



Catalytic Transformations of 4-tert-Butylphenol in Hydrogen Peroxide Solutions in the Presence of Titanium Oxide Compounds and Titanosilicates

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Authors' contributions

This work was carried out in collaboration between all authors. All authors read and approved the final manuscript.

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ABSTRACT

The selective oxidation of 4-tert-butylphenol by H₂O₂ solutions in the presence of titanosilicate catalysts could become a promising alternative for the 4-tert-butylcatechol production. In this study the catalytic transformations of 4-tert-butylphenol in hydrogen peroxide solutions were investigated in the presence of the titanium oxide samples of different phase composition and the samples of crystalline and amorphous titanosilicates. The primary product of the 4-tert-butylphenol conversion in the presence of both hydrated and amorphous TiO₂ forms was 4-tert-butylphenol ether. The maximum selectivity value of the latter was 80 mol.%. The 4-tert-butylcatechol formation selectivity reached its maximum in the presence of the anatase TiO₂ form but did not exceed 20 mol.%. The TS-1 microporous crystalline titanosilicate was shown to exhibit low activity in the 4-tert-butylphenol transformation due to the steric limitations on the diffusion of the substrate molecules towards catalytic active centers. Mesoporous amorphous titanosilicates were more selective in the 4-tert-butylcatechol formation than the titanium oxide compound samples. It was found that the

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mesoporous titanasilicate content in the reaction mix, temperature and the experiment duration affected both the 4-tert-butylphenol conversion and the 4-tert-butylcatechol formation selectivity. The maximum 53 mol.% formation selectivity value of the 4-tert-butylcatechol was shown to occur over the amorphous mesoporous titanasilicate containing 1.9 wt.% of Ti, the 4-tert-butylphenol conversion value being equal to 42 mol.%.

Keywords: 4-tert-butylphenol; 4-tert-butylcatechol; hydrogen peroxide; titanium oxide; titanasilicate.

1. INTRODUCTION

4-tert-Butylcatechol (TBC) was widely used as a restraining agent in the diene hydrocarbons polymerization; as a stabilizing additive for polymer materials, unsaturated aldehydes, synthetic ethylcellulose-based resins; as an oxidation preventer for animal fat, oil and wax [1-4].

Well-known techniques for TBC synthesis were based on the alkylation of catechol by isobutylene or isobutanol in the presence of inorganic acids, mainly sulphuric acid [3,4]. The industrial production process was conducted in two stages: first, by the alkaline melting of o-chlorophenol or o-phenylsulphonic acid they obtain the starting catechol, which, in its turn, was alkylated over KU-2 cationite with isobutyl alcohol. The drawbacks of the process were the following: the formation of di- and tri- alkyl catechol derivatives, the undesired waste effluent formation, and the complex production technology.

The selective oxidation of 4-tert-butylphenol (TBP) by H_2O_2 solutions in the presence of titanasilicate catalysts could become a promising alternative for the TBC production. However, there was no information in the literature regarding this matter.

Despite the fact, that to date two types of titanasilicate (Ti-MFI and Ti-MWW) were used in the industry, the TS-1 remained the industrial standard catalyst for oxidation reactions [5-7]. TS-1 was a crystalline microporous material of the ZSM-5 zeolite structure, where a number of silicon atoms in the lattice were substituted by the isomorphous titanium atoms. It was possible to expect that this catalyst would be low effective for the bulky TBP molecules on account of the steric restrictions. Therefore, the aim of this study was to investigate the reaction of TBP oxidation by hydrogen peroxide solutions in the presence of crystalline and amorphous titanosilicates and titanium oxides of different phase composition and porous structure.

2. EXPERIMENTAL DETAILS

2.1 Catalyst Preparation

The conversion of TBP in hydrogen peroxide solutions was studied in the presence of titanium oxide samples of different phase composition and in the presence of mesoporous amorphous and crystalline microporous titanasilicate samples. The $TiO_2 \cdot nH_2O$ samples designated as TiO_2^{100} , TiO_2^{250} , TiO_2^{350} , TiO_2^{450} and TiO_2^{550} were obtained by the hydrolysis of $TiCl_4$ in an ammonia-alcohol solution. NH_4Cl was further removed by the stages of rinsing and thermal treatment at different temperature (100-550°C). The mesoporous amorphous titanasilicate catalyst samples were prepared by the sol-gel technique using the commercially available "Ethylsilicate-40" oligomer oligoetoxyxiloxane mix (TOR 2435-427-05763441-2004) and titanium chloride alcohol solutions [8,9]. The prepared samples were calcined at 550°C for 4 h in the atmosphere of air. The titanium content in the samples of TSm series was 1.0, 1.9, and 3.7 wt.%. The same technique was used to prepare the SiO_2 sample starting from the same oligoetoxyxiloxane mix. A sample of TS-1 crystalline titanasilicate containing 1.9 wt.% of Ti was synthesized according to the technique described in [5].

2.2 Catalysts Analysis

Compositions of the synthesized titanosilicates were analyzed with the energy-dispersive X-ray fluorescent Shimadzu EDX-800HS spectrometer equipped with the rhodium anode X-Ray tube operating at the voltage of 15-50 kV and the current of 20-1000 μA , the pinhole of 3-5 mm, under vacuum.

The phase composition of samples was determined with the DRON-4-07 X-ray diffractometer using MoK_{α} emission at 35 kV, 30 mA and the goniometer focusing made according to the Bragg-Brentano technique. General XRD patterns were recorded with the scanning increment of 0.02° and the exposure time at each

point equal to 5 s. The qualitative and quantitative phase analysis was performed using the Re&Se (the RIR method) application program with the PDF-2 ICDD 2011 powder database.

The incorporation of titanium atoms into the silicate framework was evaluated by the Advance BRUKER Vertex 70V Fourier IR-spectrometer. The sample pellets were press-molded with KBr, placed into the working cell and calcined at 100–500°C followed by recording the IR absorption spectra within the range of 4000–400 cm⁻¹.

The porous structure characteristics were determined by the low-temperature nitrogen adsorption-desorption technique at 77K using the Micromeritics ASAP-2020 sorption meter. Prior to the analysis the samples were evacuated at 100–350°C for 6 h. The specific surface square area was calculated by BET method at the relative partial pressure of $p/p_0=0.2$. The pore size distribution was calculated using the desorption curve and the BJH method, the total pore volume being determined by BJH at the relative partial pressure of $p/p_0=0.95$. The volume of micropores in the presence of mesopores was determined using the t-method by Halsey [10].

2.3 4-tert-Butylphenol Transformations

Catalytic

The TBP conversion runs were performed using the bench-scale setup with the batch isothermal reactor equipped with the stirrer (200 rpm), backflow condenser, and thermometer. A 5 ml aliquot of acetonitrile, 0.09 g TBP, and the calculated amount of the catalyst (0.10–0.66 g) were loaded into the reactor and stirred until the temperature became constant. Then a required aliquot of the aqueous 35% H₂O₂ solution (0.12–0.36 ml) was added into the reactor and the reaction start time was recorded. The feed TBP concentration was 0.12 mol/L; the TBP to H₂O₂ molar ratio of the corresponding concentrations in the feed ($C_{\text{TBP}}^0/C_{\text{H}_2\text{O}_2}^0$) was 1/2 and 1/6. The experiments were run at 35, 50 and 75°C in the presence of 2.5–15 wt.% of the catalyst in the mass of the feed reaction mix. The duration of runs varied from 20 to 60 min. The grain size of the catalyst fraction used was 80–100 μm. In the preliminary experiments it was shown that under the reported conditions the reaction occurred in the kinetic region. The reaction mass obtained as a result of the experiment was separated from the catalyst by filtering, and the residual H₂O₂ content was determined by the iodometric titration technique [11]. The high molecular

weight products of the oxidative condensation were removed by filtering the reaction mix through the column loaded by the silica gel bed (the fraction of 100–200 μm). The products analysis was carried out by HPLC (HP 1050 with UV-detector) equipped with a C18 reverse-phase column and operated at 275 nm using 70% CH₃CN in water as a mobil phase. An internal substance, biphenyl, was used to quantify the residual TBP and products. The high molecular weight products of the oxidative TBP condensation were analyzed to determine the element composition [12].

3. RESULTS AND DISCUSSION

3.1 Catalysts Characterization

According to the X-Ray diffraction analysis, the TiO₂¹⁰⁰ sample was the hydrated titanium dioxide. The TiO₂²⁵⁰ sample was X-Ray amorphous, whereas the TiO₂³⁵⁰, TiO₂⁴⁵⁰ and TiO₂⁵⁵⁰ samples represent the anatase form.

On the X-Ray diffraction pattern of the TS-1 analog the reflections were observed at the following 2θ values: 7.9; 8; 8.8; 8.9; 23.0; 24.4 и 29.3 (Fig. 1). Those values were characteristic for the above indicated crystalline microporous titanosilicate [5].

All titanosilicate samples (TSm series) prepared by the sol-gel synthesis were amorphous.

In the IR-spectra of TS-1 sample and the samples of TSm series the absorption band observed at ~960 cm⁻¹ (see Fig. 2) witnessed the formation of the Ti-O-Si bond [13,14].

In Table 1 the porous structure characteristics of samples studied in this work as the catalysts for the reaction of TBP oxidation by aqueous H₂O₂ solutions were presented. It can be seen that the hydrated titanium oxide possess neither micro- nor mesopores. The volume of mesopores in TiO₂ samples calcined at 250, 350, 450 and 550°C were close and amounted 0.26–0.27 cm³/g. The volume of micropores decreased from 0.07 cm³/g in TiO₂²⁵⁰ sample down to 0.02 cm³/g in TiO₂⁵⁵⁰ sample. The specific surface area diminished in the series of TiO₂²⁵⁰, TiO₂³⁵⁰, TiO₂⁴⁵⁰ and TiO₂⁵⁵⁰ samples from 230 to 50 m²/g. The porous structure characteristics varied both due to the phase transition and to the partial agglomeration of the porous structure of the material.

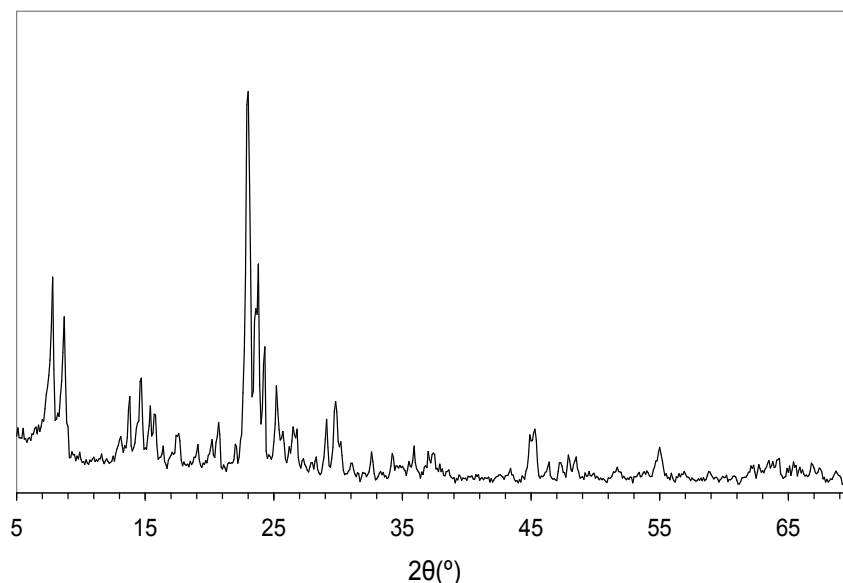


Fig. 1. XRD pattern of TS-1 sample

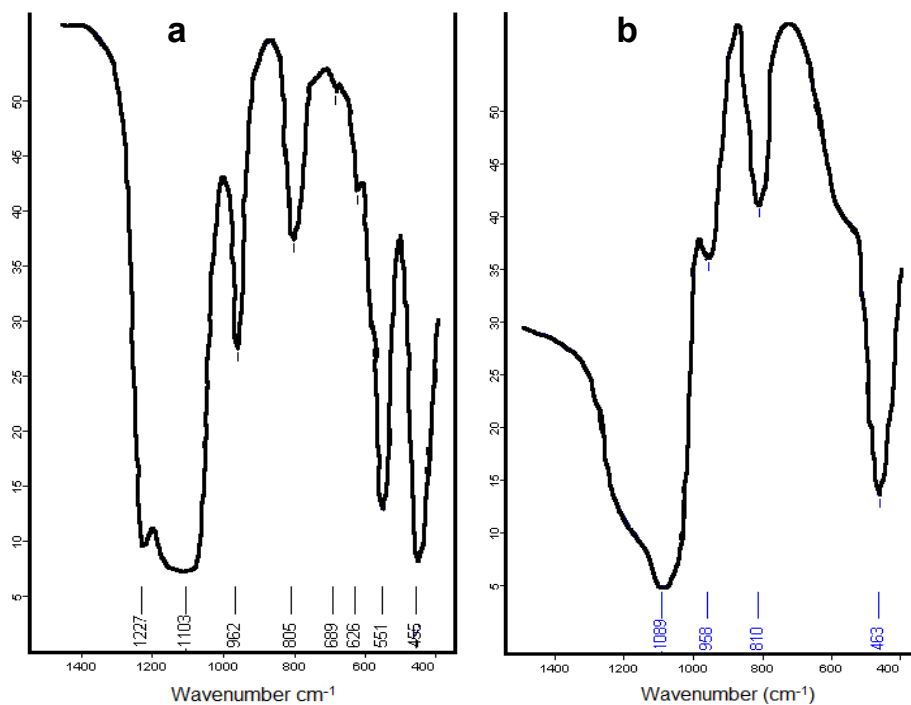


Fig. 2. IR-spectra of TS-1 (a) and mesoporous TSm-2 (b)

It was shown that as the Ti content in mesoporous titanosilicates got higher, the specific surface area and the total pore volume were slightly decreased. This variation in the porous structure characteristics was attributed in [15] to the fact that when the Ti content in the

titanosilicate increases, a part of it could exist as a separate oxide phase, leading to the variations in the porous structure.

In Fig. 3 the adsorption-desorption isotherms of nitrogen were presented for TS-1 and TSm-1

samples. It can be seen that the TS-1 sample was characterized by the isotherm of Type I without the hysteresis loop. This isotherm was inherent to the microporous materials. The isotherm of TSm-1 sample according to the IUPAC classification [10] had the hysteresis loop of H1 type. Those loops were characteristic of the porous systems with a combination of meso- and macropores. Analogous isotherms with the H1 hysteresis loop were also

obtained for the samples with the higher titanium content.

The pore size of the obtained mesoporous materials of the TSm series was within the range of 2 to 7 nm (see Fig. 4). The volume of micropores was close to zero. Thus, all synthesized titanosilicates of the TSm series had the mesoporous structure with a rather narrow pore distribution by the diameter.

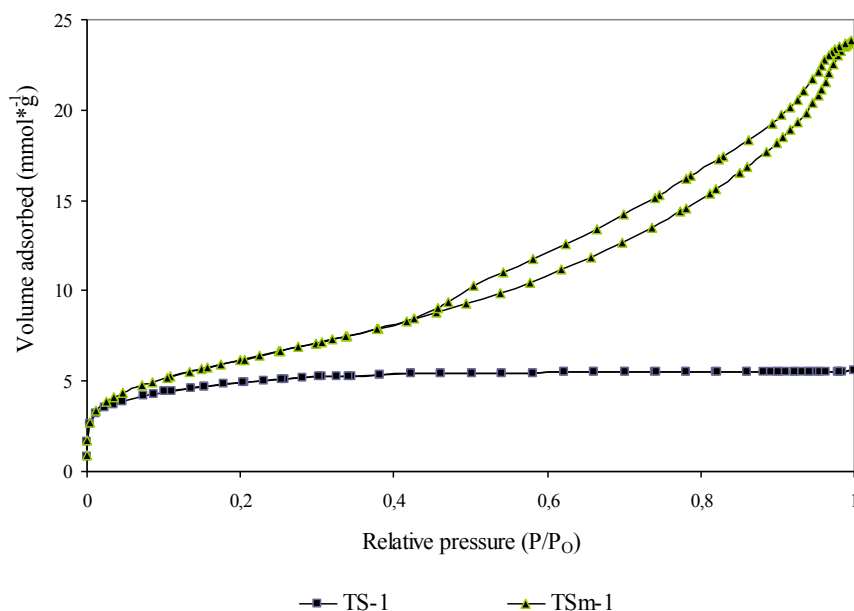


Fig. 3. Adsorption-desorption isotherms of porous titanosilicates

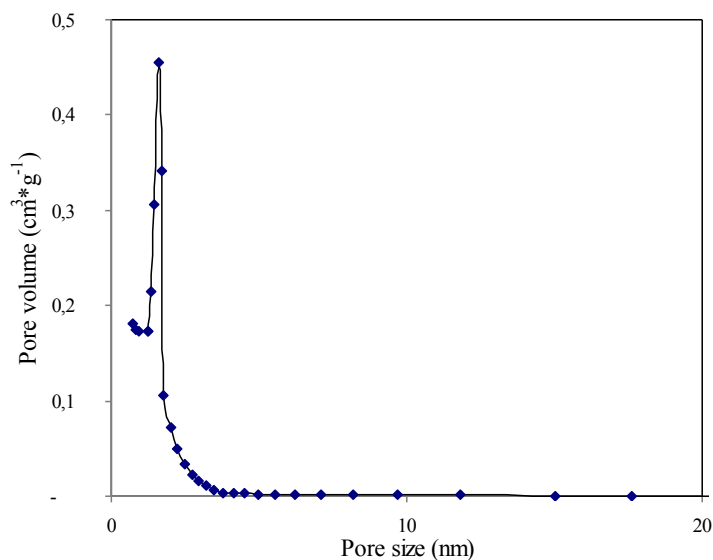


Fig. 4. Pore size distribution by volume for the TSm-1 sample

Table 1. Porous structure characteristics of the synthesized samples

Sample	Ti content (wt.%)	Specific surface area by BET (m ² /g)	Mesopore volume (cm ³ /g)	Micropore volume (cm ³ /g)
SiO ₂	0	557	0.99	0.03
TiO ₂ ¹⁰⁰	59.9	35	0	0
TiO ₂ ²⁵⁰	59.9	230	0.27	0.07
TiO ₂ ³⁵⁰	59.9	90	0.27	0.02
TiO ₂ ⁴⁵⁰	59.9	59	0.27	0.02
TiO ₂ ⁵⁵⁰	59.9	50	0.26	0.02
TS-1	1.9	360	-	0.21
TSm-1	1.0	560	0.99	0.04
TSm-2	1.9	505	0.92	0.05
TSm-3	3.7	495	0.89	0.05

3.2 TBP Transformations

The preliminary runs were conducted to demonstrate that there were no transformations of TBP and H₂O₂ in the absence of a catalyst. It should be also pointed out that none of the investigated catalysts caused any transformations of TBP without hydrogen peroxide. The gaseous phase composition (either air or nitrogen gas) did not affect neither the TBP conversion nor the reaction product composition. Thus, under the studied conditions both the catalyst and H₂O₂ must simultaneously present in the reactor for any oxidative transformations of TBP to occur. Silicon oxide exhibited no activity both in the H₂O₂ decomposition and in TBP transformations.

In Table 2 results of the TBP oxidative transformation studies in the presence of titanium oxide compounds of different phase composition were presented. It can be seen that in the presence of H₂O₂ the TBP transformation was observed over all the oxides investigated. As the duration of runs got longer from 20 to 60 min, the

TBP conversion value over the hydrated titanium oxide TiO₂¹⁰⁰ sample increased from 39 up to 57 mol.%. As the molar ratio TBP/H₂O₂ was changed from 1/2 to 1/6 in favor of H₂O₂, the TBP conversion also increased from 39 up to 58 mol.% for the same duration of the run. The H₂O₂ conversion in those runs was 85-93%.

It should be pointed out that the primary product of the TBP conversion in the presence of the hydrated (TiO₂¹⁰⁰) and amorphous (TiO₂²⁵⁰) titanium oxide species was the 4-tert-Butylphenyl ether (TBPE) (Fig. 5).

The maximum selectivity value for the latter was 80 mol.%, and the TBC formation selectivity did not exceed 2 mol.%. Besides, the high molecular weight products of the oxidative TBP condensation were formed, namely, chromane, chromene and flavan derivatives, i.e., tars. The element composition of those corresponded to the gross formula of CH_{2.0-2.4}O_{0.6-0.8}, and the formation selectivity ranged from 18 up to 81 mol.%.

Table 2. Catalytic transformations of TBP in the presence of TiO₂ samples of different phase composition

Sample	Time (min)	TBP/H ₂ O ₂ mol.ratio	Conversion H ₂ O ₂ (%)	Conversion TBP (mol.%)	Selectivity TBC (mol.%)	Selectivity TBPE (mol.%)
TiO ₂ ¹⁰⁰	20	no H ₂ O ₂	-	0	0	0
	20	1/2	92	39	2	70
	60	1/2	93	57	2	65
TiO ₂ ²⁵⁰	20	1/6	85	58	2	80
	60	1/2	98	67	5	37
TiO ₂ ³⁵⁰	60	1/2	97	30	19	3.5
TiO ₂ ⁴⁵⁰	60	1/2	97	28	20	0.5
TiO ₂ ⁵⁵⁰	60	1/2	94	30	19	0

Reaction conditions: 10 wt. % of the catalyst, c⁰(TBP)=0.12 mol/L, c(CH₃CN)=19 mol/L, 75°C.

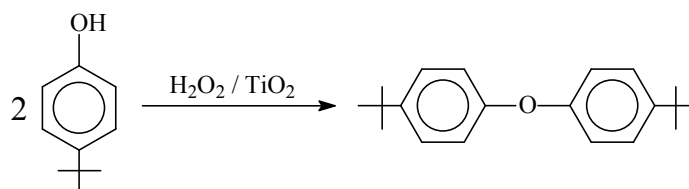


Fig. 5. Scheme of the TBPE formation in the presence of TiO_2 samples

Over the amorphous titanium oxide TiO_2^{250} sample the TBP conversion under the matching conditions was higher than over the TiO_2^{100} sample, probably on account of the larger specific surface area (see Table 1). Meanwhile, the TBPE formation selectivity was considerably lower and did not exceed 37 mol.%, and tars became the primary product of the TBP conversion.

Under the same experimental conditions over the anatase samples the TBP conversion decreased to 28-30 mol.%. The TBPE formation selectivity was even lower than for the amorphous TiO_2 ; no ether was detected in the reaction products over the TiO_2^{550} sample. After the thermal treatment within the range of temperature of 350 to 550°C the formation selectivity of TBC, hydroquinone, and quinone over TiO_2 samples was not more than 20, 1, and 3 mol.%, respectively. Tars were the primary TBP conversion product, too.

The calculations showed that the H_2O_2 conversion values indicated in Table 2 were significantly higher than those necessary for the oxidative conversions of TBP. Hence, a decomposition process of the oxidizing agent molecule into water and oxygen molecules occurred in parallel.

So far as the conversion of TBP in the acetonitrile-aqueous H_2O_2 solutions was

concerned, the results obtained witnessed the fact that in the sequential transition from the hydrated to the amorphous titanium oxide and further to the anatase, the transformation of catalytic active centers on the surface of those materials caused the change in their catalytic properties. Primarily, the centers catalytically active in the oxidative TBP condensation and the H_2O_2 decomposition were formed. The formation selectivity of TBPE and tars could be as high as 80 and 81 mol.% respectively, meanwhile the maximum TBC formation selectivity did not exceed 20 mol.%.

Catalytic properties of the synthesized titanosilicate samples were investigated in the oxidative TBP transformations (Fig. 6) in the H_2O_2 acetonitrile-aqueous solutions. The results were shown in Fig. 7. It can be seen that the TBP conversion in the presence of the TS-1 sample did not exceed 3 mol.%. The low activity of the crystalline microporous titanosilicate in the TBP transformation was attributed to the steric restrictions on the diffusion of TBP to the catalytic active centers. In the same time, the centers remained available for the much more less in size H_2O_2 molecules. It was proven by the rather high conversion factor of the oxidizing agent occurred due to the decomposition of the latter in the pores of the TS-1 sample.

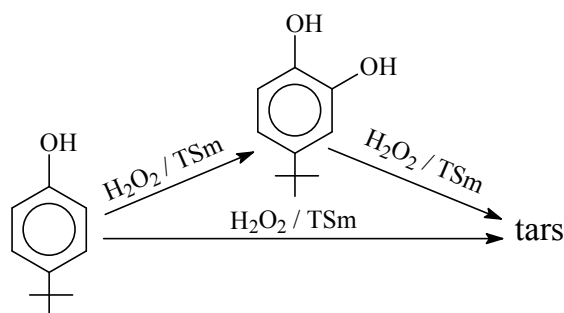


Fig. 6. Scheme of the oxidative TBP transformations in the H_2O_2 acetonitrile-aqueous solutions in the presence of titanosilicate samples

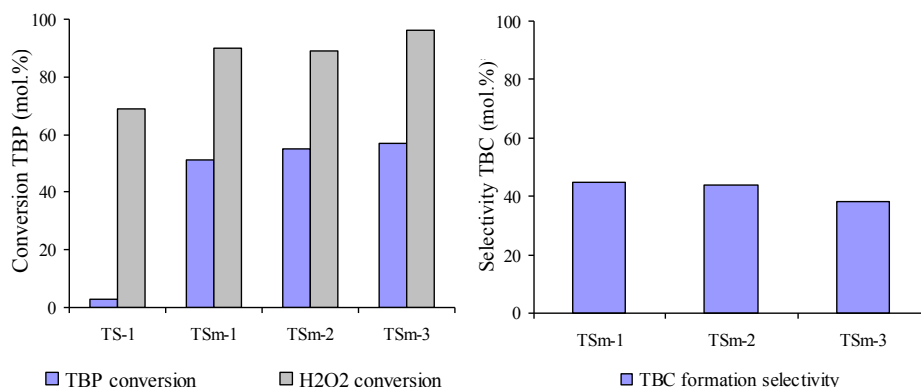


Fig. 7. The conversion of TBP, H₂O₂ and the TBC formation selectivity in the presence of titanosilicate samples (reaction conditions: 10 wt.% of the catalyst; 75°C; 60 min)

Under the conditions indicated in Fig. 7 the TBP conversion amounted 55 mol.%. It should be pointed out that TBPE was not formed over the samples of the TSm series. The TBC formation selectivity was 44 mol.%. Tars were also present in the TBP conversion products. However, the formation selectivity of them was less than over the anatase samples at the same conversion values. A contribution of the decomposition reaction of the oxidizing agent molecules into water and oxygen molecules was also less.

As the content of Ti increased from 1.0 to 3.7 wt.% (the transition from TSm-1 sample to the TSm-3 sample), the TBP conversion values slightly increased from 51 to 57 mol.%, whereas the TBC formation selectivity decreased from 45 to 38 mol.%.

Thus the mesoporous titanosilicates synthesized in this work were more selective in the TBC formation than the titanium oxide samples of different phase composition (see Table 2).

According to the data reported in [16-18], the Ti atoms of the crystalline titanosilicate TS-1 existed in the tetrahedral environment of SiO₄-groups. By reacting with H₂O₂ molecules they formed hydroperoxocomplexes selective in phenol hydroxylation. Similarly, Ti atoms in the oxide were in the octahedral oxygen environment and exhibited activity in the H₂O₂ decomposition. Our results proved this conclusion.

During the condensation stage of synthesizing amorphous titanosilicates, the incorporation of Ti atoms in the silica matrix was possible through the partial substitution of silicon atoms in the silicon-oxygen tetrahedrons. The process was

accompanied by the formation of the active centers similar to those in the TS-1. Therefore, the TSm samples were more selective in the TBC formation than the titanium oxide ones. Meanwhile, the titanium complexes could precipitate as the highly dispersed crystalline hydroxide phase. After the thermal treatment it became the dioxide phase, and the active H₂O₂ decomposition centers were formed on the surface of it.

3.3 Effect of Reaction Parameters

Results of the studies presented in Table 3 illustrated the effect of temperature, the catalyst content in the reaction mix, and the TBP/H₂O₂ molar ratio on the TBP and H₂O₂ conversion. The effect of the different duration of runs on the formation selectivity of TBC and tars in the presence of TSm-2 sample was also presented.

It can be seen that the TBP and H₂O₂ conversion values were minimum in the presence of 2.5 wt.% of titanosilicate at 35°C, being 11 and 23 mol.% for 60 min, respectively. The increase in temperature up to 75°C caused more than 3-fold increase in the TBP and H₂O₂ conversion up to 38 and 76 mol.%, respectively. As well, the increase in temperature from 35°C up to 75°C led to the increase in the TBC formation selectivity from 35 up to 42 mol.% for 60 min duration of the reaction, the corresponding increase in the TBP conversion values being from 11 to 38 mol.%. The maximum TBC formation selectivity in the presence of 2.5 wt.% amount of the catalyst at 75°C was 42 mol.% at the TBP conversion of 38 mol.%.

Table 3. The effect of the reaction temperature and TSm-2 catalyst content on the conversion of TBP, H₂O₂ and the TBC formation selectivity

Catalyst loading (wt.%)	T (°C)	TBP/H ₂ O ₂ mol.ratio	Time (min)	Conversion H ₂ O ₂ (%)	Conversion TBP (mol.%)	Selectivity TBC (mol.%)
2.5	35	1/2	20	10	8	10
		- \ -	60	23	11	35
	50	- \ -	20	16	9	16
		- \ -	60	35	16	36
	75	- \ -	20	43	16	27
		- \ -	60	76	38	42
5	50	1/2	20	25	16	23
		- \ -	60	56	31	38
10	35	1/2	20	22	15	31
		- \ -	60	41	25	47
	50	- \ -	20	39	28	38
		- \ -	60	79	38	52
	75	- \ -	20	51	35	38
		- \ -	60	89	54	43
15	35	1/2	20	21	21	43
		- \ -	60	58	32	48
	50	- \ -	20	58	36	53
		- \ -	60	92	40	53
	50	1/4	20	52	37	39
		- \ -	60	79	46	43
20	50	1/4	20	72	39	35
		- \ -	60	100	48	40

Reaction conditions: $c^0(\text{TBP})=0.12 \text{ mol/L}$, $c(\text{CH}_3\text{CN})=19 \text{ mol/L}$.

In the presence of 10 wt.% of the catalyst the increase in temperature from 35 up to 75°C led to the higher TBP conversion from 25 to 54 mol.% and the H₂O₂ conversion from 41 up to 89 % for 60 min reaction time. Under the analogous reaction conditions (the temperature, duration) the increase of the catalyst concentration from 2.5 up to 10 wt.% resulted in the substantial increase in the final product yield. The TBC formation selectivity values were higher at the higher TBP conversion value, namely, the maximum TBC formation selectivity was 52 mol.% at the TBP conversion of 38 mol.%.

An increase in the catalyst content from 10 up to 15 wt.% allowed to maintain rather high TBC formation selectivity values (48 and 53 mol.% at 35 and 50°C, respectively) as well as the higher TBP conversion (32 and 42 mol.% at 35 and 50°C, respectively).

An increase in the oxidizing agent quantity (the higher TBP/H₂O₂ molar ratio from 1/2 to 1/4) resulted in the slightly higher TBP conversion from 40 to 46 mol.%. However, the TBC formation selectivity markedly decreased from 53 to 43 mol.%. If the catalyst concentration was increased up to 20 wt.%, other things being equal, the TBP conversion did not increase

(probably on account of the insufficient oxidizing agent quantity), and the TBC formation selectivity decreased from 43 to 40 mol.%.

The application of a polar solvent was known [16] as the favorable factor to decrease the homolytic H₂O₂ decomposition that yielded various radical oxo-intermediates and led to the non-selective oxidation. Besides, similar to the oxidation of phenol by aqueous H₂O₂ solutions over the TS-1, we may assume that the reaction of the selective TBP oxidation to TBC in the presence of titanium hydroperoxocomplexes also occurred according to the electrophilic substitution mechanism. There was a number of recommended solvents for that substitution, namely, water, methanol, ethanol, acetic acid, acetone, acetonitrile, DMSO, DMPA, nitromethane, sulpholane [19]. In Fig. 8 the results of the TBP oxidation by aqueous H₂O₂ solution in the presence of TSm-2 sample were presented for different solvents, namely, acetonitrile, acetone, and ethanol. In acetone and ethanol solvents the TBP conversion values were close, the TBC formation selectivity being higher in acetone than in ethanol. The highest TBP conversion of 54 mol.% and the highest TBC formation selectivity of 43 mol.% were observed in the acetonitrile medium.

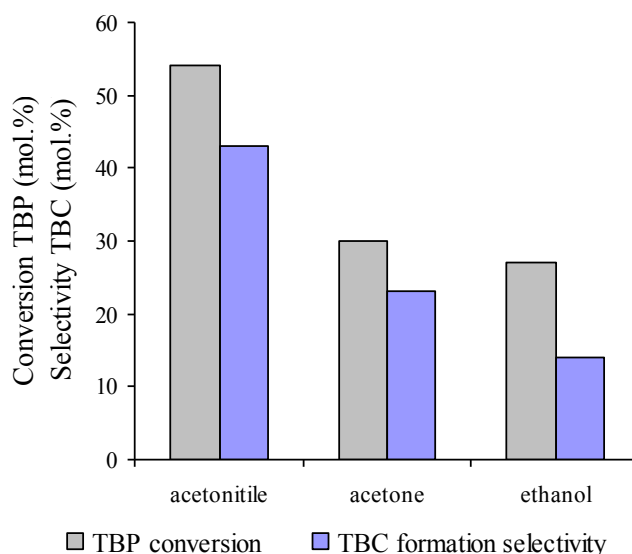


Fig. 8. The effect of solvent type on the TBP conversion (1) and on the TBC formation selectivity (2) in the presence of TSm-2 sample (reaction conditions: 10 wt.% of the catalyst, $c^0(\text{TBP})=0.12 \text{ mol/L}$, $c^0(\text{H}_2\text{O}_2)=0.24 \text{ mol/L}$; 75°C, 60 min)

4. CONCLUSION

The effect of chemical and phase composition of the titanium-containing porous materials on their catalytic activity in the 4-tert-butylphenol oxidation in acetonitrile-aqueous solutions was investigated. It was found that the variation in the phase composition of titanium oxide compounds could be used to control their catalytic properties. The maximum selectivity of the 4-tert-butylphenol ether formation in the process reached 80 mol.%, and the maximum selectivity of the 4-tert-butylcatechol formation did not exceed 20 mol.%.

It was found that the TS-1 microporous crystalline titanosilicate exhibited low activity in the 4-tert-butylphenol transformation in acetonitrile-aqueous H_2O_2 solutions due to the steric restrictions on the diffusion of the substrate molecules into the channels of the catalyst.

Mesoporous titanosilicates with the Ti content within the range of 1.0 to 3.7 wt.% showed as good activity in the transformations under study as the titanium oxide compounds. However, they were superior in the selectivity of 4-tert-butylcatechol formation. The maximum 53 mol.% selectivity of 4-tert-butylcatechol formation was reached at the temperature of 50°C for 60 min reaction time in the presence of 15 wt.% of the mesoporous titanosilicate containing 1.9 wt.% of Ti. The 4-tert-butylphenol conversion in the process was 42 mol.%.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

- Gogotov AF, Amosov VV, Tayursky VA, Ivanova AV, Voitik VS, Stankevich VK Scale tests of 4-tert-butylpyrocatechol as a polymer formation restraining agent in pyrocondensates. Production and Application of Elastomers. 2002;1:3-9.
- Gogotov AF, Amosov VV, Ivanova AV, Baranov OI, Puchenin EV, Vavilov AV, Stankevich BK Full-Scale Tests of Tert-Butylpyrocatechol as a Restraining Agent for Producing EP-300 and "Pyrotol" at the Angarsk Polymer Plant. Oil Processing and Petroleum Chemistry. 2004;3:31-33.
- USSR Patent No. 592812. Ponomarenko V.I., Tolstikov G.A., Chausov S.A., Irkhin B.L., Levandovsky B.T; 1978
- Xamis J, Nasek J. Pyrocatechol. alkylation./ Chem. Prumyst. 1964;14:245-250.
- U.S. Patent No. 4410501. Taramasso M., Perego G., Notari B; 1983.
- Clerici MG, Kholdeeva OA. Liquid phase oxidation via heterogeneous catalysis: Organic synthesis and industrial applications. Wiley, New Jersey; 2013.

7. Wu P, Kubota Y, Yokoi T. A career in catalysis: Takashi tatsumi. ACS Catal 4:23-30.
8. RU Patent No. 2420455. Veklov VA, Kutepov BI, Talipova RR, Grigorieva NG, Dzhemilev UM, Drozdov VA; 2009.
9. RU Patent No. 2422361. Veklov VA, Kutepov BI, Talipova RR, Grigorieva NG, Dzhemilev UM, Drozdov VA; 2009.
10. Karnaukhov AP. Adsorption. Texture dispersed and porous materials. Nauka, Novosibirsk; 1999.
11. Pozin ME. Hydrogen Peroxide and Peroxide Compounds. Goskhimizdat, Moscow; 1951.
12. Pilipenko AT, Pyatnitsky IV. Analytical chemistry: In two books: Book 2. Khimiya, Moscow. 1990.
13. Biz Sophie, Ocelli Mario L. Synthesis and characterization of mesostructured materials. Catal. Rev.-Sci. Eng. 1998; 40:329-407.
14. Beck C, Mallat T, Burgi T. Nature of active sites in sol-gel TiO₂-SiO₂ epoxidation catalysts. J. Catal. 2001;204:428-439.
15. Brinker CJ, Scherer GW. Sol-gel science: The physics and chemistry of sol-gel processing. Academic Press, London; 1990.
16. Ratnasamy P, Srinivas D, Knozinger H. Active sites and reactive intermediates in titanium silicate molecular sieves. Adv. Catal. 2004;48:1-169.
17. Chang Won Yoon, Kurt F. Hirsekorn, Michael L. Neidig, Xinzhen Yang T. Don tilley mechanism of the decomposition of aqueous hydrogen peroxide over heterogeneous TiSBA15 and TS-1 selective oxidation catalysts: Insights from spectroscopic and density functional theory studies. ACS Catal. 2011;1:1665-1678.
18. Notari B. Microporous crystalline titanium silicates. Adv. Catal. 1996;41:253-334.
19. Raihardt K. Solvents and Media Effects in Organic Chemistry. Mir, Moscow; 1991.

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