ternary catalytic systems, {$Ni^{II}(acac)_2$+ L^2 + PhOH} (L^2 is *N*-metyl-2-pyrrolidone (MP), hexamethylphosphorotriamide (HMPA),) and the majority of active binary systems. These results by L.Matienko and L.Mosolova are protected by the Russian Federation patent (2004).

The advantage of these ternary systems is the long-term activity of *in situ* formed complexes $Ni^{II}(acac)_2\cdot L^2\cdot PhOH$. The best results were obtained in the case of catalysis with the system {$Ni^{II}(acac)_2$ + NaSt + + PhOH} (Fig. 1).

The high efficiency of three-component systems {$Ni^{II}(acac)_2$ + MSt + PhOH} (M = Na, Li) in the reaction of selective oxidation of ethylbenzene to *a*-phenyl ethyl hydroperoxide was associated with the formation of extremely stable binuclear heteroligand complexes $Ni(acac)_2\cdot MSt\cdot PhOH$. The stability of complexes $Ni^{II}(acac)_2\cdot MSt\cdot PhOH$ can be associated with the formation of intramolecular H-bonds [5].

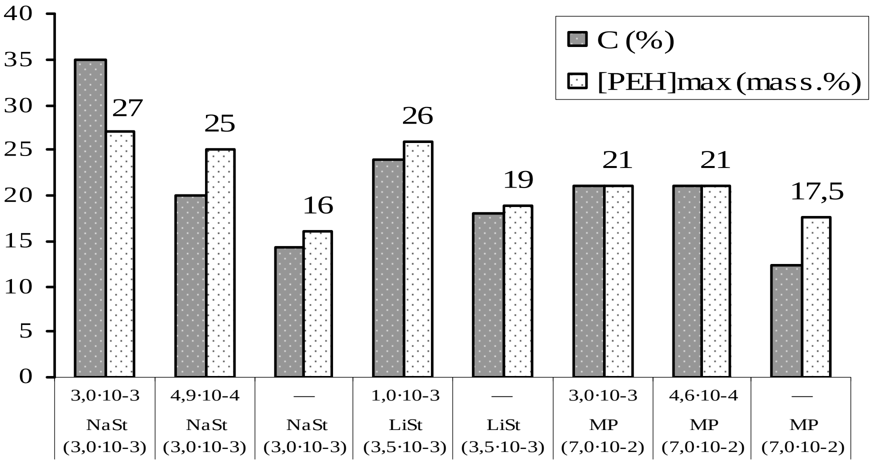


Fig. 1. Values of conversion *C* (%) (I row), maximum values of hydroperoxide concentrations $[PEH]_{max}$ (mas %) (II row) in the reactions of ethylbenzene oxidation in the presence of triple catalytic systems $\{Ni(II)(acac)_2+L^2+PhOH\}$ (L^2 = NaSt, LiSt, MP: [PhOH], mol/l – on the axis of abscises (the top number); $[L^2]$, mol/l – on the axis of abscises (the bottom number)). $[Ni^{II}(acac)_2]=3.0\cdot10^{-3}$ mol/l. Temperature is 393 K

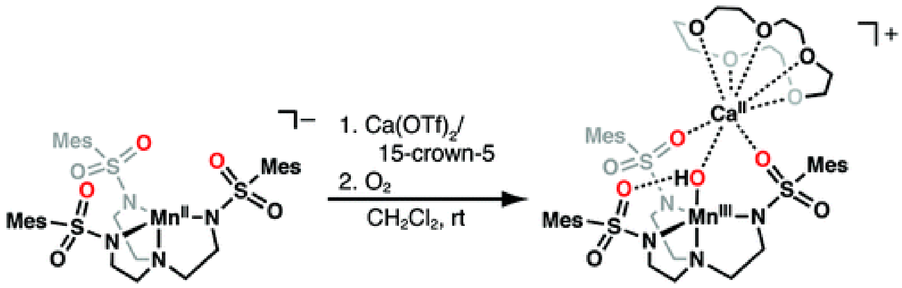
Nanostructure science and supramolecular chemistry are fast evolving fields that are concerned with the manipulation of materials that have important structural features of nanometer size (from 1 nm to 1 *m*m) [6, 7]. The self-assembled systems and self-organized structures mediated by transition metals are considered in connection with the increasing research interest in chemical transformations with the use of these systems [8].

Earlier we applied AFM technique for the evidence of the possibility of stable supramolecular structures formation in the process of ethylbenzene oxidation to the to *a*-phenyl ethyl hydroperoxide in the presence of systems $\{Ni^{II}(acac)_2 + L^2\}$ [9].

In this paper we applied AFM technique for research the possibility of supramolecular structures formation in the process of ethylbenzene oxidation to *a*-phenyl ethyl hydroperoxide at catalysis with three-component systems $\{Ni^{II}(acac)_2+NaSt+PhOH\}$: $\{Ni^{II}(acac)_2+NaSt+PhOH\} \rightarrow Ni^{II}(acac)_2\cdot NaSt\cdot PhOH \rightarrow \{Ni^{II}(acac)_2\cdot NaSt\cdot PhOH\}_n$

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 [10]. 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 [11].

The adducts of metals salts of constant valency with *b*-diketonates and *N,N'*-ethylene *bis*-(salycylideniminates) of Co^{II}, Ni^{II}, Cu^{II} are known [12, 13]. Thus the coordination of metals salts of constant valency M′L (M′ – metal of constant valency) with complexes of transition metals ML^1 is carried out through ligand (complexes of nickel and copper with the Shiff bases, copper acetylacetonate: ML^1— M′L (bonds L^1— M′) (I type). In other cases – anions of metals salts of constant valency are coordinated with ions of transitional metal (acetylacetonates of nickel and cobalt: L^1M—L M′ (bonds M—L) (II type)). For example, in complexes $[15\text{-Crown-5}\supset Ca(II)–(\mu\text{-}OH)–Mn^{III}MST]^+$ calcium ions are bound with $[MST]^{3-}$-ligand of Mn complex ($[MST]^{3-}$-tripodal ligand *N,N′,N′′*-[2,2′,2′′-nitrilotris(ethane-2,1-diyl)]tris(2,4,6-trimethylbenzenesulfonamido) [14]:



Earlier we received kinetic and spectrophotometry (UV spectra) proofs in favor of complexes formation of *bis*(acetylacetonate)nickel, $Ni^{II}(acac)_2$, with NaSt of II type, M—L, namely, $(acac)_2$ Ni — St(Na) [2, 3].

We discovered that the introduction of phenol together with the $\{Ni(acac)_2 + L^2\}$ catalyst in the reaction system in the initial stage of ethylbenzene oxidation is one of the most efficient methods of designing catalytic systems for the ethylbenzene selective oxidation to *a*-phenyl ethyl hydroperoxide. The high efficiency of three-component systems $\{Ni(acac)_2{+}MSt{+}PhOH\}$ (M = Na, Li) in the reaction of ethylbenzene selective oxidation to *a*-phenyl ethyl hydroperoxide was associated with the formation of extremely stable heteroligand complexes $Ni(acac)_2{\cdot}MSt{\cdot}PhOH$ [4]. The stability of these triple complexes throughout oxidation process allowed us to assume the formation of stable supramolecular structures due to H-bonding [5].

2. Experimental

AFM SOLVER P47/SMENA/ with Silicon Cantilevers NSG11S (NT MDT) with a curvature radius 10 nm, tip height: 10–15 µm and cone angle ≤ 22° in a taping mode with resonant frequency of 150 KHz was used.

The polished Silicone surface chemically modified was used as the substrate.

Waterproof modified Silicone surface was exploited for the self-assembly-driven growth due to H-bonding of complexes $Ni(II)(acac)_2{\cdot}NaSt{\cdot}PhOH$ with the Silicone surface. The saturated chloroform ($CHCl_3$) solution of the complex $Ni(II)(acac)_2{\cdot}NaSt{\cdot}PhOH$ (1:1:1) was put on the surface, maintained for some time, and then the solvent was deleted from the surface by means of the special method – spin-coating process.

In the course of scanning of investigated samples it has been found, that the structures are fixed on the surface strongly enough due to H-bonding. The self-assembly-driven growth of the supramolecular structures formation on the basis of complexes $Ni(II)(acac)_2{\cdot}NaSt{\cdot}PhOH$ due to H-bonds and perhaps the other non-covalent interactions was observed on the Silicone surface. One can watch these structures with a big height and volume. In check experiments it has been shown that for binary systems $\{Ni(II)(acac)_2{+}NaSt\}$, and $\{Ni(II)(acac)_2{+}PhOH\}$ the formation of the similar structures (exceeding the height of 2–10 nanometers) is not observed.

Ethylbenzene (RH) was oxidized with dioxygen at 393 K in a glass bubbling-type reactor in the presence of three-component systems $\{Ni(II)(acac)_2{+}L^2{+}PhOH\}$ (L^2=NaSt)) [4].

Analysis of oxidation products. a-Phenyl ethyl hydroperoxide (PEH) was analyzed by the iodometry. By-products, including methylphenylcarbinol (MPC), acetophenone (AP), and phenol (PhOH) as well as the RH content in the oxidation process were examined by GLC [4].

The order in which PEH, AP, and MPC formed was determined from the time dependence of product accumulation rate rations at $t \to 0$. The variation of these rations with time was evaluated by graphic differentiation ([4], see Fig. 2).

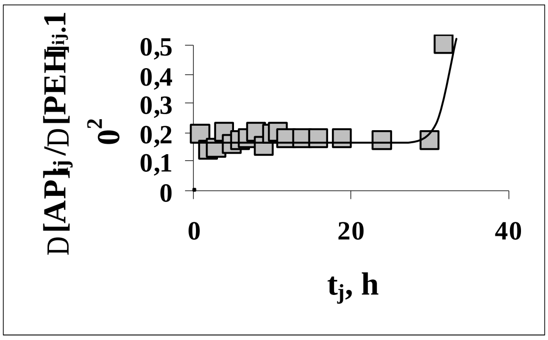


Fig. 2. Dependence of $\Delta[AP]_{ij}/\ \Delta[PEH]_{ij}{\cdot}10^2$ on time t_j in the course of ethylbenzene oxidation, catalyzed with complexes $Ni(II)(acac)_2{\cdot}NaSt{\cdot}PhOH$, 393 K.

3. Results and Discussion

Earlier we established, that the increase in the initial rate of the ethylbenzene oxidation with dioxygen, catalyzed with $Ni^{II}(acac)_2$ in the presence of additives of metalloligand MSt (M = Li, Na, K), is due to the higher activity of the formed complexes $Ni^{II}(acac)_2 \cdot MSt$ in the micro stages of chain initiation and/or decomposition of PEH with a free radical formation. The participation of the catalyst $Ni^{II}(acac)_2{\cdot}MSt$ in micro steps of chain propagation and, probably, in chain termination must also be taken into account [2]. The results found in [14] illustrate the possibility that redox-inactive metal ions can be used to facilitate the activation of dioxygen (see the abstract scheme of [14], above), which will be coordinated with our data.

At catalysis with triple complexes the parallel formation of *a*-phenyl ethyl hydroperoxide, acetophenone and MPC was observed ($w_{AP\ (MPC)}/w_{PEH} \neq 0$ at $t \to 0$, $w_{AP}/w_{MPC} \neq 0$at $t \to 0$) throughout the reaction of ethylbenzene oxidation). A more considerable increase in the selectivity (S_{PEH}) in the catalysis by $Ni(acac)_2{\cdot}L^2{\cdot}PhOH$ (L^2 = NaSt, MP) complexes as compared with non-catalytic oxidation was associated with the change in the route of acetophenone and methylphenylcarbinol formation (AP and MPC form in parallel with PEH rather than as a result of its decomposition as observed in the non-catalytic ethylbenzene oxidation) and with the inhibition of the PEH heterolytic decomposition (see, for example, Fig. 2).

Thus, the triple complexes Ni(II)(acac)$_2$·NaSt·PhOH unlike binary complexes Ni(II)(acac)$_2$·NaSt seem to be not active in the reaction with hydroperoxide, but active in the reactions of chain initiation (O_2 activation) and the chain propagation (Cat+$RO_2^\bullet$→) (and, probably, in chain termination). In these systems dioxygen activation may be promoted through the formation of intramolecular H-bonds [2]. The role of intramolecular H-bonds is established by us in the mechanism of catalytic complexes {Ni(II)(acac)$_2$·L^2·PhOH} (L^2 = *N*-methyl-pirrolidon-2) formation in the process of ethylbenzene oxidation with molecular oxygen [4].

At the same time the high efficiency of three-component systems {Ni(acac)$_2$+MSt+PhOH} (M = Na, Li) in the reaction of selective oxidation of ethylbenzene to *a*-phenyl ethyl hydroperoxide was associated with the formation of extremely stable heteroligand complexes Ni(acac)$_2$·MSt·PhOH, which resulted in the considerable increase in the degree of conversion of ethylbenzene to PEH and in the yield of *a*-phenyl ethyl hydroperoxide. The stability of heterobinuclear heteroligand complexes Ni(acac)$_2$·MSt·PhOH seems to be due to formation of supramolecular structures {Ni(II)(acac)$_2$·NaSt·PhOH}$_n$ as a result of intermolecular (phenol-carboxylate) H-bonds and possibly the other non-covalent interactions [5].

The possibility of triple complexes Ni(II)(acac)$_2$·NaSt·PhOH association to supramolecular structures is followed from the analysis of AFM data, received by us in this work. Results are presented in the Figs. 3-5 and Table.

Figs. 3-4 demonstrated three-dimensional and two-dimensional AFM image (30x30 and 10×10 μm) of the structures on the basis of triple complexes Ni(II)(acac)$_2$·NaSt·PhOH formed at drawing of the uterine solution on the surface of modified silicone.

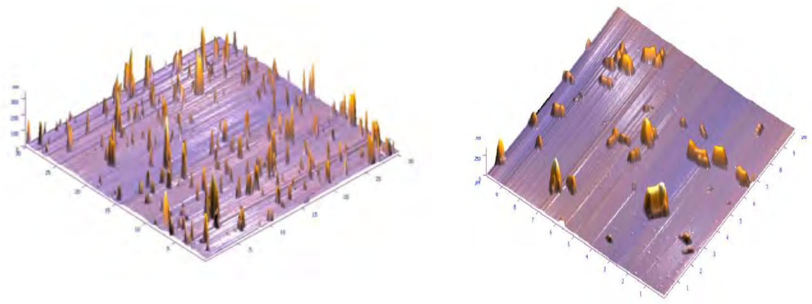


Fig. 3. The AFM three-dimensional image (30×30 and 10×10 μm) of the structures formed on the surface of modified silicone on the basis of triple complexes Ni(II)(acac)$_2$·NaSt·PhOH

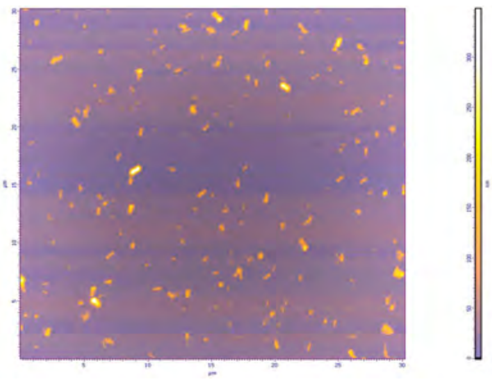


Fig. 4. The AFM two-dimensional image (30×30 μm) of nanoparticles on the basis of Ni(II)(acac)$_2$·NaSt·PhOH formed on the surface of modified silicone

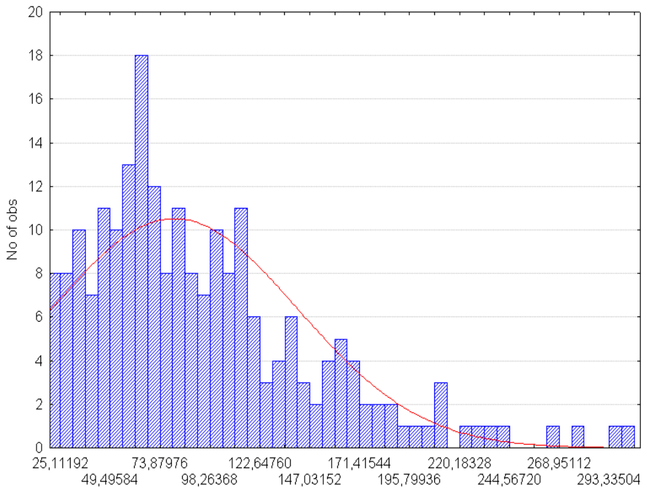


Fig. 5. Histogram of height mean values (nm) of the AFM images of nanostructures based on Ni(II)(acac)$_2$·NaSt·PhOH, formed on the surface of modified silicone

Table

The mean values of area, volume, height, length, width of the AFM nanoparticle images on the basis of Ni(II)(acac)$_2$·NaSt·PhOH formed on the surface of modified silicone

Variable	Mean values	Confidence -95.000 %	Confidence +95.000 %
Area, μm^2	0.13211	0.11489	0.14933
Volume, μm^3	14.11354	11.60499	16.62210
Height (*Z*), nm	80.56714	73.23940	87.89489
Length, μm	0.58154	0.53758	0.62549
Width, μm	0.19047	0.17987	0.20107

In the Fig. 5 the histogram of nanoparticles mean height on the basis of Ni(II)(acac)$_2$·NaSt·PhOH is presented. As one can see, structures are various at heights from 25 to ~ 250–300 nm for maximal values. The distribution histogram shows that the greatest number of particles is particles of the mean size of 50-100 nm at height.

The Table shows the mean values of area, volume, height, width, length of nanoscale structures on the basis of triple complexes Ni(II)(acac)$_2$·NaSt·PhOH formed on the surface of modified silicone.

We revealed an interesting fact that the length of the formed nanoparticles in the XY plane exceeds the width of nanoparticles about three times (Table).

4. Conclusions

Thus, in the present work we applied AFM method at first for the analytical purposes to research the possibility of the supramolecular structures formation on the basis of heterobinuclear heteroligand triple complexes Ni(II)(acac)$_2$·NaSt·PhOH.

We have shown what the self-assembly-driven growth seems to be due to H-bonding of triple complexes Ni(II)(acac)$_2$·NaSt·PhOH with the surface of modified silicone, and further formation supramolecular nanostructures {Ni(II)(acac)$_2$·NaSt·PhOH}$_n$ due to directional intermolecular (phenol-carboxylate) H-bonds [5], and, possibly, other non-covalent interactions (van Der Waals-attractions and *p*-bonding).

These data support the very probable supramolecular structures appearance on the basis of heterobinuclear heteroligand triple complexes Ni(II)(acac)$_2$· NaSt·PhOH in the course of the ethylbenzene oxidation with dioxygen, catalyzed by three-component catalytic system {Ni(II)(acac)$_2$+NaSt+PhOH} and therefore the high values of the ethylbenzene oxidation conversion into *a*-phenyl ethyl hydroperoxide at the selectivity S_{PEH} preservation at the level not below S_{PEH} = 90 % in this process.

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СЕЛЕКТИВНЕ ОКИСНЕННЯ ЕТИЛБЕНЗОЛУ МОЛЕКУЛЯРНИМ КИСНЕМ У a-ФЕНІЛЕТИЛГІДРОПЕРОКСИД, КАТАЛІЗОВАНЕ ПОТРІЙНОЮ КАТАЛІТИЧНОЮ СИСТЕМОЮ {Ni(acac)$_2$+NaSt(LiSt)+PhOH}. ФОРМУВАННЯ НАНОСТРУКТУР {NI(II)(ACAC)$_2$·NAST·PHOH}$_n$ ЗА ДОПОМОГОЮ МІЖМОЛЕКУЛЯРНИХ Н-ЗВ'ЯЗКІВ

Анотація. *Розглянуто роль внутрішньо- та міжмолекулярних Н-зв'язків в механізмах каталізу потрійними гетеробіядерними гетеролігандними комплексами Ni^{II}(acac)$_2$·NaSt(LiSt)·PhOH, які включають нікель і редокс-неактивний метал Na(Li), в реакціях окиснення етилбензолу молекулярним киснем в a-фенілетилгідропероксид. З використанням методу атомно-силової мікроскопії досліджено можливість формування стабільних супрамолекулярних наноструктур на основі потрійного комплексу Ni^{II}(acac)$_2$·NaSt·PhOH, за допомогою міжмолекулярних Н-зв'язків.*

Ключові слова: *наноструктура, потрійний комплекс Ni^{II}(acac)$_2$·NaSt·PhOH, Н-зв'язки, каталіз, етилбензол, окиснення, a-фенілетилгідропероксид.*