CATALYTIC OXIDATION OF CYCLIC COMPOUNDS INTO DICARBOXYLIC ACIDS. NEW PERSPECTIVES.


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This paper summarizes some of the traditional and new data on obtaining dicarboxylic acids with hydrogen peroxide or molecular oxygen in the presence of homogeneous and heterogenized transition metal complexes. Particular attention is given to liquid-phase oxidation of alicyclic unsaturated hydrocarbons and their functionalized derivatives in the presence of mesoporous metal-silicalites and peroxometallic complexes immobilized on a carbon material.

Keywords: Homogeneous, Heterogeneous catalyst, oxidation, hydrogen peroxid, dioxide, unsaturated hydrocarbons, dicarboxylic acid

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Introduction

Aliphatic dicarboxylic acids, in particular, such as adipic, suberic, sebacic products are in the range of bulk chemical industry. Modern production of C6-C10 dicarboxylic acids is based on a two-phase process involving oxidation of the corresponding cycloalkane or cycloalkene in the presence of cobalt- or boron-containing catalysts with molecular oxygen in to mixture of cycloalkanol and cycloalkanone and subsequent treatment of this mixture by nitric acid with compounds of vanadium (V) and copper (II) [1-4]. Production of these acids under the above scheme is realized by well-known companies such as DuPont, BASF, Stamicarbon, Asahi Chemical, Koch, etc. Oxidation of cyclohexane by air oxygen in the first stage proceeds by a radical mechanism. With a high degree of conversion of the substrate the reaction is nonselective...
and is often accompanied by formation of a considerable number of deep and destructive oxidation products. Therefore, on an industrial scale conversion of cyclohexane does not exceed 4 – 5%. The second stage proceeds through formation of various intermediates. In particular, in the oxidation of a mixture of cyclohexanol and cyclohexanone with concentrated nitric acid, adipic acid is formed via an intermediate 6, 6 – nitrohydroxyiminohexanic acid. In so doing the process is accompanied by accumulation of oxidative and low molecular weight acids - glutaric, succinic, oxalic acid in the oxide as well, which requires the creation of additional process units in the overall scheme to obtain a commercial product in pure form. Use of 57 – 60% nitric acid in the process leads to release of significant quantities of toxic nitrogen oxides (N₂O, NOₓ).

Currently, at all existing plants, there are additional processing units for processing or removal of these oxides [1, 2].

Over the last 10 – 15 years a new trend has appeared, aimed at obtaining the C₆-C₁₂ aliphatic dicarboxylic acids, bypassing the stage of oxidation with nitric acid. The process is done by using soluble or heterogenized complexes of transition metals and the most environmentally friendly oxidant - hydrogen peroxide or molecular oxygen in the triplet state. However, scientific materials on the catalytic oxidation of alicyclic hydrocarbons and their oxygenated derivatives are available, mainly, in separate articles of scientific magazines and journals. With the exception of several reviews [4, 5], compiled by the publications at the end of the last century, most of the recent materials in the last years have not been generalized.

This paper provides academic and scientific results of studies on the catalytic oxidation of alicyclic unsaturated hydrocarbons and diols in the presence of metal highly dispersed materials, undertaken by IPCP of ANAS in recent years.

Homogeneous catalysts for oxidation of C₆-C₁₂ alicyclic hydrocarbons and their derivatives into dicarboxylic acids by hydrogen peroxide and dioxyge

To selective oxidation reactions of alicyclic unsaturated hydrocarbons in the liquid phase, flowing through an ionic mechanism, in the first place, belongs the synthesis of dicarboxylic acids using catalytic systems based on peroxopolyoxocomplexes of transition metals in combination with various carriers of active oxygen from the molecule of H₂O₂. As the oxygen carrier quaternary ammonium salts are often used [6-11]. In particular, very good results have been obtained in the oxidation of cyclohexene with peroxotungstenphosphatic complex and cetyltrimethylammonium. The yield of adipic acid for 6 hours reaches 56% [6]. Oxidation of cyclohexene with hydrogen peroxide in the presence of a catalytic system of Na₂WO₄ and compounds of bis-quaternary ammonium is recommended to be carried out at 80°C with the use of organic solvents or in their absence. In the latter case, the aim product yield reaches 75% [7].

A.G. Tolstikov, et al. [8] investigated in detail the influence of various factors on the formation of "in situ" active peroxopolyoxotungstenphosphatic complexes in conjunction with quaternary ammonium cations and on the oxidation of various organic substrates, including cyclohexene and cyclooctene with their participation.
The oxidation of cyclohexene to adipic acid by 30%-H_2O_2 in the presence of Na_2WO_4 and [CH_3(n-C_8H_17)3N]HSO_4 [9-11] or [CH_3(n-C_8H_17)3N]_3 [PO_4 {WO(O_2)_2} 4] catalyst [12], proceeds through the stages of formation of cyclohexane-1,2-diol. The absence of other information about formation and expenditure of such compounds as the corresponding epoxides, unsaturated alcohols and ketones prevents us from quantifying the effect of hydroxyl-containing intermediates on the stage of accumulation of the target product in the oxidate [13]. R. Noyori, et al. [10, 11] have carried out a more detailed study of the oxidation of cyclohexene in the presence of tungsten oxides and quaternary ammonium salts have shown that the accumulation of adipic acid proceeds through successive stages of the epoxidation of substrate, hydrolysis of the oxirane intermediate, oxidation of diol to oxyketone, conversion of the latter to oxylactone by Baeyer-Villeger and further to anhydride. Advanced form of this reaction is the oxidation of cyclohexene using microwave heating [14]. The technique is based on the use of a system consisting of tungsten compounds and quaternary ammonium salts used as the interphase oxygen carrier. Microwave irradiation reduces the reaction time and speeds up the accumulation of adipic acid in the oxidate.

The use of quaternary ammonium salts, separation of which is a very labour-intensive process and requires additional power consumption, which is a major drawback of the above studies. On the other hand, the used anion [(SO_4) {W_2O_2(μ-O_2)2(O_2)2}]_2^-, though it is one of the best peroxocompounds for effective transport of active oxygen, is readily converted to double-nuclear complex and rapidly loses its activity.

Replacing the quaternary ammonium salts with oxalate, phosphate or borate complex increases selectivity for adipic acid to 96% [15-19]. With H_2WO_4: H_3PO_4: C_6H_{12}: H_2O_2 = 1:1:40:176 molar ratio yield of adipic acid of high purity is 88.2% [16]. Use of the above organic and inorganic acids as a carrier of oxygen in the oxidation of cyclohexene has also led to the formation of certain amounts of low molecular weight dicarboxylic acids, in particular, glutaric acid [15].

Using preliminarily prepared complexes such as [CsH_{17}Me_3N]_4 W_{10} O_{32}, [C_8H_{17}Et_3N]_4 W_{10} O_{32}, [C_{12} H_{25}Et_3N]_3 W_{10} O_{32}, [PhCH_2 (C_5H_5N)]_4 W_{10} O_{32} and [C_{12} H_{25}(C_5H_5N)]_4 W_{10} O_{32} in this reaction at a temperature of 72 – 80ºC or in a boiling solution improves yield of adipic acid to 78 – 85% [20, 21]. The applied catalytic systems are not soluble in water, but under the influence of H_2O_2 dissolve in the solution and form homogeneous active forms. After complete consumption of H_2O_2 catalysts again sedimentate, and as a result of the introduction of a new portion of hydrogen peroxide soluble forms of active complexes are recovered.

In [22] oxidation of cyclohexene with hydrogen peroxide is carried out in the presence of tungsten and molybdenum heteropolycomplexes prepared by the interaction of the corresponding heteropoly acids with glycine. Tungsten-containing samples exhibit a higher activity in their presence the yield of product is 95% with 99.8% selectivity.

The use of ionic liquid (CH_2)_4 SO_3 • HMIm increases the conversion of cyclohexene at 0 – 5ºC up to 100% [23]. The selectivity of the reaction by adipic acid is 96.7%, and 92.3% after the extraction in a pure form. The used ionic liquid (CH_2)_4 SO_3 • HMIm is repeatedly recycled to
the process. The option of oxidation of cycloolefins into the corresponding dicarboxylic acids with NaNO₂ in a solution of trifluoroacetic acid, is also known [24]. The high yield of dicarboxylic, particularly adipic acid is achieved in the presence of an equimolar amount of NaNO₂ and molecular oxygen. When using NaNO₂ in more than three-fold excess, substrate oxidation is carried out in a nitrogen medium.

Soluble transition metal compounds of V⁶⁺ and VI⁺ groups were used for the oxidation of other cyclic unsaturated hydrocarbons and their derivatives with oxygen function [25-27]. Thus, the selective oxidation of cyclopentene to glutaric acid in the presence of H₂O₂ and tungstic acid is recommended to be carried out with oxalic acid as a complexing agent [25]. With the concentration of H₂O₂ - 50%, the amount of catalyst – 1.5%, molar ratio of H₂O₂: cyclopentene 4,4:1, H₂WO₄: H₂C₂O₄ 1:1, 85°C temperature and the duration of 6 hours glutaric acid output was 92.3%. Varying of the acidity of the medium contributes to regulation of the selectivity of the reaction. Thus, it is known that [26, 27], in the oxidation of furfural with hydrogen peroxide in the presence of soluble vanadium compounds change in acidity of the medium results in practically quantitative yield of succinic acid. The main source of raw materials to produce C₈–C₁₂ aliphatic dicarboxylic acids may be cyclic dimers and trimers of butadiene - 1, 3 – cyclooctadiene – 1,5, cyclododecadiene – 1,5, cyclododecatriene – 1,5,9 and their hydrogenated analogues with such oxidants as molecular oxygen, ozone, nitric acid or hydrogen peroxide [3, 28 – 30]. The particular interest in these acids is due to their use in the manufacture of polyamide resins, frost-resistant plasticizers, aviation oils, etc. [31]. On an industrial scale, these acids are produced in limited quantities by firms DuPont de Nemour (USA) and Chemische Werke Huls (Germany) [3].

In English patent [32] suberic acid with a yield of 74% is obtained by oxidation of cyclooctene by 45% nitric acid in the presence of vanadium pentoxide and manganese nitrate (II). Cyclododecene oxidation with hydrogen peroxide in the presence Re₂O₇ in acetic acid medium gives decanedicarboxylic – 1, 10 – acid with a high yield [33]. More selective transport of active oxygen from hydrogen peroxide is provided by tungstate or sodium phosphotungstate [34, 35].

A number of papers described single - stage oxidation of cyclohexane and its oxygen-containing derivatives by triplet oxygen or H₂O₂ to adipic acid [36-40]. In the oxidation of cyclohexane by molecular oxygen with iron porphyrinate at a temperature of 140°C, a pressure of 2.5 MPa, catalyst concentration 1,33-10% 5mol and duration of 8hours the yield of adipic acid on converted cyclohexane reached 21.4% [36, 37].
Recently it was reported about the potentially new process of obtaining adipic acid in one stage from cyclohexane using a catalyst system with a stable lipophilic carboxylic acid and small amounts of manganese and cobalt salts [38].

When using bis-(2-pyridylmethyl) amine complexes mononuclear bis-(2-pyridylmethyl) amine complexes of iron (III) are active in the oxidation of cyclohexane with hydrogen peroxide or butylhydroperoxide in solution of acetonitrile under mild conditions [41]. Higher results are obtained by oxidation of the substrate H$_2$O$_2$, in that case the yield of a mixture of cyclohexanol and cyclohexanone (molar ratio 1.5:1) reaches 30%. In this instance, adipic acid is formed in negligible quantity. Its higher yields are achieved by resing bis(2-pyridylmethyl) amine complexes of copper (II) [42]. The total yield of cyclohexanol, cyclohexanone, cyclohexane hydroperoxide and adipic acid for 24 h was ~ 69%.

Using the method of biomimetic oxidation of cyclohexane, cyclohexanone, by the complex of iron (III) in the H$_2$O$_2$-acetonitrile at 50ºC leads to the yield of mixture of cyclohexanol and adipic acid to 27% [43].

In the literature there is a report of obtaining dicarboxylic acids, in particular, adipic acid, by oxidation of cycloalkanes with molecular oxygen in the presence isoamyl nitrite [44, 45]. The main product of the reaction at T \( \leq 120 \, ^\circ\mathrm{C} \) temperature is a mixture of the corresponding cycloalkanol, cycloalkanone and dicarboxylic acid.

Oxidation of cyclohexanone by 30% H$_2$O$_2$ in the presence K$_{10}$Na$_2$P$_2$W$_{16}$O$_{60}$ heteropolycomplex at a ratio of tungsten: sulfosalicylic acid (ligand): cyclohexanone: H$_2$O$_2$ = 2:1:100:400, boiling point of the mixture (98 ºC) and 5 hours reaction time leads to the yield of adipic acid, separated in pure form, 76.7% [46].

When using a mixture of Na$_2$WO$_4$ • 2H$_2$O and sulfosalicylic acid as the catalyst the yield of adipic acid reaches ~ 80% [47]. The authors of [39, 40] have shown that the oxidation of
cyclohexanone to adipic acid by 30%-H₂O₂ with Na₂WO₄ • 2H₂O and oxalic acid proceeds through an intermediate stage of formation of ε-caprolactone.

In [48-50] for the oxidation of cyclohexene, cyclohexanol, cyclohexanone and cyclohexane-1, 2-diol by 30%-H₂O₂, amphiphilic complexes of oxydiperoxytungsten and nitrogen-containing surfactants, simultaneously playing the role of a catalyst and a phase transfer agent, were used. The main reaction product is adipic acid, which yields ~90% in the oxidation of cyclohexene at 90°C for 20 h. Complexes containing the anions of peroxyxylodiphenyl showed low activity in this reaction. According to the authors of [51, 52] during the oxidation of cyclohexene, cyclohexanol and cyclohexanone in the presence of µ-oxocluster complexes of cobalt and manganese at 80 – 150°C achieved the same yield of adipic acid as in the process, effected by using HNO₃ as oxidizing agent, is achieved.

The high yield of adipic acid is obtained by oxidation of cyclohexanone by the air oxygen in the presence of heteropoly anionic complexes of molybdenum and vanadium, with the structure of Keggin H₅[PMo₁₀V₂O₄₀]₉aq (aq-10-30 H₂O) in acetic acid solution [53, 54]. In the reaction products, along with adipic acid glutaric and succinic acids are also contained. In particular, at a pressure of 1 atm O₂, at 70°C and 7 h. duration the yield of adipic, glutaric and succinic acid is 50, 19 and 3%, respectively. In the presence of Cu(NO₃)₂ out put of adipic acid (at T = 110°C, >τ = 8 hours) reaches 72% [4].

The advantage of the above catalytic oxidation of cyclohexanone by dioxygen over the well known industrial method of producing adipic acid, through oxidation stage of a mixture of cyclohexanone and cyclohexanol by nitric acid, is a high corrosion resistance of the system employed and the absence of toxic nitrogen oxides in the gaseous reaction products.

Co-liquid-phase oxidation of o-xylene and cyclohexanone in the presence of CuCl₂·2H₂O at atmospheric pressure and temperature of 60 – 90°C for 10 h leads to their conversion of 74 and 97%, respectively. O-tolualdehyde (42%) and o-toluic acid (31.7%) were obtained from o-xylene, and adipic acid formed from a cyclohexanone with a yield of 93.3% [55].

Oxidation of cyclohexanone in the presence of redox systems of Co²⁺/³⁺ or Mn²⁺/³⁺ in the solution of acetic acid at 80-85°C mainly leads to the accumulation of glutaric acid (≥ 80%) [56].

Another option of adipic acid has been proposed previously [57] by oxidizing epoxycyclohexane by Jones reagent under mild conditions. The yield of adipic acid at 20°C for 20 minutes is 60%. As a by-product, up to 20% of cyclohexanone is formed. The disadvantage of this method is to accumulation of a significant amount of highly toxic chromium-bearing waste, disposal of which requires more energy.

The process of oxidation of cycloalkanols and cycloalkanones, in any case, is accompanied by the formation of dicarboxylic acids with fewer carbon atoms. To get higher (C₅-C₁₂) dicarboxylic acids containing no admixture of the lower homologues, it is proposed to use as a substrate vicinal alicyclic diols, high reactivity of which provides the possibility of the process under mild conditions with hydrogen peroxide and sodium salts of molybdenic, tungstic, phosphotungstic and vanadic acids [34, 35, 58].
These processes are characterized by high yields of C₅-C₁₂ dicarboxylic acids, the absence of toxic nitrogen oxides, high corrosion resistance and are recommended for industrial implementation [34, 35].

In the oxidation of cyclopentane-1, 2–diol with aqueous of H₂O₂ in the presence of a homogeneous catalyst H₂WO₄ and interfacial oxygen carrier a high yield (∼ 90%) of glutaric acid is achieved [59].

W-containing systems are also successfully used in the oxidation of cyclohexane-1, 2-diol by 30%-H₂O₂ [10, 11, 60-62] to adipic acid.

Catalytic oxidation of cyclooctane 1, 2-diol by 30%-H₂O₂ is recommended to be carried out in the heterophase system liquid-liquid, where the solvent for diol is toluene [34, 35]. Efficient conversion of hydrogen peroxide in this system is provided by tungstate or sodium phosphotungstate in the presence of which high yields and purity of suberic acid (∼ 92%) are obtained. To the authors’ [34] opinion, the presence of 2-hydroxycyclooctanone and cyclooctane-1, 2-dione, established by chromatographic method, shows a sequence of transformations of starting, diol according to the scheme:

In the first stage of the scheme, of the two reaction centers in the molecule of the original diol, only one can interact with peroxyanion owing to hydrogen bonds, which facilitate the formation of six-membered transition state,

in which redistribution of electron density leads to a weakening of the C-H and O-H bonds. Breakage of these bonds and coordinated transfer of hydrogen atoms on peroxy fragment contributes to the oxidation of diol to α-ketoalcohol (IV) and the regeneration of MeO⁻ anion.

Version of the direct oxidation of -α-oxyketone in α-diketone [34] is unlikely, since as a result of redistribution of electron density C-C bond between the hydroxy- and carbonyl-containing fragments strongly weakens, and as a result of coordination of peroxyanion with the carbonyl fragment by the ion-dipole mechanism the further oxidation of α-oxyketone proceeds through the intermediate stages of formation of the oxylactone [10, 39, 40] by the scheme:
Heterolytic rupture of the bond that takes place in weakly acidic media, leads to accumulation of suberic acid, bypassing the stages of formation of the corresponding aldehydoacid [34, 35]. Catalytic oxidation of cyclohexane-1,2-diol to adipic acid (or its esters) is carried out smoothly by dioxygen in the presence of a catalytic H$_5$[PMo$_{10}$V$_2$O$_{40}$]aq / ROH [63] system:

The advantage of this process is the use of molecular oxygen, as well as the absence of onium salts as oxygen carrier.

III Heterogeneous catalysts of oxidation hydrocarbons on the basis of mesoporous silicalites and other supporters. Methods to increase their activity

Homogeneous catalysts used in oxidation reactions of C$_6$ - C$_{12}$ alicyclic hydrocarbons and their derivatives, interact with components of the conversion to the substrate, which leads to a partial shift of the transition metals to the target products and their pollution. As a result of this interaction it is necessary to purify the reaction products from the catalysts, separation and recovery of which is a difficult technological problem.

One possible cardinal solution of this question is the transfer to heterogeneous catalysts synthesized by sol-gel method or catalyst systems immobilized on solid supporters. The advantages of using the above catalysts are more stable active complexes in fixed form, the ease of their separation from the products of oxidation and reuse, as well as the variation of catalyst activity by altering the surrounding of the active centers by adding various components. In immobilization of soluble compounds on solid supporters there is a problem with washing-out of the active phase [64]

Presently, one of the most promising heterogeneous catalysts of liquid-phase oxidation of organic compounds are titanium amorphous silicalites TS-1, with the structure of zeolite ZSM-5 (MFI), TS-2, with the structure of zeolite ZSM-11 (MEL) [64, 65], mesoporous titanium-containing zeolites and silicalite with a large pore size [66]. Some of them, in particular, TS-1 and TS-2, due to the high hydrostability and activity in oxidation reactions with H$_2$O$_2$ found a practical application on an industrial scale. In particular, using TS-1-H$_2$O$_2$ system the Italian company Enichem developed capacity the process of oxidation of phenol to hydroquinone and
catechol with the unitof the 10000t/year [67, 68]. These narrow-porous zeolites (pore size 0.53-0.56 nm) are effective in the oxidation of alcohols [69], epoxidation of linear C₃-C₆ olefins [70, 71], the oxidation of alkanes [72, 73], etc. Unlike the TS-1, TS-2 silicalite epoxidation of allyl alcohol, cyclohexene and styrene selectively conducts with the adduct of urea and hydrogen peroxide [74]. However, these systems are only effective in the oxidation of organic compounds with molecular kinetic diameters <0.6 nm (the linear structure hydrocarbons, phenol). Selective oxidation of substrates with a diameter of molecules 0.6 nm (cyclohexene, cyclooctene, cyclododecene, norbornene, etc.) was carried out with the use of mesoporous and amorphous silicalites, such as Ti-MCM-41, Ti-MCM-48, Ti-SBA-15 containing transition metals and other molecular sieves are redox system [66]. Examples of some of the reactions are listed in Table 1.

**Table 1.** Oxidation of organic compounds by hydrogen peroxide in the presence of heterogeneous catalysts.

<table>
<thead>
<tr>
<th>The starting compound</th>
<th>The reaction products</th>
<th>catalyst</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propylene</td>
<td>epoxypropane</td>
<td>TS-1</td>
<td>[70]</td>
</tr>
<tr>
<td>Pentene-1</td>
<td>1,2-epoxypropane</td>
<td>TS-1</td>
<td>[71]</td>
</tr>
<tr>
<td>Phenol</td>
<td>Catechol, hydroquinone</td>
<td>TS-1</td>
<td>[68]</td>
</tr>
<tr>
<td>Hexene-1</td>
<td>1,2-epoxyhexane, hexane-1,2-diol</td>
<td>Ti-MCM-41</td>
<td>[76]</td>
</tr>
<tr>
<td>Cyclopentene</td>
<td>glutaraldehyde</td>
<td>WO₃/SiO₂</td>
<td>[77, 78]</td>
</tr>
<tr>
<td>Cyclohexene</td>
<td>epoxycyclohexane</td>
<td>Ti-MCM-41, xerogel Ti/B-SiO₂</td>
<td>[74]</td>
</tr>
<tr>
<td>Cyclohexene</td>
<td>Mixture of epoxycyclohexene, cyclohexane-1,2-diol, cyclohexene-3-ol and cyclohexene-3-one</td>
<td>Ti-MCM-41, Ti-MMM</td>
<td>[76, 79]</td>
</tr>
<tr>
<td>Cyclooctene</td>
<td>Epoxycycloctane</td>
<td>Mo-MCM-41, Mo-MCM-48, Mn-SiO₂</td>
<td>[80]</td>
</tr>
<tr>
<td>Cyclododecene</td>
<td>Epoxycyclodecane</td>
<td>Ti-MCM-48, Ti-MCM-41, TiO₂-SiO₂</td>
<td>[87]</td>
</tr>
<tr>
<td>Limonene</td>
<td>Mixture of 1,2-epoxylimonene,carvone, carveollimonone -1,2-diol</td>
<td>Ti-MCM-4, Zn-phosphate and chrome molecular sieve</td>
<td>[85]</td>
</tr>
<tr>
<td>Norbornene</td>
<td>3-oxatricyclo [3.2.1.02.4] octane, bicyclo [2.2.1] heptane-2,3-diol</td>
<td>Ti-MCM-41, Mn-SBA-15</td>
<td>[76]</td>
</tr>
<tr>
<td>Styrene</td>
<td>Mixture of styrene oxide, 1-phenyl ethane -1,2-diol and benzaldehyde</td>
<td>Ti-MCM-41, Ti-HMS, Ti-MCM-48</td>
<td>[90]</td>
</tr>
<tr>
<td>Stilbene</td>
<td>stilbene epoxide</td>
<td>W-SPA-15, vitamin B₁₂ on Al-MCM-41</td>
<td>[93]</td>
</tr>
</tbody>
</table>
As it can be seen from these data, mesoporous metal silicalites and amorphous silicate, characterized in comparison with TS-1 and TS-2 by a higher hydrophilic nature, exhibit relatively high activity in the reactions of epoxidation and dihydroxylation of cyclic unsaturated hydrocarbons (cyclohexene, cyclooctene, cyclododecene, norbornene, limonene, and others), which have co larger size of molecules as compared with the linear hydrocarbons [66]. Pore sizes of mesoporous materials make it possible to use as an oxidizer, not only H$_2$O$_2$, but also organic peroxides (in particular, tert-butyl hydroperoxide) [76]. However, in the latter case, the yields of the target products are not high. Thus in the oxidation of norbornene by tert-butylhydroperoxide in the presence of Ti-MCM-41 the yield of the corresponding epoxide is 42% and 8% of the diol [76, 104]. α-Pinene in this catalytic system is selectively converted (~100%) in to the corresponding epoxide, but the conversion of the substrate does not exceed 11% [99]. The use of an organic peroxide, in this case, is due to washing-out titanium ions from the silicate matrix under the action of an aqueous solution of H$_2$O$_2$ matrix and destruction of the porous structure of the catalyst.

The high hydrophilicity of mesoporous systems leads to the deactivation of zeolites for the sorption of polar products and solvent in their pores. The high hydrophilicity of the zeolites is due to the low ratio of Si / Al (it should be noted that the increase in the ratio of Si / Al has little effect on the activity of these systems [101]). Creation of a hydrophobic surrounding around the active site contributes to the solution of the problem of catalyst stability and desorption of polar oxidation products.

In order to prevent the transition of the active component from the above catalytic systems in to the liquid phase it is intended to carry out hydrophobilization of their surfaces by silylation [106, 107] or introduction of hydrophobic reagents to in the silicate matrix during the synthesis of mesoporous metal-silicalite [103, 108]. Increasing the hydrophobicity of mesoporous titanium silicalites promotes the preservation of their structure and activity, and thereby reuse of these zeolites.

The modification of mesoporous or amorphous silicon-containing materials or by transition metal compounds (Lewis acids) enhances the rate of hydrolysis of the epoxide ring and the accumulation of the corresponding diol in the oxidate. [104]. By Fe(ClO$_4$)$_3$ on a silicagel supporter a stable non-hygroscopic agent is obtained , it can be used in the reactions of formation and rupture of the carbon-oxygen bonds in organic compounds, in particular, obtaining of the vicinal diols [109]. The epoxidation of cyclohexene at the room temperature is catalyzed by Ni (Acac)$_2$ · H$_2$O complex encapsulated by sol-gel method to SiO$_2$ [110] or by using Na$_2$...
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(PV$_2$Mo$_{10}$O$_{40}$) supported on TiO$_2$ nanoparticles [111], Ti-MCM-48, Ti-MCM-41 and Ti-HMS titanium silicates are active in the oxidation of styrene by hydrogen peroxide in to benzaldehyde. The selectivity of the reaction is 77-85% with 10-28% conversion of the substrate [90, 91]. The introduction of aluminum into the mesoporous SBA-15 silicalite directly in its synthesis or during post-synthesis with the subsequent application of titanium, leads to the formation of active catalytic system of one-step oxidation of cyclohexene by tert-butyl peroxide to adipic acid. The yield of the target reaches 80% at 80° product C and the reaction time 24h. The intermediate is trans-cyclohexane-1, 2-diol [94, 95]. Both of the catalysts retain their activity and can be recycled to the reactor. The selectivity of the reaction is determined by the stereochernistry of the resulting intermediate. In particular, in the presence of Ti-containing aluminophosphate molecular sieve TARO-5 adipic acid in the absence of organic solvent is formed as follows [96]:

In [97] oxidation of cyclohexene to adipic acid was carried out with hydrogen peroxide in the presence of mesoporous silicalites Ti-MMM-2 and Ce-SBA-15. With the molar ratio of H$_2$O$_2$ : substrate 3.6:1, temperature of 80° C, duration of 72 hours the yield of the target product is 33 and 18%, respectively. The resulting adipic acid reacts with Ti-MMM-2, which leads to washing-out of titanium ions from the catalyst composition and their transition to a solution. Ce-SBA-15 has a more stable activity. However, this catalyst is inclined to deactivation due to agglomeration of cerium ions and the formation of less active nanocrystals of Ce (IV) and Ce (III) oxides [97]. Higher yields of adipic in oxidation of cyclohexene by 30%-H$_2$O$_2$ are obtained on oxotungstic silicalite W-SBA-15 containing tetrahedrally coordinated tungsten in the absence of organic solvents (yield 55%) [98]. The W-SBA-15 catalyst containing a mixture of W$^{4+}$, W$^{5+}$ and W$^{6+}$ retains its activity and can be recycled into the system for the oxidation of the substrate.

In the literature there is also a new report on oxidation of cyclohexane with molecular oxygen to adipic acid using samples of metalcontaining zeolite ZSM-5 (MFI) and hydroxyphthalimide [99]. The highest selectivity for the target product is achieved with Mn (II) ZSM-5 [99]. When using zeolite molecular sieve of ALPO-31 (Fe-aluminophosphate-31) type with a pore diameter of less than 0.54 nm, cyclohexane is easily adsorbed in the micropores of this system, at the same time the desorption rate of the primary products of its oxidation, that is cyclohexylhydroperoxide, cyclohexanol and cyclohexanone is low. The resulting intermediates undergo further oxidation with oxygen to adipic acid, which is then easily desorbed into the liquid phase. Under these conditions large-porous Fe-ALPO-5 selectively conducts oxidation of cyclohexane to cyclohexanone and cyclohexanol (yield to 60%) [100, 101].
transition of the stage of the interaction of substrate with oxygen inside the micropores, promotes growth of selectivity.

Porphyrrinates of Co, Mn, Fe encapsulated to zeolite NaX, compared with supporters obtained from silicic acid, montmorillonite or polystyrene, exhibit high selectivity in the oxidation of cyclooctane to cyclooctanone and cyclooctanol by air oxygen [102]. Ratio of ketone: alcohol is at the level of the reaction carried out in a solution of the above mentioned porphyrinate-metals.

Analysis of materials on one-step oxidation of cyclanic hydrocarbons to the corresponding dicarboxylic acids with homogeneous catalysts or redox forms of molecular sieves in the presence of oxygen or H$_2$O$_2$ shows that they, unlike their unsaturated analogues are characterized by low efficiency and they are of no interest in terms of realization on an industrial scale. Oxidation of cyclic unsaturated hydrocarbons with hydrogen peroxide is conducted in the presence of amorphous mesoporous oxidic [83, 84, 112, 113] and metallocontaining polymeric materials [114-117]. In [107] by the sol-gel method, obtained mesoporous mixed ZrO$_2$-SiO$_2$ oxides of different composition and with a surface modified by methyl groups, were obtained, they show high activity in the oxidation of cyclohexene with hydrogen peroxide in to cyclohexanediol. The specific surface and porous structure of the synthesized catalysts are regulated by their degree of methylation.

The activity of covalently fixed Mn-salen complex on amorphous mesoporous SiO$_2$ in the epoxidation reaction of cyclooctene as compared with the activity of the corresponding homogeneous catalyst is practically not reduced [83, 84]. For modification of the above porous supporter it was prenoculated with (3-aminopropyl) - or (3-iodopropyl) trimethoxylane. Immobilization of the Mn (3 +) and Mn (4 +)-salen complexes on silica was carried out by means of a peptide or ester bond [84]. Heterogeneous Mn (4 +)-salen complexes exhibit a more stable and higher activity, they can be used repeatedly in epoxidation reaction of cyclooctene. At the same time, Mn (3 +)-salen complexes are less effective and largely contribute to unproductive decomposition of hydrogenperoxide.

High activity in the oxidation of unsaturated hydrocarbons is exhibited by the complexes, obtained by reacting of compounds of Mn (2 +), Co (2 +), Ni (2 +) and Cu (2 +) with bis-(2-oxyanil) dibenzene supported on Al$_2$O$_3$ [109 , 114].

In the presence of complexes of Mn (2 +) and acetylacetonate of N, N'-ethyl bisalicylidimenimate, ethylenediamine or 2, 2'-dipyridine ligand supported on Al$_2$O$_3$, major products of oxidation of cyclohexene by 30%-H$_2$O$_2$ are the corresponding oxirane and vicinal diol [117].

MoO(O$_2$)$_2$ containing copolymers of tetraethoxylane and N, N'-chelate ligands obtained by the sol-gel method have a large specific surface and exhibit a stable activity in liquid-phase epoxidation of cyclooctene [118]. In addition to mesoporous systems, for the selective oxidation of cycloolefins, it is proposed to use forms of hydroxyapatite or hydrotalcite modified by transition metals [74, 119-122]. Thus, oxidation of cyclooctene by urea H$_2$O$_2$ in the presence of H$_2$WO$_4$ supported on apatite leads to a high yield of the corresponding epoxide [74].
Co\(^{2+}\) cations supported on ion-exchange method on hydroxyapatite, exhibit high selectivity in the epoxidation of styrene in DMF solution under mild conditions [119]. In the process, DMF was subjected to oxidation into N-(hydroxymethyl) N-methylformamide, which is a carrier of active oxygen from H₂O₂ to the substrate.

In [120], the oxidation of cyclohexene with 30% H₂O₂ in the presence of compounds of Mo supported on synthetic hydrotalcite Mg₃Al(OH)₆(CO₃)₀.₅ H₂O, has been studied. Samples containing ionic form of MoO₄²⁻, are active in the formation of cyclohexene hydroperoxide and catalysts containing Mo⁴⁺ ions selectively carry out epoxidation of the substrate.

Hydrotalcite is applied also for the induction of ultrasonic irradiation epoxidation reaction of olefins and \(\alpha, \beta\)-unsaturated ketones with hydrogen peroxide [121, 122].

Catalysts prepared by Pd supported on Cu-Mg-Al hydrotalcites are active in the reaction of liquid phase oxidation of limonene [123]. Oxidation proceeds by a radical chain mechanism whereby Pd is involved in the formation of allyl radicals, activating the CH bond, as well as adducts by breaking the C = C bond and copper cations catalyze the decomposition of are hydroperoxides formed during the oxidation with the emergence of radical intermediates. The reaction products are 1,2- and 8,9-epoxylimonenes, cis- and trans-carveols and carvone.

Regioselective opening of oxirane ring with aliphatic alcohol and water can be effectively achieved in the presence of iron perchlorate (3+) supported on SiO₂ [109].

Single-stage dihydroxylation of cyclohexene and norbornene proceeds selectively with the participation of urea - H₂O₂ system or H₂O₂-dioxane solution in the presence of a mixture of bentonite and kaolinite (5:1 ratio), and their coked forms, modified by Mo (V), W (VI) and Co (II) halogenides, [124-125]. Synthesized diols are further recommended for obtaining of the corresponding dicarboxylic acids.

Thus, analysis of literature data on the oxidation of cyclic unsaturated hydrocarbons and some of their derivatives on mesoporous molecular sieves, or oxidates containing redox systems shows that these catalysts are mainly active in the implementation of stages of epoxidation of the initial substrate and hydrolysis of oxiranes in to the diols. Publications on the synthesis of dicarboxylic acids with mesoporous systems in the literature are very limited, and the data given there are conflicting. We can assume that the problem in this area is still in early stages of research.

**Evaluation of activity of modified forms of carbon materials in the oxidation of unsaturated hydrocarbons**

At the present time for the preparation of immobilized systems along with the mesoporous materials, carbon supporters are used as a supporter [126-128].

Carbon materials are regular or chaotically arranged crystallites with fragments of the structure of graphite [119, 130]. A certain part of the surface carbon atoms are active and can form various oxygen-containing functional groups, in particular, hydroxyl, carbonyl, carboxyl, lactone, and quinoid, etc. [130, 131].

The presence of interconnected and isolated pores of different shapes and sizes in the bulk structure provides the possibility of using carbon materials, which differ in structure and
dispersity, in the oxidation catalysis [132-134]. In particular, for the oxidation of alcohols, saturated and unsaturated hydrocarbons, highly dispersed amorphous carbon materials [126-128, 135], foliaceous compounds of graphite [133] and fullerenes of different composition [134, 136, 137] were used.

In the course of the epoxidation of styrene into acetonitrile, carbon materials obtained by grafting of salen-complex Mn (3+) to the surface of active coal oxidized by air [127, 128] were tested. It is established that the heterogenized catalysts are chemoselective for formation of styrene epoxide, are resistant to leaching and can be used repeatedly.

In [126], liquid-phase oxidation of α-pinene with oxygen at 70-90°C is carried out with Pd, Pt, Ru, Rh, Ir supported on carbon material.

Catalytic activity in the oxidation of cyclohexene by molecular oxygen and the decomposition of cyclohexylhydroperoxide is exhibited by foliaceous compounds of graphite modified by Co, Mn, Fe, Mo, etc chlorides. On MoCl₅-modified forms of catalyst, reaction proceeds till the formation of epoxycyclohexane[133].

Catalytically active centers of modified forms of the foliaceous graphite are chlorides, located either between the carbon grids, or on the edges of the crystallites of graphite [133]. In the reaction, a small part of the salt, from the graphite proceeds into solution. However, after pretreatment of catalysts by a solution of cyclohexenyl hydroperoxide in cyclohexene, chloride washing-out stops, and their activity and selectivity remains practically unchanged. On the basis of the reaction products and some of the kinetic regularities, the authors surmised oxidation of cyclohexene with a foliaceous graphite proceeds by radical-chain heterogeneous-homogeneous mechanism.

The catalytic functions of C₆₀, C₇₀- fullerenes and fullerene-containing carbon structures in the oxidation of unsaturated hydrocarbons, including α- and β-pinenes, 4-methylcyclohexene, limonene are considered in [134, 135]. The main reaction products are viscous polymerlike compounds containing peroxide fragments. In the process of oxidation fullerenes partially decompose and dissolve in solution. According to [136], at 70 °C and the duration of 376h fullerenes in quantities of 5-20 ppm sharply increase concentration of hydroperoxides in jet fuel samples containing a significant amount of polycyclic olefins. In the aerobic oxidation of n-decane in the presence of C₆₀,C₇₀- fullerene products of catalytic conversion of hydroperoxides - alcohols, ketones and lactones are obtained [137]. In this case, the carbon atoms of the fullerene, which are in the sp²-hybrid state, and have acceptor properties, actively attract electrons and free radicals [138] and thereby promote acceleration of the oxidation process and the formation of various oxygen-containing compounds.

It is known that fullerenes and molecular-sieve carbon materials modified with transition metals can be active and selective catalysts for reactions under mild conditions [138, 139]. Harder reaction conditions lead to their structural changes or partial homogenization of fullerenes metals in the liquid phase. In order to improve the thermal stability of fullerene-containing catalysts, the inoculation of C₆₀ to the surface of various supporters, in particular, SiO₂, by using compounds containing amine [140], pyridine [141], phenanthroline [142] fragments or alkyl and alkoxyderivative silanes [143], is applied. The fullerene-containing
obtained by this way, systems exhibit high selectivity in hydroformylation reactions of hydrogenation and hydroformylation of organic compounds [138]. Works devoted to the oxidation of hydrocarbons and their derivatives with their participation are few [135, 136], and they mainly examine the possibility of applying metal-containing fullerenes.

Microstructured carbon materials MCM with immobilized in them transition metal compounds of Mo (V), W (VI), Co (II) show high activity in the oxidation of cycloolefins with hydrogen peroxide into vicinal diols [144] and dicarboxylic acids [145, 146].

Microstructured (X-ray amorphous) metal-carbon materials, are prepared by the interaction of individual powders of chromium, molybdenum, tungsten and cobalt or their binary mixtures, as well as molybdenum and tungsten blue (a mixture of MoO₃Br₃ or WO₃Br₃ oxohalogenides, where n = 1, 2, m = 2-4) obtained by the method described in [147, 148] with carbon tetrachloride or bromoform at 75-76°C. As an activator of CCl₄ (CHBr₃), metallic aluminum was used [149]. After filtration, the obtained metal-containing carbon nanoparticles are dried at 20-30°C and thermotreated at 170-180°C until no AlCl₃ separates.

It is known that the oxidation of low-soluble in water cycloolefins in the presence of 30% aqueous H₂O₂ occurs at the phase interface. Application of microstructured carbon material in pseudohomogeneous system makes the process possible without the use of phase transfer agents – salt of the quaternary ammonium cation by the intensive mixing of the reaction mixture.

(500-600 rotations min⁻¹) According to [150], the intensity of mixing of two-phase solutions fluids increases only up to a certain level, despite an increase in speed, intensity of mixing, and consequently, the magnitude of the surface area of the interface are not changed. The use of dioxane solution of H₂O₂ [146] as an oxidizing agent facilitates the interaction of cycloolefins and the formed "in situ" catalytic complex in the entire volume of the reaction mixture. In this case, the intensity of mixing of the reaction mixture does not significantly affect the yield of the reaction products, i.e. organic solvents ensuring homogenization of the liquid phase and removing the effect of hydrodynamic parameters of bias do not contribute to yield of dicarboxylic acids.

Use of binary mixture of oxohalogenides and halogenides of Mo (V, VI), W (VI), and Co (II) highly dispersed on carbon nanoparticles, in the presence of aqueous H₂O₂ leads to their hydrolytic conversion and formation of «in situ» carbonaceous peroxomolybdencocobalt systems of [MeO (O₂)ₚ HlgₘCoBr₂]ₙ / MCM (where p = 1 and 2, m = 1 and 2, n = 1-4) [151]. In this case the ditransition of salt from the carbon matrix into the solution practically does not occur and the catalyst is easily separated from the reaction mixture by hot filtration. On these catalysts yield of dicarboxylic acids (adipic, 3-methyladipic, 1.3-cyclopentanedicarboxylic) is 82-85% [145-146]. Oxidation of cycloolefins in the presence of the aforementioned metal-carbon materials proceeds as in the case of homogeneous catalysts by aconsecutive scheme[60, 11, 152]. The primary reaction product is epoxide, then converting in an acidic medium into the corresponding dihydric alcohol. Oxidation of the latter leads to the accumulation of dicarboxylic acid in the system.
Conclusion

Methods for the selective functionalization of saturated and unsaturated alicyclic hydrocarbons into oxygen-containing compounds, and especially into the dicarboxylic acids, which are alternative to commercialized two-step acid production, using nitric acid as an oxidant are aimed at solving important technological and environmental problems. This review covers the materials on catalytic oxidation of hydrocarbons above with hydrogen peroxide or dioxygen over the past 10 years. The presented data show that for the solution of this problem, studies are carried out in two directions.

1. The development of homogeneous catalysts based on soluble transition metal compounds or heteropolyacids with phase transfer agents, salts of quaternary ammonium cations. The implementation of these methods is difficult due to the emerging new problem of separation of alkyl derivatives of ammonium and their recycling into the process. Part of the problem is solved by using organic or mineral acids. Researches in this area require further development.

2. Development of the concept of effective oxidation catalysts based on mesoporous silicalites of transition-metals or carbon materials of various structures and modifications. The creation of such catalytic systems enables us to develop new environmentally friendly technologies for different types of oxygen-containing compounds, including, dicarboxylic acids. In this case the problem of the separation of catalysts from reaction products and re-use them is solved. The prospects of using the above systems in heterogeneous catalytic processes, is shown, in particular, by the development and commercialization of a number of new large-tonnage processes with their participation. Oxidation of phenol by hydrogen peroxide into the catechol and hydroquinone with 10000t/year capacity (firm «Enichem», Italy), obtaining of cyclohexanoneoxime with 12000t/year (Enichem) and 600000t/year («Sumimoto», Japan) capacity, propylene oxide with 300000t/year capacity ( BASF, Dov Chemical, "Solvay", Belgium) are the first steps in this direction.

Immobilized catalytic systems prepared on the basis of microstructured and other forms of carbon materials have been studied to a lesser degree. It can be assumed that this trend will develop in the future.

REFERENCES

7. Wang Qinbo, Li Xi, Wang Lijun et al. Kinetics of p-Xylene Liquid-Phase Catalytic Oxidation to
16. Cao F., Jiang H., Gong H. Direct catalytic oxidation of cyclohexane to adipic acid with catalyst system tungsten / inorganic acid ligands // China Synthetic Fiber Ind. 2004, v. 27, №6, p. 34


73. Laha S.C., Kumar R. Highly Selective Epoxidation of Olefinic Compounds over TS-1 and TS-2 Redox Molecular Sieves Using Anhydrous Urea–Hydrogen Peroxide as
76. Lu Guang, Li Xinyong, Qu Zhenping et al. Selective oxidation of cyclopentene to glutaraldehyde over the WO₃/SiO₂ catalyst // Appl. Surface Sci. 2008 v. 255, N5, p. 3117-3120
83. Lutz T., Papp, P. A new method of immobilization of the complex Mn-SALIN on the modified silica and its catalytic activity in epoxidation reactions of cyclooctene // Thro. and rolled. 2007 v. 48, N1, p. 185-191


98. Danhong Yang, Mingdeng Liu, Wenjun Zhao, Lin Gao A comparative oxidation of cyclohexene catalyzed by N-hydroxyphthalimide and ZSM-5 supported Co(II), Mn(II), Ni(II), Zn(II), Fe(III) with molecular oxygen in the absence of solvents and reductants // Catal. Commun. 2008 v. 9, N14, p. 2407-2410


