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Catalysts for Obtaining 2,3,5-Trimethyl-1,4-benzoquinone, a Key Intermediate for the Synthesis Vitamin E

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Abstract

The development of catalytic methods for the oxidation of organic compounds those fit contemporary environmental requirements represents a complicated and highly urgent task, especially for the processes of fine and pharmaceutical chemistry. This review summarizes data concerning the catalytic oxidation methods developed during the last 20 years for converting 2,3,6-trimethylphenol into 2,3,5-trimethyl-1,4-benzoquinone, a key intermediate for the synthesis of vitamin E. Also considered catalysts during 2,3,6-trimethylphenol hydroxylation in to 2,3,5-trimethyl-1,4-hydroquinone are considered, too.

Key words: 2,3,6-trimethylphenol, 2,3,5-trimethyl-1,4-benzoquinone, oxidation

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INTRODUCTION

In today's world, an ever-deteriorating quality and ecological purity of the ambient air, natural waters (rivers, lakes, and seas), soil, and drinking water is observed, especially within industrialized areas. In this context, increasing importance in the development of catalytic processes is acquire by the following trends:

– Environmental technologies based on catalytic processes [1]: purifying vehicle exhaust; purifying smoke fumes from combined heat power plants; purifying industrial effluents and gaseous emissions.

– Modernizing the existing facilities and the development of new energy-efficient and waste-free technologies [2]: increasing the yield of target products; using the by-products as a feedstock; simplifying the processes *via* improving the technological scheme and the structure of reaction units; novel catalysts and catalytic processes; reducing the energy consumption.

The latter line is especially important for fine and pharmaceutical chemistry, because the most of the products of these industries (pesticides, dyes, fragrances, textile auxiliary substances, vitamins and medicines) exhibit a complex structure, which results in multi-stage

TABLE 1

Scale of production and E-factor parameters for some segments of the industry

Segments of the industry	Scale of production, t/year	*E*-factor
Petroleum refining	10^6–10^8	<0.1
Basic chemistry	10^4–10^6	<1–5
Fine chemistry	10^2–10^4	from 5 up to >50
Pharmaceutical chemistry	10 –10^3	from 25 up to >100

processes for the preparation thereof being connected with a lot of wastes and wastewaters [3]. These industries exhibit the highest values of *E*-factor that characterizises the ratio of unreacted substances and wastes to target products (in kg/kg of the target product) reflecting the economical efficiency and environmental safety of the technologies used (Table 1).

A special place among the products of these industries is taken by vitamins, organic substances with different structure essential for life, the biological catalysts of chemical reactions or the reagents of photochemical processes occurring in a living cell. In human and animal organisms, vitamins can not synthesized, coming therein only from the environment [4].

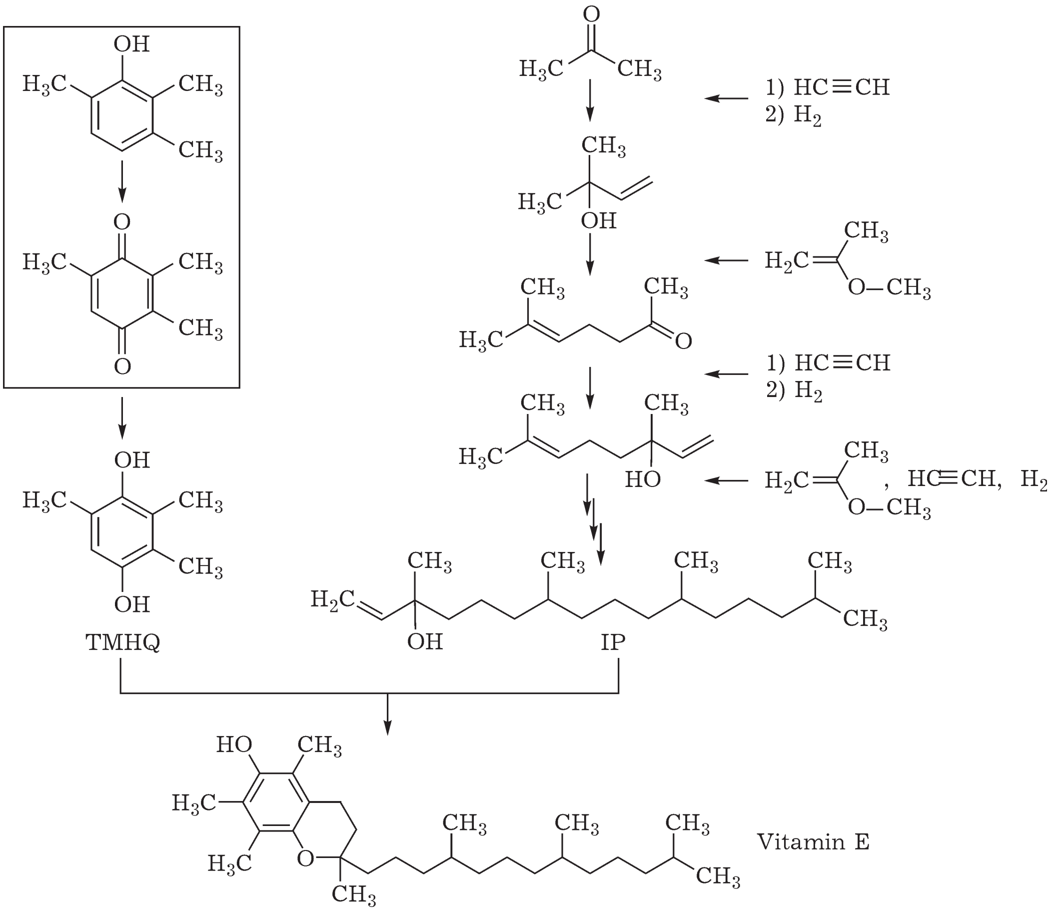
For example, modern industrial method for the synthesis of vitamin E (α-tocopherol) involves three basic stages (Scheme 1) [5]:

1) synthesis of isophytol (IP);

2) synthesis of 2,3,5-trimethyl-1,4-hydroquinone (TMHQ);

3) between IP and TMHQ.

The first key building block isophytol can be synthesized using a variety of approaches based on a combination of C_2 and C_3 chain elongation reactions, since acetone or citral. Scheme 1 demonstrates one of the IP synthesis strategies based on using multiple key building blocks (acetone, acetylene, hydrogen and methylisopropenyl ether) and on repeating the typical reactions such as C_2 elongation reaction *via* inter-



Scheme 1. Synthesis of vitamin E from isophytol with trimethylhydroquinone.

action with acetylene followed by hydrogenation, as well as the reaction of C_3 elongation *via* interaction with methylisopropenyl ether.

It is seen that for the industrial production of TMHQ, the second key building block in the synthesis of vitamin E, the major starting material is presented by 2,3,6-trimethylphenol (TMP) oxidized into 2,3,5-trimethyl-1,4-benzoquinone (TMBQ) with further hydrogenation. The oxidation reaction is usually carried out in the presence of an aqueous $CuCl_2$ solution containing the additives of Li^+, NH^+ chlorides and other salts with the use of oxygen as an oxidizer [6].

The last stage in the industrial synthesis of α-tocopherol is based on the reaction between isophytol and TMHQ. Typically, this reaction is catalyzed by a combination of a Lewis acid and a Brøensted acid, such as $ZnCl_2$ + HCl.

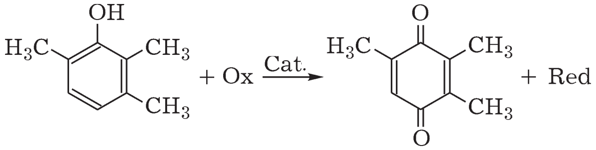
The function of vitamin E in a human organism are numerous and manifold. It is used for the prevention and treatment of many diseases [4]. Thus, this vitamin favours the metabolism of fats, maintains a normal activity of nerve fibres in the muscles, facilitates the clinical course of cardiovascular diseases. It is also used in agriculture as a part of premixes for adequate animal nutrition ration to increase the productivity [7].

The oxidation of TMP into TMBQ represents a key reaction in the synthesis of vitamin E, which reaction occurs with a low productivity, insufficient selectivity level (up to 94 %) to be accompanied by a significant number of hazardous by-products (organochlorine congeners of dioxins) those must be carefully removed and utilized. These disadvantages cause a low environmental safety and low economical efficiency of the existing commercial method of TMBQ obtaining, as well as an increase in the cost of the target product (vitamin E).

Currently, the world production level of vitamin E is greater than 25 000 t/year [5, 8], and the fraction of synthetic product reaches 90 % of total production. That is why the development of an environmentally safe and cost-efficient method for producing TMBQ is of extreme urgency.

CATALYSTS FOR TMP OXIDATION INTO TMQ

There are many known methods for preparing the TMBQ *via* catalytic TMP oxidation using different oxidants such as oxygen, hydrogen peroxide, tretbutylhydroperoxide (TBHP), *etc.* in the liquid phase according to the following reaction:



Copper chloride catalysts

A wide spread within the 1970–1990′s was obtained by the application of cupric (II) chloride $CuCl_2$ solution as a catalyst in the presence of molecular oxygen. In the earliest research works concerning the oxidation of TMP the reaction was carried out in the system of miscible solvents, which prevented complete separating the product from the catalyst. In this regard, the major improvement in the later industrial processes consisted in carrying out the mentioned reaction in a two-phase system. In the most of the studies the reaction was carried out in a homogeneous manner in the presence of different aqueous-organic solvent mixtures and different complexing agents (alkali, alkaline earth, transition, rare earth metal, and ammonium halides).

So, the authors of [9, 10] investigated the TMP oxidation by atmospheric oxygen in a two-phase system in the presence of copper (II) halide with an alkali metal halide in the environment of an aliphatic alcohol containing from 5 to 10 carbon atoms. The best yield of TMBQ (97.2–97.6 %) at a 100 % TMP conversion level was obtained using $Li[CuCl_3] \cdot 2H_2O/LiCl$ system as a catalyst, with the molar ratio TMP/$Li[CuCl_3]/LiCl = 1 : 0.25 : 0.75$. The reaction was carried out in 1-hexanol during 4 h at 60 °C with the oxygen content in the gas phase being more than 40 %. As the main by-product, 2,2′,3,3′,6,6′-hexamethyl-4,4′-biphenol (BP) was isolated. The authors of [11] succeeded in reaching the same selectivity level (97.7 %) using $FeCl_3/CuCl_2$ system as a catalyst (the molar ratio TMP/$CuCl_2$ / $FeCl_3 = 1 : 0.75 : 1.5$) in the same solvent at 70 °C during 1 h. The advantage of the latter system consisted in the use of a cheap co-catalyst, in decreasing the reaction time in the simplicity of obtaining the catalyst aqueous phase *via* mixing the solutions of individual components.

The authors of [12] obtained TMBQ *via* TMP oxidation with oxygen in the presence of a catalyst containing copper (II) halide and an alkali or alkaline earth metal halide. The reaction was carried out in a two-phase reaction medium consisting of water and an aliphatic alcohol that contains from 12 to 18 carbon atoms. The yield equal to 94.9 % with a complete conversion level of TMP was achieved using $CuCl_2/MgCl_2$ system (molar ratio $TMP/CuCl_2/MgCl_2 = 1 : 1 : 1$) at 80 °C during 3 h in an environment of dodecanol-1. It was assumed that the use of such alcohols as solvents provides the best explosion safety of the process for obtaining TMBQ and allows one to facilitate the isolation of TMBQ by means of distillation. The fact is that these alcohols are characterized by a very high flash point, which provides a very great difference between the reaction temperature and the flash temperature of the solvent. However, a disadvantage of this system consists in the fact that the solvent is solid at a room temperature, which hampers the use thereof to a considerable extent.

With the same purpose, the authors of [13] carried out the oxidation of TMP in the presence of carboxylic acids containing from 8 to 11 carbon atoms. The best yield (92.3 %) was obtained under using $CuCl_2/CrCl_3$ system as the catalyst at a molar ratio $TMP/CuCl_2/CrCl_3 = 1 : 1 : 2$ and at the temperature of 90 °C during 8 h. As the solvent, a mixture of octanoic, nonanoic and decanoic acids was used.

The authors of a patent [14] achieved a 94 % yield of TMBQ in the course of reaction performed at 60 °C during 4 h with the use of benzene/ethanol mixture (volume ratio 2 : 1) as a solvent in the presence of $CuCl_2 \cdot 2H_2O/LiCl$ in the two-phase system (at a molar ratio $TMP/CuCl_2/CuCl_2/LiCl = 1 : 1 : 4$).

The authors of [15] succeeded in reaching a 80 % selectivity level at a 100 % conversion level of the substrate, using 1.5 mass % of $CuCl_2$ as a catalyst and 2.8 mass % of $NH_2OH \cdot HCl$ as a co-catalyst. The reaction was carried out in acetic acid at a room temperature. As an oxidant there was a 10–25 % excess of TBHP used. The main advantage of the work consisted in changing from a stoichiometric amount of the catalyst to a catalytic amount thereof, which allowed researchers to avoid the formation of 4-chloro-2,3,6-trimethylphenol as a by-product. However, in this case there was a significant reduction in the selectivity level observed.

A 98.2 % yield was obtained on a heterogeneous catalyst prepared by applying cuprous chloride, ammonium chloride, and alkali metal chloride onto aluminum hydroxide in the presence of phosphoric acid (with the ratio between $Al(OH)_3/H_3PO_4/CuCl/NH_4Cl/LiCl \cdot H_2O = 1 : 0.04 : 0.5 : 0.02 : 0.22$) either in the solution of anhydrous primary aliphatic C_2–C_4 alcohol or in methyl cellosolve, ethyl cellosolve or a mixture of ethyl cellosolve with ethanol (OK-30) [16]. The reaction was performed during 3 h at a temperature of 30–35 °C and a mass ratio $TMP/OK\text{-}30/C_2H_5OH = 1 : 0.5 : 7.9$.

The authors of [17] investigated the oxidation of TMP by molecular oxygen in the presence of cuprous chloride (II)/hydroxylamine hydrochloride system as the catalyst. The reaction was carried out at an oxygen pressure of 114.7 kPa in an alcoholic solution at 40 °C. The advantage of this system consisted in changing from the stoichiometric amount of $CuCl_2$ to a catalytic amount thereof with maintaining a relatively high selectivity level (molar ratio $TMP/CuCl_2 \cdot H_2O/NH_2OH \cdot HCl = 20 : 1 : 2$), which allowed the authors to avoid the formation of 4-chloro-2,3,6-trimethylphenol. The best TMBQ yield was obtained in the course of a 2 h reaction in the presence of *t*-BuOH as a solvent, being equal to 96 % at a complete TMP conversion level. However, it was found that hydroxylamine is partially decomposed in the course of the reaction, therefore it is required for continuously adding the reagent. There were no data on reusing the catalyst presented therein. The replacement of $NH_2OH \cdot HCl$ by alkylamines resulted in some loss of selectivity [18]. The yield amounting to only 84.4–85.5 % was obtained in the course of 4 h reaction in the presence of secondary amines, such as $(CH_3)_2NH \cdot HCl$, $(C_2H_5)_2NH \cdot HCl$, $(i\text{-}C_3H_3)_2NH \cdot HCl$, as well as $n\text{-}C_4H_9NH_2 \cdot HCl$ at a 100 % conversion level of TMP and at the molar ratio $TMP/CuCl_2 \cdot H_2O/amine = 10 : 1 : 1$.

The authors of [19] obtained TMBQ by means of TMP oxidation with oxygen, using $CuCl_2/MgCl_2$ system as a catalyst. After the optimization, the selectivity level with respect to

TMBQ in such a system amounted to 90.0 % at the substrate conversion level equal to 98.5 %.

The authors of [20] performed the TMP oxidation with molecular oxygen in the presence of a $CuCl_2$-poly(4-vinylpyridine) catalyst ($CuCl_2$-PVPy). A 25 % cross-linked PVPy appeared the most stable. In his presence of the mentioned catalyst, the TMBQ yield in the first cycle was 92.0 % with a complete TMP conversion level. The reaction was performed at 80 °C and P_{O_2} = 10 atm in the environment of DMSO–C_6H_6 (volume ratio 1 : 3) during 24 h. At the second cycle of testing there was an insignificant decrease observed in the selectivity level (88 % with respect to TMBQ), but at the third cycle the conversion of the substrate was already incomplete (88 % for TMBQ at 98 % with respect to TMP).

In recent years, an increasing number of studies appear wherein ionic liquids are used as solvents. Owing to a low volatility, flammability, high polarity, low coordination ability with respect to catalysts and to good chemical and thermal stability, ionic liquids are considered by many authors as a promising replacement of flammable and volatile organic solvents. However, as demonstrated by the examples below, the use of ionic liquids for the TMP oxidation into TMBQ still requires the presence of some amount of an organic solvent.

So, the selectivity level equal to 98 % at a complete TMP conversion level was achieved using copper (II) chloride as a catalyst in an ionic liquid such as 1-butyl-3-methylimidazolium chloride, [BMIm]Cl [21, 22]. The reaction was carried out at a temperature of 60 °C and an oxygen pressure equal to 10 bar during 5 h. The disadvantages of this method alongside with a long reaction time, low productivity, and high reaction pressure consisted in the use stoichiometric amounts of components as well as of *n*-butanol as a co-solvent. In the case of using a catalytic amount of [BMIm] $CuCl_3$ (2.5 mol. %) the selectivity level was equal to 86 % with respect to TMBQ.

The yield equal to 88.6 % only at a complete TMP conversion level was obtained with the use of a copper chloride catalyst (stoichiometric amount) at 60 °C at a fivefold excess of 1-butyl-3-methylimidazolium tetrafluoroborate as a solvent and *n*-hexanol as a co-solvent in the course of 2 h [23]. Increasing the reaction temperature up to 75 °C and the reaction time up to 5 h with reducing the amount of both catalyst and ionic liquid down to 10 mol. % resulted in an increase of the selectivity level up to the 96.1 % [24]. However, the repeated using the ionic liquid led to an almost 4 % decrease of the selectivity level.

Besides the duration of the reaction and poor productivity, and high reaction temperature values in some cases, almost all of the mentioned copper chloride catalysts have one major drawback: they cause the chlorination of a part of TMBQ and by-products into environmentally hazardous organochlorine compounds related to dioxin. Such compounds should be thoroughly separated and destructed, since they could interact with DNA and proteins to damage them with causing harm to an organism. This requires for introducing additional process stages and for an increased production costs.

In order to eliminate the chlorinating ability of $CuCl_2$ catalyst it was required for significantly reducing the concentration of chloride ions in solution. However, resulting from this the catalyst partly lost the activity, since in the absence of a great excess of chloride ions the copper ions lost their oxidative properties due to a significant decrease in the oxidation potential of the system. In the cases when the authors succeeded in changing the stoichiometric amount of $CuCl_2$ by a catalytic amount thereof, the maintaining of the selectivity level required for making the reaction conditions much more severe. For the last 20 years, there appeared many papers in the literature concerning the oxidation of TMP into TMBQ in other systems, but all of them exhibit different degree of success, as well as they have the limitations associated with requiring a great excess of oxidant, high temperature values and large amounts of organic solvents. Let us consider these methods in detail.

Heteropolyacids

In the early 70-ies of the last century, the authors of [25] first used heteropolyacids (HPA) in the composition of catalysts (homogeneous catalyst Pd + HPA) as reversibly acting oxidants. Since then, the catalysis by heteropoly compounds (HPC) became widespread and be-

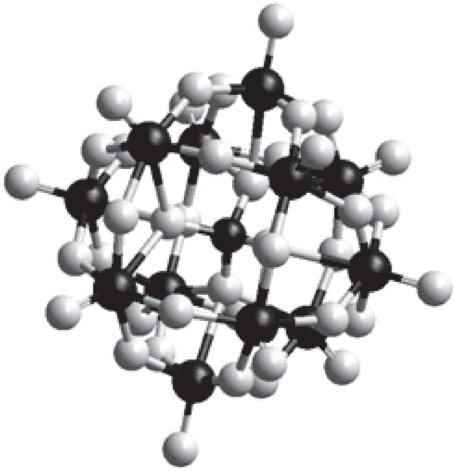


Fig. 1. Heteropolyanion of Keggin structure $[PMo_{12}O_{40}]^{3-}$. Bright atoms – oxygen, the central black atom – phosphorus, the remaining atoms are molybdenum.

gan to develop intensively. Heteropoly compounds were used successfully both in acidic and oxidative catalysis either as single component catalysts or in the composition of multicomponent catalysts of homogeneous and heterogeneous embodiments [26, 27]. These catalysts were tested also in the reaction of obtaining the TMBQ. Thus, the authors of a patent [28] used P–Mo, Si–Mo or P–Si–W HPA Keggin structures and their salts as a catalyst for the oxidation of TMP by hydrogen peroxide (60 % solution). The best yield equal to 78.3 % was obtained using P–Mo HPA (Fig. 1) (molar ratio TMP/HPA = 0.01–0.03) in acetic acid at the temperature of 30 °C for 5 h. The mentioned method is characterized by a low yields and by a complicated product and catalyst separation procedure, since the organic solvent under use was mixed with water.

The authors of [29] proposed a method for the synthesis of TMBQ where the oxidation of TMP was performed with the use of oxygen in the presence of HPA such as $H_{3+x}PMo_{12-x}V_xO_{40}$ (HPA-x, where x = 2, 4, 6) having a Keggin structure. The maximum TMBQ yield observed in this system with the use of HPA-4 was equal to 86 % at a complete TMP conversion level. The reaction was carried out in an environment of AcOH–H_2O at a ratio AcOH/H_2O = 95 : 5, thereby increasing the concentrations of H_2O in acetic acid resulted in a significant reduction in selectivity. When using such catalysts, no formation of chlorination products happened, whereas the catalysts themselves exhibited a high initial activity. However, the acetate method of TMBQ synthesis had not obtained further development since the selectivity was low, and the catalyst was deactivated rather quickly.

The process developed by the authors of [30–32] is to all appearance, the most promising. In the mentioned works, the oxidation of TMP was carried using oxygen in a two-phase system in the presence of modified non-Keggin HPA-x' solutions having a gross composition such as $H_aP_zMo_yV_xO_b$, where $1 \le z \le 3$; $8 \le y \le 16$; $1 \le x' \le 12$; $a = 2b - 6y - 5(x' + z)$; $40 \le b \le 89$. The reaction was carried out in an environment of non-branched primary alcohol containing from 6 to 9 carbon atoms at a temperature of 60 °C during 15 min. Such a method allowed obtaining TMBQ with the selectivity level up to 99.5 % at a 100 % TMP conversion level. The advantages of the catalyst also consisted in the stability in multi-cycled testing and high productivity (430–630 g TMBQ/($L_{cat} \cdot$ h)). However, the process using solutions non-Keggin HPA has not been completely optimized till now.

Phthalocyanine complexes

Phthalocyanine complexes of transition metals are becoming more and more attractive as potential catalysts for oxidation processes because of a relatively low cost, easy processing on a large scale, as well as chemical and thermal stability thereof. The authors of [33, 34] studied the oxidation of TMP by TBHP solution on the catalyst prepared by fixing iron tetrasulphophthalocyanine on SiO_2 and MCM-41 surface. Using catalysts containing monomeric phthalocyanine complexes on the surface (Fig. 2, *a*), only 21–47 % of TMBQ was formed within 2 h of the reaction at the 95–98 % conversion level of TMP. The best result (up to 88 % of TMBQ at 96 % TMP conversion level) was obtained using a catalyst d-FePcS/SiO_2 containing dimeric complexes (see Fig. 2, *b*).

Repeated studies of the catalytic activity on this catalyst demonstrated that the TMP conversion level remains approximately equal during three cycles (96, 97 and 93 %), but the yield of TMBQ exhibit a significant decrease (77, 69 and 51 %). According to the authors of [33, 34],

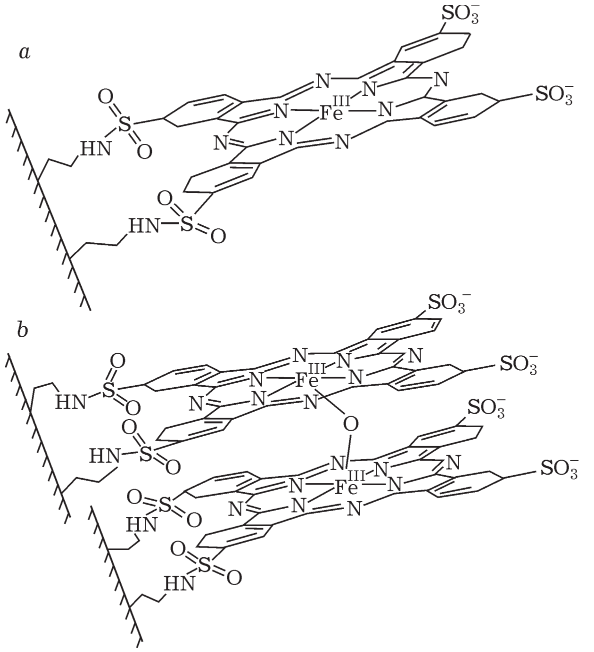


Fig. 2. Schematic representation of monomeric (*a*) and the dimeric (*b*) FePcS catalysts fixed on a silicon substrate.

this could be caused by a gradual transformation of selective dimeric complexes into a less selective monomer in the course of the reaction.

In the further publications, the authors revealed that the stabilization of the dimeric structure by a covalent binding of free sulphochloryl groups remaining after fixing the complex on the substrate resulted in a slight increase in the selectivity level [35, 36]. Thus, in the case of using *N*,*N*′-diethyl-1,3-propanediamine as a stabilizer, in the course of a 2 h reaction in 1,2-dichloroethane at 30 °C the authors succeeded in achieving a 87 % TMBQ yield at 97 % TMP conversion level, whereas using *N*,*N*′-diethylenediamine they obtained 82 % TMBQ yield at 91 % TMP conversion level. The use of 1,3-propanediol resulted in a worse result (56 % of TMBQ at a 95 % conversion level).

The selectivity with respect to TMBQ remained insufficiently high, therefore the authors of [37] attempted to stabilize the dimer structure *via* immobilizing the complexes of iron tetrasulphophthalocyanine within a sol-gel material (aerogels and xerogels). However, such catalysts demonstrated a very low activity in the oxidation of TMP. The authors of [37] attributed this fact to complications in the diffusion of the substrate and the oxidant into the pores of the catalyst and to a partial occlusion of pores with large molecular aggregates FePcS, formed in the course of preparing the sol-gel material. The best selectivity level of 43 % at a 95 % conversion level was obtained on the xerogel EP in 1,2-dichloroethane during 2 h of reaction at 30 °C with TBHP as an oxidant. The authors of [38] used as the catalyst iron tetrasulphophthalocyanine fixed on TiO_2 substrate ($FePcS{-}TiO_2$). Owing to the association between the metal complex and catalytically active inorganic substrate due to combining the two different catalytic sites in a single material, the authors planned to obtain a catalyst with improved catalytic properties. However, as the result of TMP oxidation under the same conditions, the TMBQ yield was equal to only 57 % at a 96 % conversion level of TMP.

In another paper, a 100 % selectivity level with respect to TMBQ at a complete TMP conversion level was achieved in a homogeneous system consisting of iron tetrasulphophthalocyanine and potassium peroxomonosulphate in a methanol/water environment (at a ratio 8 : 1). The reaction was performed at a room temperature for 5 min at a molar ratio [FePcTS]/TMP/$KHSO_5$ = 1 : 300 : 1200 [39]. However, despite the excellent conversion and selectivity at an extremely low reaction time, the second cycle resulted in rapid FePcTS deactivation associated with oxidative degradation of the catalyst in the presence of $KHSO_5$. So, for the system with [FePcTS]/TMP/$KHSO_5$ = 1 : 300 : 600 for three experimental cycles the conversion level of TMP was equal to 97.3, 48.6 and 2.7 % , respectively. Using cobalt tetrasulphophthalocyanine as a catalyst at the same content of components resulted in significantly worse paremeters already at the first cycle of the reaction (TMP conversion level 69.2 %) and in the formation of a significant amount of BP. In both cases (FePcTS and CoPcTS) there occurred unproductive $KHSO_5$ decomposition and an excess of oxidant was required.

Heterogeneous titanium silicate catalysts

Another relevant line of improving the multistage process for the preparation of vitamin E consists in developing an efficient method for obtaining TMQ based on the use of a heterogeneous catalyst. Once in the early 80-ies of the last century, the Italian Enichem Co. had developed microporous catalyst TS-1 for the selective oxidation of hydrogen peroxide [40], creating mesoporous titanium analogues for the oxidation of large organic molecules has became an urgent task [41].

In this connection it should be noted that over the past 10 years there were many mesoporous titanium silicate heterogeneous catalysts of different nature developed (mixed oxides TiO_2-SiO_2, titanium-containing mesoporous mesophase materials Ti-MMM, Ti-MMM-2, Ti-SBA-15, Ti/SiO_2), whose activity and selectivity in the TMP oxidation reaction are significantly different. Let us consider such catalysts in more detail.

The authors of [42] investigated the oxidation of TMP Ti and V containing mesoporous mesophase silicate catalysts (Ti- and V-MMM, respectively) synthesized under alkalescent conditions using surfactants. As an oxidant they used 30 % H_2O_2 solution 30 % H_2O_2. It was assumed that the main advantage of a novel process performed on these catalysts would consist in easy separation of the catalyst from the product (TMBQ), the absence of chlorinated derivatives and no contamination of the target product by transition metal compounds. However, V-MMM was completely unstable compound, since in the presence of 30 % H_2O_2 solution the vanadium atoms are quickly washed out into the solution. Titanium based catalysts are more stable. So, in the presence of Ti-MMM in the course of optimization there was achieved an 86 % TMBQ selectivity level at a complete TMP conversion [42, 43]. The reaction was carried out in acetonitrile at 80 °C during 30 min. It was found that despite the resistance to washing out the titanium the catalytic properties of Ti-MMM are worsened with a repeated use, which could be associated with destructing the catalysts by water; it should be also noted that these catalysts axhib it a low productivity. Furthermore, alongside with the target reaction, the Ti-MMM and V-MMM catalyzed H_2O_2 decomposition, so the complete conversion of the substrate requires for a great excess of oxidant (H_2O_2/TMP molar ratio = 3.5).

The authors of [44] investigated TMP oxidation in the presence of Ti-MMM-2, prepared by mixing the three solutions ($C_{16}H_{33}N(CH_3)_3Br + TiOSO_4 + Na_2Si_2O_5$) in an acidic medium followed by the filtration, drying and calcination of the precipitate obtained. The target reaction was carried out at 80 °C in acetonitrile with a molar ratio TMP/H_2O_2 = 1 : 3.5 during 25 min. The yield of TMBQ under these conditions was equal to 81 % at a complete conversion of TMP. The advantages of this catalyst consisted in the absence of leaching the active ingredient. According to the authors of [44], Ti-MMM-2 combines a high catalytic activity (due to a considerable availability of titanium and a high dispersion level thereof) and hydrothermal stability to represent a promising catalyst for the oxidation of large organic molecules using H_2O_2. However, there are no data reported in the paper concerning the activity of the catalyst in the subsequent reaction cycles. Moreover, the conclusion about the hydrothermal stability was made by the example of caryophyllene oxidation (six cycles), whose conditions (20 °C, molar ratio TMP/H_2O_2 = 1 : 1.2) are much milder than the oxidation conditions for TMP.

Mixed oxides TiO_2-SiO_2 appeared much more stable [45–59]. In the presence of them at a complete TMP conversion level there was TMBQ obtained with the selectivity of 95–98 % (under the same reaction conditions.) Nevertheless, despite the absence of leaching Ti, the analysis of the data reported by the authors of [45, 46, 49] allows one to conclude that the catalyst based on mixed oxides TiO_2-SiO_2 is not stable enough, too. Owing to the hydrolytic instability of a porous carrier structure and irreversible oligomerization of titanium on the surface during repeated use of the catalyst, the electivity is worsened ($S_1 = 98$ %, $S_2 = 94$ %, $S_3 = 90$ %), and in the third cycle there is incomplete TMP conversion observed. Furthermore, this catalyst, like Ti-MMM, leads to hydrogen peroxide decomposition and exhibits no good productivity.

The authors of [50] investigated the catalytic properties of the synthesized hexagonally packed mesostructured titanium silicates such as SBA-15 by the example of TMP oxidation by aqueous solution of H_2O_2. In spite of the stability of the Ti-SBA-15 structure with respect to the hydrolysis by aqueous H_2O_2 solution and to leaching Ti, the catalytic activity of these catalysts was much lower than that of Ti-MMM. In none of the experiments, the authors succeeded in achieving a complete TMP conversion (after 6 h of the reaction at 80 °C in acetonitrile, the conversion was equal to only 57 %). Furthermore, at the second and third reaction cycles, there was a significant decrease observed in the yield of TMBQ. As the authors of [50] suggested, such a deterioration of the catalytic properties as compared to the Ti-MMM could be explained by a lower dispersion of titanium and by increasing the thickness of silicate walls.

In the case when titanium silicate materials such as TiSCMS and Ti-MCM-41 were used as a catalyst [51] (those represent solid, non-porous particles of SiO_2, coated by a mesoporous titanium-silicate shell) the TMBQ yield was equal to 77 % at 99 % level of TMP conversion for Ti-SCMS and 72 % at 92 % conversion for Ti-MCM-41. The reaction was carried out in the presence of a 3.5-fold excess of H_2O_2 and MeCN as a solvent at 80 °C during 30 min. The stability data concerning the catalyst did not reported in the paper. Similar selectivity and conversion level values (79 and 98 %, respectively) under the same conditions of the reaction were obtained using similar particles with a non-porous core of silica and mesoporous titanium silicate shell, as a catalyst, but containing paramagnetic iron oxide nanoparticles in the nucleus [52]. It was assumed that the main advantage of such a catalyst consists in the ease of the separation from the reaction mixture by using a constant external magnet. However, such catalyst exhibited reduction in the activity due to the adsorption of solvent on the surface, which required for drying prior to reuse.

One of the best results among heterogeneous catalysts has been achieved with the catalysts prepared by means of grafting different titanium derivatives (mono-, bi- and tetranuclear complexes) onto the surface of commercial mesoporous silica with different textural characteristics [53, 54]. It was assumed that such a method of synthesis could allow creating a catalyst with a good separation and uniform distribution of active sites on the surface, which would combine the main advantages of homogeneous catalysts (activity and selectivity) and heterogeneous catalysts (ease of separation and reuse). Separate samples of the catalysts obtained (*e. g.*, Ti/SiO_2 on a Nippon Kasei Chemical Co. support with the content of Ti equal to 3.63 mass %) appeares resistant with respect to leaching, and demonstrated good results for the four cycles of the reaction (at the first cycle, the selectivity was equal to 99 % at 100 % TMP conversion) . The reaction was carried out in acetonitrile at 80 °C during 30 min. However, the drawbacks of these systems consisted in necessary using a 3.5–4-fold excess of 70 % H_2O_2 solution, a low productivity and long catalyst preparation for re-use (drying and calcination the catalyst at 560 °C for 5 h are required).

Recently, in the literature there appeared a paper [55] concerning the oxidation of TMP in the presence hierarchical mesoporous zeolites TS-1 of a new type such as Ti-TUD-1 and c-Ti-TUD-1. Unlike their microporous analog, the new catalysts demonstrated a much greater efficiency in the oxidation of larger organic molecules, but still lost with respect to other mesoporous Ti-containing catalysts (Ti-MMM, mixed oxides $TiO_2–SiO_2$, Ti/SiO_2 grafted catalysts). So, for the Ti-TUD-1 the conversion level of TMP for five cycles decreased from 86 to 42 %. Catalyst s-Ti-TUD-1 was more stable: at the first cycle the conversion level was about 99 %, at the second one being of 86 %, whereas the three subsequent cycles exhibited reducing the value down to 80 %, remaining approximately constant. The reaction was carried out in the presence of H_2O_2 solution (30 %) at 80 °C. In the course of the hydrothermal treatment during 48 h the Ti-TUD-1 retained 79 % of the surface area, whereas the s-Ti-TUD-1 appeared a more stable: the loss of area was equal to only 7 %. Furthermore, s-Ti-TUD-1 demonstrated an increased resistance with respect to leaching.

The authors of [56] studied the oxidation of TMP on mixed xerogels $TiO_2–SiO_2$ prepared by means of a sol-gel method using titanium isopropoxide and vanadium acetylacetonate as precursors. The reaction was performed during 4 h at a room temperature (20 °C) in ethanol using 70 % solution of H_2O_2 as the oxidant. The conversion level equal to 93 % was achieved on catalyst Ti100-200 (without V); the yield of TMBQ was equal to 96 %. In the case of using VTi95-200 (5 % V) as a catalyst the selectivity level with respect to TMBQ was equal to 99 %, substrate conversion level was however equal to only 90 %. Further increasing the vanadium content in the catalyst resulted in reducing the conversion and selectivity levels. Despite the absence of leaching, reusing the VTi95-200 catalyst resulted in some reduction in the activity. The TMP conversion level in the second cycle amounted to 88 % with the TMBQ selectivity equal to 94 %.

The authors of [57] obtained TMBQ *via* TMP oxidation by hydrogen peroxide adsorbed on the surface of titanium dioxide xerogel, as well on the surface of TiO_2 modified by cellulose powder (TiO_2–PTs). The reaction was performed in the absence of an organic solvent at 24 °C during 2 h. The adsorption of TMP performed *via* adding a weighed sample portion of TiO_2 xerogel or composite TiO_2–PTs at 62 °C TMP melt prepared. It was assumed that the absence of solvent could allow developing a more environmentally safe way to prepare TMBQ and to significantly simplify the technology of producing vitamin E. However, the best selectivity with respect to TMBQ on TiO_2 xerogel was achieved for the sample with a molar ratio TiO_2/TMP = 34 to amount to only 70.7 % at 99.1 % substrate conversion level (molar ratio H_2O_2/TiO_2 = 1.5). The results obtained using the composite were even worse. Despite the stability of the cellulose matrix of the composite under the reaction conditions and a higher specific surface area, as compared to xerogel, within the range of O_2/TMP = 2.7–9.5 the TMBQ selectivity level was equal to only 40–45 % at about 99 % conversion level of the substrate.

Salts, mixed oxides, molecular sieves, complex compounds

One of the best results in the selectivity level was achieved by means of TMP oxidation by Fenton's reagent under mild conditions in an aqueous phase [58]. The reaction was performed using a 5 % solution of H_2O_2 (fourfold excess) with $FeSO_4$ (5 mol. %) as a catalyst at 45 °C during 3 h. The important advantages of such a system mentioned by the authors in addition to the selectivity level of 99.9 % at a complete conversion of TMP (1 mmol) consisted in the absence of an organic solvent, non-toxicity, relative cheapness and a high solubility of the catalyst in water. However, this method could not compete with the existing commercial process, since the catalyst productivity in the reaction under investigation is low. There is no data concerning the stability of the catalyst in this paper.

A high selectivity level (100 %) was obtained by the authors of [59] in the course of TMP oxidation over a nano-octahedral manganese oxide molecular sieve K-OMS-2 synthesized with the help of microwave irradiation, using TBHP as an oxidant (molar ratio TMP/TBHP = 1 : 2). The reaction was carried out in acetonitrile at 80 °C during 4 h. However, in spite of such a good result, the authors of [59] did not reported data concerning the hydrolytic stability of the catalyst and its activity in the course of repeated use.

Furthermore, there are papers available in the literature concerning the oxidation of TMP by hydrogen peroxide in a ternary catalytic system consisting of $FeCl_3 \cdot H_2O$, pyridine-2,6-dicarboxylic acid, and various benzylamines [2, 60]. The maximum yield of TMQ equal to 79 % at the TMP conversion level >99 % was obtained using *n*-butylbenzylamine. Besides a low product yield, the disadvantage of this system consisted in requiring for the reaction to occur at 0 °C.

The system of $M(acac)_n$/3-methylbutanal/O_2/1,2-dichloroethane (M = Co, Mn, Fe, Cu, Pd; acac = acetylacetone) at a room temperature during the 48 h of the reaction demonstrated a very low result with respect to the oxidation of TMP [61]. The conversion level of the substrate equal to 100 % was achieved only in the case of $Fe(acac)_3$, but the yield of TMBQ amounted to only 6 %. The best selectivity level with respect to TMBQ equal to 34 and 32 % was observed in the case of $Co(acac)_2$ and $Mn(acac)_3$ at the conversion level equal to 66 and 85 % , respectively.

The catalytic oxidation of TMP [62] by a 30 % aqueous solution of H_2O_2 (TMP/H_2O_2 = 1 : 10) over spinel $CuCo_2O_4$ (1 mol. %) prepared by means of a sol-gel method using inorganic salts provided TMBQ selectivity level equal to 87.4 % at a more than 99 % TMP conversion level. The reaction was performed at a room temperature (25 °C) for 6 h with gradually adding H_2O_2 solution in the presence of acetic acid. Advantages of this catalyst consisted in the absence of leaching and in the retention of the activity within five reaction cycles.

The authors of [62] examined also the photo-oxidation of TMP into TMBQ under visible light irradiation ($\lambda > 400$ nm) using a system such as hypocrellin/$CuCo_2O_4$ (HC/CCO) as a catalyst obtained by means of physical adsorption of hypocrellin A and B (a compound naturally occurring in fungi *Hypocrella bambusae*) (see Fig. 3) in acetone at ambient temperature [63]. The reaction was carried out in air, in the environment of ethanol at 25 °C during 12 h. The system demonstrated an excellent selectivity with respect to TMBQ (100 %), but the best TMP conversion level was equal to only 7.8 % (mass ratio HC/CCO = 15 : 100). In the case of a repeated use of such catalysts, the active component was observed to be washed out, which resulted in the loss of photocatalytic activity of the catalyst and in decreasing the conversion level of TMP in the subsequent cycles of the reaction.

The authors of [64, 65] performed TMP oxidation with a 30 % aqueous H_2O_2 solution (TMP/H_2O_2 = 1 : 2.3) in the presence of hematin from a protoporphyrin complex containing one hydroxyl ligand. The reaction proceeded in 90 % acetic acid at 4 °C during 10 min (molar ratio TMP/hematin = 8). Under such conditions, the authors managed to achieve the selectivity level with respect to TMBQ equal to 99.1 %. However, they nowise discuss the conversion of the initial substrate and the problem of product isolation.

For the system consisting of $CuFe_2O_4$, HCl, dichloroethane and hydrogen peroxide the yield of TMBQ amounted to only about 45 % in the course of TMP oxidation at 60 °C during 4 h [66].

The authors of [67, 68] investigated the catalytic activity of M-POMs (M = Ti, Zr) in the reaction of TMP oxidation by H_2O_2 solution. However, these processes have demonstrated a very low selectivity level and incomplete conversion of the initial substrate.

CATALYSTS FOR TMP HYDROXYLATION INTO TMHQ

A great number of papers [69–82] was devoted to catalytic TMP hydroxylation by a 30 % hydrogen peroxide solution (TMP/H_2O_2 molar ratio = 3 : 1) directly into 2,3,5-trimethyl-1,4-hydroquinone (TMHQ). Although such a reaction in the synthesis of vitamin E would allow abandoning a two-stage process of obtaining TMHQ (the TMP oxidation into TMBQ and a subsequent hydrogenation of TMBQ into trimethyl-1,4-hydroquinone) with significantly simplifying the process, the mentioned one-stage process appeared much less efficient. In all the cases considered, researchers observed the formation of a TMBQ and TMHQ mixture with a significant amount of by-products at a very low conversion level of the starting substrate (less than 50 %).

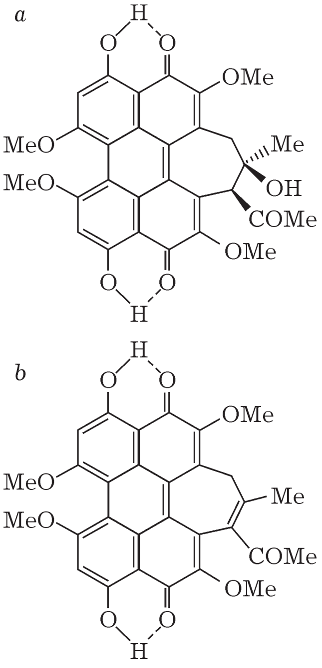


Fig. 3. Hypocrellins A (*a*) and B (*b*).

So, the authors of [69] obtained TMHQ with the yield of 54.6 % *via* TMP hydroxylation using a mixture of AcOH/H_2O_2/HCl. The reaction was carried out at a molar ratio of TMP/AcOH/H_2O_2/HCl = 1 : 6.5 : 6.5 : 2.5 with the use of petroleum ether as a solvent during 1.5 h.

The authors of [70–73] studied a direct hydroxylation of TMP investigated in the presence of mesoporous titanium silicates MTS-*n* (*n* = 5, 8, 9, 9A) synthesized *via* assembling appropriate precursors with a polymeric surfactants. The main objective of the authors was to create catalysts those combine the advantages of zeolites (the ability of high temperature oxidation) and mesoporous materials (large pores). The advantage of these systems consisted in a better hydrothermal stability as compared to Ti-MSM-41 and SBA-15 due to the introduction of primary and secondary zeolite units in the mesoporous walls. At the same time, the activity of these systems was low. For the sample MTS-5, the reaction conversion with respect to TMP amounted to only 16.2 %, whereas for MTS-8 the value was 13.6 % (with the formation of 13.9 and 9.3 % by-products therefrom, respectively) [72]. Using MTS-9, during the same time the TMP conversion level was equal to 18.8 %, 12.2 % being by-products [70, 71]. In all the cases the reaction was carried out using acetonitrile as a solvent at 80 °C and at molar ratio TMP/H_2O_2 = 3 : 1. The disadvantage of these catalysts also consisted in a low thermal stability. In the course of calcinating therm before the next cycle of the reaction, there occurred a reorganization of the titanium coordination environment resulting in decreasing the catalytic activity. So, after calcination at 550 °C during 4 h the specimen MTS-5 synthesized in an alkaline medium demonstrated the TMP conversion level amounted to 13.2 %, whereas MTS-8 synthesized in a strongly acidic medium, exhibited the value equal to 8.4 %. The modification of the synthesis method for samples MTS-9 (by adding ammonium salts) resulted in reducing the crystallization rate and increasing the condensation level of the building blocks, which allowed obtaining MTS-9A samples with a better thermal stability [73]. Owing to this fact, after calcination (6 h at 550 °C) the second reaction cycle during 2 h resulted in achieving almost the same conversion level of TMP as it was in the first cycle, however, this value was still insignificant (17.9 and 18.1 %, respectively). The best stability was demonstrated by sample MTS-9A-1.2 prepared with the addition of 1.2 g of NH_4Cl.

The authors of [74] investigated the hydroxylation of TMP by means of H_2O_2 solution in the presence of catalysts prepared by impregnation of the surface of mesoporous materials such as MCM-41 and SBA-15 with a finely dispersed TS-1 (JQW-1 and JQW-2). The reaction was carried out in acetone at45 °C for 5 h. The best result in the case of JQW-1 was obtained at a ratio n(Si)/n(Ti) = 33 the product yield values corresponded to 71.3 % of TMHQ, 15.6 % of TMBQ and 13.1 % of other products; the TMP conversion level amounted to 17.1 %. For sample JQW-2 (n(Si)/n(Ti) = 35) the yields corresponded to 70.6 % of TMHQ, 15.2 % of TMBQ, 14.2 % of by-product; the TMP conversion level being of 16.3 %. Performing the reaction in the presence of a Ti-JQW-5 catalyst (highly stable mesostructured heteroatom-substituted AlPOs) in acetonitrile at 80 °C during 4 h resulted in the formation of 63.7 % of TMHQ, 21.2 % of TMBQ and 15.1 % of by-products; the TMP conversion level being equal to 13.1 % [75].

The authors of [76, 77] used Si-P-Mo and Si-PW HPA Keggin structures as catalysts applied onto SBA-15 *via* encapsulation and impregnation methods. It was assumed that such a hybrid catalyst would have a larger pore size, thick walls and a high hydrothermal stability of zeolites, alongside with unique acidic and redox properties inherent in heteropolyacids, whereas the heterogeneous nature thereof should provide a much more ready separation of the catalyst from the reaction products as to compare with homogeneous systems. For 2 h, the reaction in acetonitrile at 80 °C on catalysts HPMo/SBA and HPW/SBA applied by means of impregnation resulted in the conversion level equal to 21.2 % (64.5 % TMHQ, 28.3 % TMBQ and 7.2 % by-products) and 15.8 % (72.3 % TMHQ, 19.3 % TMBQ and 8.4 % by-products), respectively.

Encapsulated catalysts demonstrated slightly better results. The conversion level on SiPMo-8 amounted to 26.5 % (including 83.4 % of TMHQ, 11.7 % of TMBQ and 4.9 % of by-products), whereas SiPW-8 exhibited a 17.9 % conversion level (89.2 % of TMHQ, 9.5 % of TMBQ and 1.3 % of by-products). After the repeated use of each type of catalyst for five cycles, the SiPMo-8 and SiPW-8 demonstrated similar catalytic activity value (26.2 and 17.6 %, respectively) as compared with the same fresh catalyst. At the same time the conversion level obtained on the catalysts HPMo/SBA and HPW/SBA was much lower (only 4.9 and 3.0 %, respectively). This indicates that the samples of SiPMo-8 and SiPW-8 obtained *via* encapsulation are more stable with respect to liquid-phase reactions in the course of repeated use as compared with the samples obtained by means of impregnation.

The authors of [78–81] performed the hydroxylation TMP by 30 % H_2O_2 solution (molar ratio TMP/H_2O_2 = 3) over copper hydroxyphosphate $Cu_2(OH)PO_4$ during 2 h at 80 °C in acetonitrile. Despite the absence of leaching the ions into the solution, the TMP conversion level amounted to only 40.2 % (including 72.2 % TMHQ, 17.7 % TMBQ and 10.1 % of other products). The activity $Cu_4O(PO_4)_2$ catalyst obtained by means of calcination $Cu_2(OH)PO_4$ for 6 h at 850 °C, was even lower, whereas TMHQ formation was not observed at all.

The authors of [82] carried out the same reaction using a modified bimetallic mesoporous material (Sn/Ti-MS-1) as a catalyst that was synthesized *via* assembling a Sn-containing precursor TS-1 with surfactants in acidic medium. In the environment of acetonitrile at 80 °C, the TMP conversion level during 4 h amounted to 16.9 % (68.6 % TMHQ, 20.5 % TMBQ and 10.9 % by-products). After calcination, the catalyst selectivity was not changed to a considerable extent (the conversion level was equal to 15.3 %).

CONCLUSION

Already within several decades, the main industrial production method for obtaining TMBQ (a key intermediate for the synthesis of vitamin E) is being presented by a catalytic oxidation of TMP with oxygen or an oxygen-containing gas in the presence of copper (II) chloride as a catalyst. The main disadvantages of the mentioned catalyst consist in a chlorination activity, low productivity, and high corrosiveness.

Initially, the reaction of TMP oxidation into TMBQ was performed in single-phase systems (miscible solvents), which complicated the isolation of the product from the reaction mixture. The main improvement in the later industrial processes consisted in performing a targeted reaction in a two-phase system (the aqueous solution of catalyst, TMBQ and TMP solution in an aliphatic alcohol C_4–C_{10}), first implemented by Mitsubishi Co. in 1986 [6]. Owing to this, it has become possible to separate the reaction products from the catalyst by a simple phase separation. In most subsequent patents compositions of organic solvents and co-catalysts (auxiliary used alkali chlorides, alkaline earth, transition and rare earth metals) were different, but the catalyst was invariably presented by $CuCl_2$. Thus, novel methods were distinguished by simplifying the separation of reaction products from the catalyst, but the other disadvantages remained. In this regard, necessity has arisen to develop a novel process for preparing TMBQ devoid of these drawbacks.

For the past 20 years, this problem was the subject of many papers. Numerous catalysts such as heteropolyanions of Keggin structure ($H_{3+x}PMo_{12-x}V_xO_{40}$), phthalocyanine complexes, molecular sieves K-OMS-2, Fenton's reagent, mesoporous titanium silicate heterogeneous catalysts and many others, have been studied in the reaction of TMP oxidation into TMBQ. The analysis of published works demonstrated that the majority of new catalysts provide a fairly high selectivity TMP oxidation, solving the problem of chlorination and hence the problems associated with the disposal of toxic wastes. However, all the above mentioned catalysts (both homogeneous and heterogeneous) are characterized by a low productivity, whereas the most of heterogeneous catalysts are characterized by a low thermal and hydrolytic stability. In some cases, the active component is eluted into the reaction solution and the catalyst becomes unsuitable for further use after the first reaction cycle. A direct TMP hydroxylation into TMHQ that could eliminate the stage of obtaining TMBQ and in general to simplify the process of obtaining vitamin E to a great extent, appeared to be even less efficient.

In the course of developing a novel catalytic process or of introducing a novel catalyst to the existing production process of fine chemistry, the determining criterion is presented not only by the selectivity level (generally above 95 %). On should also consider the following parameters [3]:

- Productivity in TON units (turnover number, moles of reacted substrate/mole of active catalytic component);
- Catalytic activity in TOF units (turnover frequency, TON/per unit time (in h^{-1})), that should exceed 500 h^{-1} for small-scale production and 10 000 h^{-1} for large-scale production;
- The commercial availability of a catalyst, the reproducibility of its properties in the synthesis;
- The stability of the catalyst with respect to a medium, ease of product separation from the catalyst.

So, today the issue of developing environmentally safe and cost-efficient production process for obtaining TMBQ remains open. In the industry, the TMBQ is still obtained by means of TMP oxidation with oxygen in the presence of copper (II) chloride solutions.

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