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A new environmentally friendly method for the production of 2,3,5-trimethyl-*p*-benzoquinone

O.A. Kholdeeva[a,*], N.N. Trukhan[a], M.P. Vanina[a], V.N. Romannikov[a,1], V.N. Parmon[a], J. Mrowiec-Białoń[b], A.B. Jarzębski[c]

[a] *Boreskov Institute of Catalysis, 5 Acad. Lavrentiev Av., Novosibirsk 630090, Russia*
[b] *Institute of Chemical Engineering, ul. Bałtycka 5, 44-100 Gliwice, Poland*
[c] *Department of Chemical Engineering, Silesian University of Technology, Strzody 7, 44-100 Gliwice, Poland*

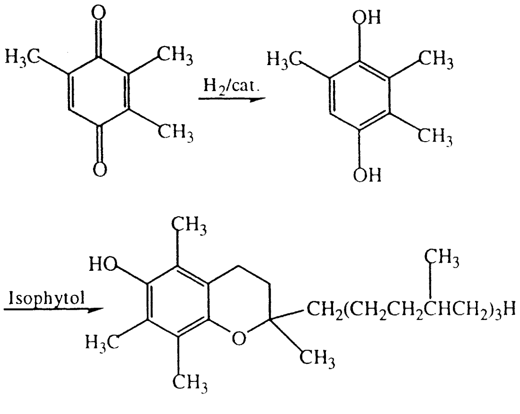
Abstract

A new environmentally friendly method for the production of 2,3,5-trimethyl-1,4-benzoquinone (TMBQ, Vitamin E precursor) based on the oxidation of 2,3,6-trimethylphenol (TMP) with aqueous H_2O_2 over various Ti-containing mesoporous silicate materials is reported. Both well-organized Ti-containing mesoporous mesophase silicate (Ti-MMM), having hexagonal arrangement of uniform mesopores, and amorphous TiO_2–SiO_2 mixed oxides (aerogels and xerogels) produced TMBQ with good to high yield. All the materials studied have been proved to operate as truly heterogeneous catalysts. No titanium leaching occurred from the solid matrixes during the oxidation process. Titanium dispersion and its accessibility were found to be crucial factors determining the catalytic properties. For samples with similar titanium loading, both the catalytic activity and TMBQ yield appeared to fall in the order TiO_2–SiO_2 aerogel > Ti-MMM > TiO_2–SiO_2 xerogel and correlate with average mesopore diameter and mesopore volume. The best results (96–98% selectivity to TMBQ at 99–100% TMP conversion) were obtained with TiO_2–SiO_2 aerogels, containing 1.7–6.5 wt.% Ti.

Keywords: 2,3,5-Trimethyl-*p*-benzoquinone; Mesoporous mesophase materials; Titanium

1. Introduction

Quinone derivatives play an important role in biosystems and are useful intermediates of fine organic synthesis. 2,3,5-Trimethyl-1,4-benzoquinone (TMBQ) is a key intermediate in the production of Vitamin E [1].



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[*] Corresponding author. Tel.: +7-383-234-4573; fax: +7-383-234-3056.
E-mail address: khold@catalysis.nsk.su (O.A. Kholdeeva).

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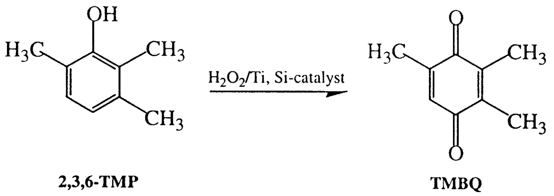
Until recently, traditional environmentally unacceptable stoichiometric oxidation of 2,3,6-trimethylphenol (TMP) with MnO_2, HNO_3 or other toxic reagents was the main route for TMBQ industrial production. Last decades, the development of environmentally friendly catalytic methods for selective oxidation of organic compounds has become a challenging goal. A number of catalytic systems for the TMP oxidation to TMBQ has been developed using "clean" and cheap oxidants, such as molecular oxygen and hydrogen peroxide. Among the catalytic systems are copper salts/O_2 [2,3], Schiff base cobalt complexes/O_2 [4,5], ruthenium salts/H_2O_2 [6], and heteropoly and isopoly compounds/H_2O_2 [7,8] or O_2 [9]. The main disadvantage of the above mentioned systems is the use of homogeneous catalysts that leads to the known problems with the catalyst separation and, therefore, may result in contamination of the target product with hazardous transition metal compounds.

Last years, mesoporous molecular sieves, such as M-MCM-41, M-MCM-48, M-HMS, M-MMM, etc., and amorphous MO_x–SiO_2 mixed oxides, where M is transition metal ion (Ti^{IV}, V^{V}, Sn^{IV}, etc.) and MMM refers to mesoporous mesophase materials, attract much attention as catalysts for selective oxidation of large organic substrates [10–22]. Recently, oxidations of TMP with H_2O_2 over (Cr)MCM-41 [23] and TiAPO-5 [24] have been reported to give TMBQ with the yield of 64 and 85%, respectively. However, substantial chromium leaching was observed in the former system, while the heterogeneity of the latter one has not been demonstrated and seems to be problematic [25]. An attempt was made to employ Fe(III) phthalocyanine catalyst immobilized onto SiO_2 in the TMP oxidation using *tert*-butylhydroperoxide as oxidant. However, the selectivity with this catalyst was good (72–80%) only in the first catalytic cycle [26]. Thus, an efficient method for TMBQ production based on the employment of a solid, stable to leaching catalyst has yet to be developed.

Here we report a new method for the TMP oxidation to TMBQ, which uses aqueous H_2O_2 as oxygen donor and mesoporous Ti-containing silicate materials as heterogeneous catalysts. Catalytic behavior of a Ti-containing mesoporous mesophase silicate (Ti-MMM), having well-developed hexagonal arrangement of uniform mesopores, and amorphous TiO_2–SiO_2 mixed oxides (both aerogels and xerogels) has been compared. An attempt was made to establish the relationship between structural and textural characteristics and catalytic properties.



2. Experimental

2.1. Materials

TMP (Fluka) was recrystallized from hexane. Hydrogen peroxide (28–74% in water) was determined iodometrically prior to use. All the other reactants were obtained commercially and used without further purification.

2.2. Catalysts

Ti-MMM sample was prepared by hydrothermal synthesis and characterized as described in [15,16]. Syntheses of TiO_2–SiO_2 mixed oxides were performed using a modified procedure of that described in [18]. Typically, 50 mmol of tetraethoxyortosilicate (TEOS) was dissolved in 225 mmol of ethanol and hydrolized with 25 mmol of water under acidic conditions for 3 h at 50 °C under reflux. Then 5.26 mmol of tetraisopropoxy titanium mixed with 10.52 mmol of acetylacetone, dissolved in 47.25 mmol of ethanol was introduced to the solution of hydrolyzed TEOS and refluxed for 2 h at 50 °C. Then the solution of ethyl silicate 40 (50 mmol of Si) in 225 mmol of ethanol was added and stirred for 10 min. After that the solution composed of 450 mmol of ethanol, 330 mmol of water and 1.6 mmol of ammonia was added to the mixture under vigorous stirring. After gelation, the alcogel was aged for 7 days at room temperature. Drying of alcogel was performed in a stream of supercritical carbon dioxide (343 K, 12 MPa) to give aerogel catalyst (sample **A2**), containing 3.05 wt.% Ti (3.70 wt.% Ti after calcination at 500 °C). Conventional drying of the alcogel in air during 4 days at 50 °C and 6 h at 100 °C yielded xerogel (sample **X2**), containing 3.39 wt.% Ti (3.90 wt.% Ti after calcination at 500 °C). The other samples were synthesized by similar procedures, varying the Si/Ti ratio from 4 to 65. The prepared TiO_2–SiO_2 mixed oxides were characterized by the nitrogen adsorption measurements, elemental analysis and DRS-UV.

2.3. Catalytic oxidation procedure

Catalytic experiments were performed under vigorous stirring in thermostated glass vessels at 80 °C. Typically, the reactions were initiated by adding 1.05 mmol of H_2O_2 to a mixture, containing 0.3 mmol of TMP, 9–100 mg of a catalyst (0.013–0.08 mmol of Ti), an internal standard (biphenyl) and 3 ml of MeCN. When the catalytic properties of samples with different Ti loading were compared, specified catalyst amounts were used in order to introduce 0.013 mmol of Ti in each case. The oxidation products were identified by GC–MS, UV–Vis and ^{1}H NMR. TMP conversion and TMBQ yield were quantified by GC. After the reaction, catalysts were filtered off, washed with MeCN and then re-used. Pure TMBQ was separated from the reaction mixture using adsorption chromatography on silica gel.

2.4. Leaching tests

The catalysts were filtered off during the oxidation process and the TMP conversion was monitored in the filtrate by GC. The filtration was performed at the reaction temperature in order to prevent a possible re-adsorption of leached titanium species. Titanium content in the catalysts was determined before and after several treatments with H_2O_2 using atomic adsorption spectroscopy.

2.5. Instrumentation

Gas chromatographic analyses were performed using a gas chromatograph “Tsvet-500” equipped with a flame ionization detector and a quartz capillary column (25 m × 0.3 mm) filled with Carbowax 20 M. GC–MS analyses of organic products were conducted using an LKB-4091 instrument. ^{1}H NMR spectra were recorded on an MSL-400 Bruker spectrometer. DRS-UV measurements were performed on a Shimadsu UV–VIS 2501PC spectrophotometer at ambient conditions. Nitrogen adsorption isotherms at 77 K were measured using a Micromeritics ASAP 2000 instrument.

3. Results and discussion

The synthesis and characterization of the Ti-MMM sample used in this study have been reported elsewhere [15,16]. The sample codes and physico-chemical characteristics for the TiO_2–SiO_2 aerogels and xerogels along with those of Ti-MMM are summarized in Table 1. Both the X-ray amorphous materials and the mesophase Ti-MMM catalyst possess high surface area, a mesoporous structure (a bimodal pore distribution in the case of xerogels) and, according to DRS-UV, have high titanium dispersion. The predomination of site-isolated titanium species is indicated by λ_{max} at 216–238 nm ([10] and references therein). The aerogels with high titanium content (**A3**, **A4**) show a long-wave shift in the UV spectrum (λ_{max} at 258 and 262 nm, respectively) along with a band broadening, thus indicating the appearance of partially oligomerized titanium species [10].

The catalytic properties of the TiO_2–SiO_2 aerogels and xerogels in the TMP oxidation with H_2O_2 are given in Table 2 in comparison with the Ti-MMM catalytic properties. Both well-organized Ti-MMM and amorphous TiO_2–SiO_2 mixed oxides appeared to produce TMBQ with good to high yield at optimal reaction conditions (TMP 0.1 M, H_2O_2 0.35 M, 80 °C, MeCN). The main by-products were 2,2′,3,3′,5,5′-hexamethyl-4,4′-biphenol and a polymeric compound, most likely polyphenylene oxide. The selectivity to TMBQ considerably enhanced with decreasing the TMP concentration and increasing the temperature [16]. The use of lower than 3.5/1 H_2O_2/TMP molar ratio resulted in uncompleted TMP conversion. At $[H_2O_2]/[TMP] = 3.5$ all the oxidant was consumed during the reaction, indicating that some unproductive peroxide decomposition occurred. Thus taking into account the stoichiometry of the target reaction (2/1), one can estimate from the data given in Table 2 that the selectivity based on H_2O_2 was quite moderate (50–60%) for

Table 1
Physico-chemical properties of the Ti, Si-catalysts studied

Sample (wt.% Ti)[a]	S_{BET} (S_{BJH})[b] (m^2/g)	$V_{p(BJH)}$[c] (cm^3/g)	d_p[d] (nm)	DRS-UV λ_{max}[a] (nm)
A1 (1.68)	770 (783)	3.03	15.49	229
A2 (3.70)	695 (713)	2.20	12.35	236
A2	968 (733)[a]	2.45[a]	13.36[a]	236
A2[e]	913 (690)[e]	2.06[e]	11.97[e]	260[e]
A3 (6.52)	651 (635)	2.41	15.18	258
A4 (16.65)	870 (838)	3.74	17.84	262
X1 (1.44)	737 (280)	0.21	2.96	216
X2 (3.90)	657 (390)	0.26	2.67	226
X3 (7.29)	519 (241)	0.17	2.87	238
Ti-MMM (1.53)	1112 (1059[f])[a]	0.91[a,g]	3.79[a,h]	218

[a] Determined after calcination at 500 °C.

[b] S_{BJH} denotes BJH cumulative desorption surface area of pores between 1.0 and 300.0 nm diameter.

[c] BJH cumulative desorption pore volume of pores between 1.0 and 300.0 nm diameter.

[d] BJH desorption average pore diameter $d_p = 4V_{p(BJH)}/S_{BJH}$.

[e] After treatment with 30% H_2O_2 and re-calcination at 500 °C.

[f] Specific mesopore surface area.

[g] Specific mesopore volume.

[h] Mesopore diameter.

Ti-MMM and TiO_2–SiO_2 aerogels. The situation was rather complicated for TiO_2–SiO_2 xerogels. Complete TMP conversion was not achieved with these catalysts even when higher than 3.5/1 H_2O_2/TMP molar ratio was employed. The reason for that seems to be lower porosity of the xerogels, resulting in blocking of active centers by the oxidation products, but not the higher rate of the unproductive peroxide

Table 2
TMP oxidation with 30% aqueous H_2O_2 over Ti, Si-catalysts[a]

Sample[b] (mg)	Time (min)	Selectivity to TMBQ[c] (%)	TMP conversion (%)	TOF[d] (mol TMP/mol Ti × min)
A1 (37)	18	96	99	4.6
A2 (17)	21	97	99	3.6
A2 (20)[e]	50	93	84	2.7
A1 (100)	10	95	98	–
A1[f] (100)	10	83	95	–
A1[g] (100)	10	84	94	–
A3 (10)	40	90	97	2.9
A3[f] (10)	40	71	63	–
A3 (51)	10	98	100	–
A3[f] (51)	10	94	100	–
A3[g] (51)	10	90	92	–
A4 (23)	160	53	91	0.17
X1 (43)	100	96	71	0.54
X2 (16)	110	92	53	0.44
X3 (9)	120	84	36	0.40
Ti-MMM (42)	25	77	100	0.92

[a] Reaction conditions: TMP 0.1 M, [TMP]/[H_2O_2] = 1/3.5, MeCN 3 ml, 80 °C.

[b] Samples were calcined at 500 °C.

[c] GC yield based on TMP consumed.

[d] Turnover frequencies determined from initial rates of TMP consumption.

[e] Uncalcined sample.

[f] Second cycle.

[g] Third cycle.

decomposition, which was found to fall in the order Ti, Si-aerogel > Ti, Si-xerogel > Ti-MMM.

Recently, we have found that the titanium content is a crucial factor, which determines the state of the active catalytic site in Ti-MMM, thus effecting the catalytic behavior [15,16]. The Ti-MMM catalysts containing 1.5–2 wt.% Ti showed the highest activity and selectivity in the TMP oxidation [16]. An increase in xerogel efficiency with lowering metal loading was also reported for H_2O_2-based oxidation of hydrocarbons [22]. The catalytic activity data given in Table 2 clearly demonstrate a similar effect of the titanium content on the catalytic activity of the TiO_2–SiO_2 mixed oxides. Such a dependence can be rationalized taking into account that less reactive Ti–O–Ti bonds form with increasing the Ti loading. This is strongly supported by DRS-UV data reported in Table 1 and elsewhere [10,14–16]. However, considerably lower activity of sample **A4**, which has good textural characteristics and UV spectrum very close to that of sample **A3**, is unclear yet.

For the samples with similar titanium loading, both the catalytic activity and the TMBQ yield turned out to fall in the order TiO_2–SiO_2 aerogel > Ti-MMM > TiO_2–SiO_2 xerogel and correlate with the average mesopore diameter and mesopore volume. The yield of TMBQ was found to increase with augmentation of the catalyst amount (Table 2). The highest TMBQ yields (96–98% selectivity at 99–100% TMP conversion) were attained over the TiO_2–SiO_2 aerogels, containing 1.7–6.5 wt.% Ti. The calcined aerogel samples produced higher TMBQ yields as compared to the uncalcined ones (Table 2). This accords with the textural data, which show that both the mesopore volume and average mesopore diameter increase after the calcination (Table 1).

A serious problem associated with the use of solid catalysts in the liquid phase, especially when using aqueous hydrogen peroxide, is the predilection for leaching of the metal ion into solution [13,14,19,23,25]. Experiments with fast catalyst filtration performed at the reaction temperature during the TMP oxidation process showed that no further TMP conversion was exhibited in the filtrate after removal of the catalyst (Fig. 1). This proves that if small amounts of the titanium species are leached from the solid matrix during the oxidation process, the observed catalytic activity is not due to these species. Thus both Ti-MMM [16] and TiO_2–SiO_2 mixed oxides operate as truly heterogeneous catalysts. According to the elemental analysis data, the total titanium content in the sample remained unchanged after several catalyst treatments with H_2O_2 (Fig. 2). This appears to be a quite rare example of true heterogeneity of mesoporous Ti, Si-catalysts in H_2O_2-based

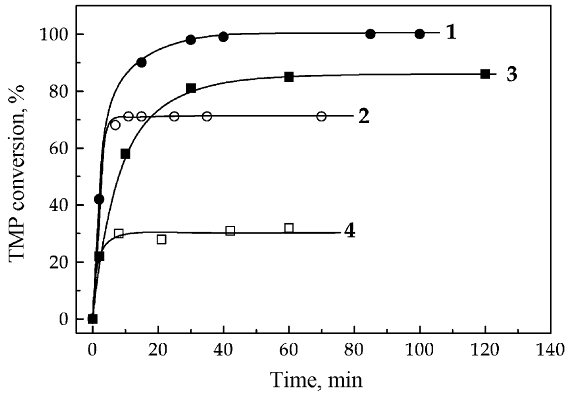


Fig. 1. TMP conversion vs. time: (1) over sample **A2**; (2) in filtrate after removal of sample **A2**; (3) over sample **X2**; (4) in filtrate after removal of sample **X2**. Fast catalyst filtration was performed at the reaction temperature at 4 and 2 min for **A2** (curve 2) and **X2** (curve 4), respectively. Reaction conditions: TMP 0.1 M, H_2O_2 0.35 M, MeCN 3 ml, 80 °C.

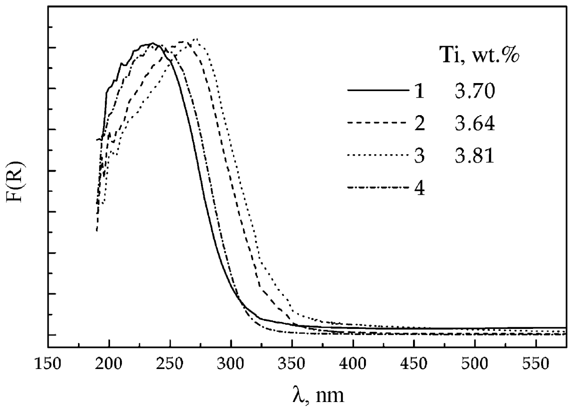


Fig. 2. UV–Vis diffuse reflectance spectra for the TiO_2–SiO_2 aerogel (sample **A2**): (1) before treatment; (2) after the first treatment with 30% H_2O_2; (3) after the second treatment with 30% H_2O_2; (4) after the first treatment with 74% H_2O_2. Treatment conditions: **A2** 23 mg, H_2O_2 0.35 M, 80 °C, MeCN 3 ml, 1 h. All the samples were calcined at 500 °C before running the spectra.

oxidations [13,14,19]. Nevertheless, some loss of the catalytic activity can be observed after the catalyst recycling, especially when small catalyst amounts are used (Table 2). This loss could not be attributed to the accumulation of organic deposit on the catalyst surface because it was observed both for samples, which were calcined at 500 °C before recycling, and for uncalcined samples. For Ti-MMM the catalytic activity loss was even higher when samples were calcined between catalytic cycles. The reason for the catalyst deactivation is most likely a negative effect of aqueous H_2O_2 on the hydrophylic catalyst surface resulting in both deterioration of the textural properties, which in turn reduces the accessibility of titanium active sites, and the formation of partially oligomerized titanium species (Table 1). The latter is indicated by a long-wave shift in the UV spectrum of the samples treated with 30% H_2O_2. Note that when the catalyst was treated with 74% H_2O_2, only slight changes in the UV spectrum were observed (Fig. 2). The problem of the catalyst stability seems to be in principle overcome either by reducing water concentration in the reaction mixture [16] or by making the catalyst surface hydrophobic [27,28].

In conclusion, the most important characteristics for the Ti, Si-catalyst-based TMP oxidation process obtained under optimal reaction conditions are given in Table 3 in comparison with characteristics of the $CuCl_2$-based process [3]. Even though hydrogen peroxide is more expensive per kilo than molecular oxygen, it can be the oxidant of choice for fine chemicals because of its simplicity of operation [25]. One can see that most of the process parameters are similar if not higher for the proposed method. Several advantages, very important for the environment, are clearly seen for the Ti, Si-catalyst-based process:

- high activity combined with high selectivity;
- true heterogeneity of the catalyst, which can be separated by simple filtration;
- no Cl-containing reactants and solvents;
- high purity of the product (lack of transition metal impurities and Cl-containing by-products);
- no corrosion problems.

Table 3
The most important characteristics for the Ti, Si-catalyst-based process of the TMP oxidation in comparison with characteristics of the $CuCl_2$-based process

Catalyst	Ti, Si-catalyst	$CuCl_2$ [3]
Catalyst state	Heterogeneous	Homogeneous
Oxidant	H_2O_2	O_2
Solvent	MeCN	Alcohols
TMP/Ti (Cu) (mol/mol)	4–23	1
TMP conversion (%)	99–100	100
Selectivity to TMBQ (%)	96–98	98
TOF_{av}. (mol TMP/mol Ti (Cu) × min)	0.44–1.26	0.005

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