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How to reach 100% selectivity in H_2O_2-based oxidation of 2,3,6-trimethylphenol to trimethyl-*p*-benzoquinone over Ti,Si-catalysts

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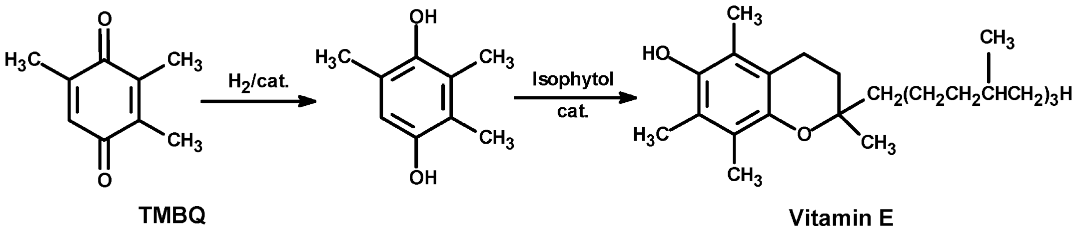
ABSTRACT

A comprehensive study of structure/activity/selectivity relationships and mechanistic aspects of the oxidation of 2,3,6-trimethylphenol (TMP) with aqueous H_2O_2 over a wide variety of titanium-silicate catalysts allowed us to infer requirements to an optimal catalyst and optimal reaction conditions for this reaction and to produce 2,3,5-trimethyl-1,4-benzoquinone (TMBQ, Vitamin E precursor) with nearly 100% selectivity at 100% substrate conversion. The main by-products in the TMP oxidation are C–C and C–O dimers, formed by coupling of intermediate phenoxyl radicals. The formation of TMBQ is favoured by (1) a poor coordinating solvent (MeCN), (2) elevated temperature (80 °C), (3) low TMP concentration (not higher than 0.1 M), (4) high H_2O_2/TMP molar ratio (ca. 3.5), and (5) low TMP/Ti ratio ($<$10–20). The crucial factors which determine the selectivity of Ti,Si-catalysts in TMP oxidation to TMBQ are mesoporosity and an optimal surface concentration (ca. 0.7–1.0 Ti atoms/nm^2) of accessible highly dispersed, probably, dimeric Ti(IV) species. The catalysts prepared by a simple, affordable and cheap synthesis methodology *via* grafting titanium(IV) precursors onto the surface of commercial mesoporous silica completely fulfil these requirements and thus can be viewed as promising catalysts for environmentally benign TMBQ production.

1. Introduction

Vitamin E is the most important fat-soluble biological antioxidant [1]. The market for Vitamin E exceeds 30,000 t/year. The key intermediate in the Vitamin E synthesis, 2,3,5-trimethyl-1,4-benzoquinone (TMBQ), is currently produced in the industry *via* oxidation of 2,3,6-trimethylphenol (TMP) with molecular oxygen (or air) in the presence of $CuCl_2$ catalyst in various solvents, including two-phase systems, whereby high TMBQ yields (>95%) are obtained [2,3 and references therein].



However, the known drawbacks of employing a homogeneous catalyst are related to its separation, recycling and product purification. The use of two-phase solvent systems partially solves these problems, but even so product contamination with traces of

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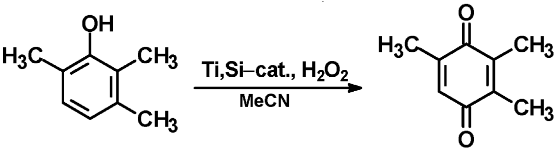
transition metal may occur due to metal complexation by organics and subsequent extraction into organic phase. Furthermore, high concentrations (close to stoichiometric) of copper chloride used [4] result in the formation of Cl-containing by-products and require special apparatus, resistant to corrosion. Therefore, the development of greener alternatives for the production of TMBQ is a challenging goal of fine chemistry.

In 2000, some of us found and patented a new method for TMP oxidation to TMBQ based on the use of aqueous H_2O_2 as oxidant and mesostructured titanium-silicate catalyst Ti–MMM [5,6].



TMBQ yield attained 80% in this method. In the same year, Sorokin and Tuel published similar results for Ti–MCM-41 catalyst [7]. One year later, we revealed that amorphous TiO_2–SiO_2 mixed oxides are even more selective catalysts for TMP oxidation [8], yields of the target quinone as high as 95–98% being attained over TiO_2–SiO_2 aerogels [9,10]. However, a substantial disadvantage of these types of Ti,Si-catalysts (Ti–MMM, Ti–MCM-41 and TiO_2–SiO_2 aerogels) was their low hydrolytic stability and, therefore, a dramatic lack of the activity after the first catalytic run [6,9,11]. Since that time, a considerable progress has been achieved in solving the problem of the hydrolytic instability of mesoporous titanium-silicates. A few hydrothermally stable catalytic materials, such as mesoporous TS-1 [12], Ti–MMM-1 [13] and Ti–MMM-2 [14,15], have been reported. The Ti–MMM-2 catalyst combined high activity in H_2O_2-based TMP oxidation with good stability of the catalytic performance. However, the selectivity to TMBQ never exceeded 80% [15], which is not enough to make this process commercially attractive. In 2003, Tuel and Hubert-Pfalzgraf prepared titanium-silicate catalysts by grafting a hexanuclear Ti cluster onto the surface of mesostructured silicates, HMS and SBA-15, and demonstrated their efficiency in TMP oxidation with H_2O_2 [16]. Very recently, we revealed that catalysts prepared by grafting titanocene dichloride onto commercial silicas, adapting the procedure developed by Maschmeyer et al. [17,18], are highly active and selective in the title reaction [19].

In this review paper, we survey a large set of the experimental data acquired for TMP oxidation with H_2O_2 over a range of titanium-silicate catalysts. A comprehensive analysis of the structure/activity/selectivity relationships and of the mechanistic aspects of the TMP oxidation reaction has allowed us to infer requirements to an optimal catalyst and optimal operating conditions and, finally, to produce TMBQ with a nearly quantitative yield.

2. Experimental

2.1. Catalysts and materials

Ti/SiO_2 catalysts were prepared by grafting titanocene dichloride (Aldrich) onto the surface of various silicas adapting the procedure developed by Maschmeyer et al. [17,18]. Four types of supports were used, namely, two commercial non-ordered mesoporous silicas obtained from Grace and Nippon-Gosei (designated as A and B, respectively), a pyrogenic non-porous Aerosil silica (C) and mesostructured MCM-41 (D). Ti–MMM-2 was prepared by a templated route following a slightly modified procedure described in Refs. [14,15]. The TiO_2–SiO_2 aerogel sample was prepared according to [8]. Silylation of the Ti/A-2 sample was carried out by treating the calcined solid (at 573 K for 1 h in air and for 2 h in vacuo) with a solution of hexamethyldisilazane (HMDS, Aldrich) in toluene (20 mL), previously dried on molecular sieves (Siliporite 3A), under argon at 383 K during 2 h, using a HMDS:SiO_2 molar ratio of 0.084. The textural properties of supports A–D as well as those of Ti–MMM-2 and TiO_2–SiO_2 aerogel are given in Table 1. All the catalysts, except for the silylated sample Sil–Ti/A-2, were calcined at 560 °C for 5 h in air prior to use in catalytic tests and physico-chemical measurements. The silylated catalyst was evacuated for 7 h at 110 °C prior to use. All the catalysts were characterized by elemental analysis, N_2 adsorption and DRS-UV measurements.

Table 1
Textural properties of the supports and catalysts

Support or catalyst	BET surface area, S ($m^2 g^{-1}$)	Mesopore volume, V ($cm^3 g^{-1}$)	Mean pore diameter, D (nm)
A (Grace)	290	1.48	20.4
B (Nippon-Gosei)	679	0.66	3.8
C (Aerosil)	333	Non-porous	–
D (MCM-41)	972	0.65	2.6
Ti–MMM-2	976	0.54	3.1
TiO_2–SiO_2 aerogel	988	3.25	13.2

TMP (98%) was purchased from Fluka and used as received. The concentration of hydrogen peroxide (27–30% in water) was determined iodometrically or by titration with $KMnO_4$. Acetonitrile was dried and stored over activated 4A molecular sieves. All the other reactants were obtained commercially and used without further purification.

2.2. Catalytic experiments

Catalytic TMP oxidations with H_2O_2 were performed under vigorous stirring (500 rpm) in thermostated glass vessels. The rate of TMP consumption remained constant while the stirring rate varied in the range of 200–1000 rpm indicating no external diffusion limitation. The catalytic performance was assessed under optimal reaction conditions identified previously [6]: TMP, 0.1 M; H_2O_2, 0.35 M; catalyst, 8–28 mg (to introduce 0.006 mmol of Ti); MeCN, 1 mL, 80 °C, 20–30 min. The oxidation products were identified by GC–MS and ^1H NMR. TMBQ yield and TMP conversion were quantified by GC using diphenyl as internal standard. After the reactions, catalysts were filtered off, washed with methanol and acetonitrile, dried in air overnight, calcined at 560 °C for 5 h and then re-used. H_2O_2 decomposition over Ti,Si-catalysts was studied at 80 °C in MeCN (4 mL) at initial concentration of H_2O_2 0.35 M in the absence of TMP. The catalyst amount was specified to introduce 0.024 mmol of Ti. Aliquots of 0.25 mL were taken during the reaction course, and H_2O_2 concentration was determined by titration with 0.01 N $KMnO_4$. TOF values for TMP oxidation and H_2O_2 decomposition were determined from the initial rates of TMP and H_2O_2 consumption, respectively.

2.3. Instrumentation

GC analyses were performed using a gas chromatograph "Tsvet 500" equipped with a flame ionisation detector and a quartz capillary column (30 m × 0.25 mm) Supelco MDN-5S. GC–MS analyses were carried out using a gas chromatograph Agilent 6890 (quartz capillary column 30 m × 0.25 mm/HP-5 ms) equipped with a quadrupole mass-selective detector Agilent MSD 5973. ^1H NMR spectra were recorded on an MSL-400 Bruker spectrometer. DRS-UV measurements were performed on a Shimadzu UV–vis

2501PC spectrophotometer. Nitrogen adsorption at 77 K was measured using an ASAP-2020 instrument.

3. Results and discussion

3.1. Factors affecting the catalytic activity

The catalytic properties of grafted Ti,Si-catalysts in TMP oxidation with H_2O_2 are presented in Table 2 along with the results of the catalytic runs acquired using some other representative Ti,Si-catalysts (Ti–MMM-2, TiO_2–SiO_2 aerogel and TiO_2–SiO_2 xerogel). It is widely accepted that catalytic activity of Ti,Si-catalysts strongly depends on the dispersion of titanium in a silicate matrix and this parameter can be characterized by DR-UV spectroscopy [11,20–24]. According to the literature, catalysts containing site-isolated Ti atoms typically show a DRS-UV band in the range of 208–230 nm depending on the coordination number of Ti(IV). The formation of Ti–O–Ti connectivities is manifested by a red shift of the position of the DRS-UV band.

We performed a comparative analysis of turnover frequency (TOF) values determined from the initial rates of TMP consumption as well as of the position of DRS-UV bands (Table 2; some representative DR-UV spectra are also shown in Fig. 1), and we observed that titanium dispersion does have a strong impact on the catalytic activity of Ti,Si-catalysts in TMP oxidation with H_2O_2. It is worth noting that Ti dispersion depends on the synthesis procedure and the surface concentration of Ti, which, in turn, depends on both the Ti loading and the specific surface area of the material. Fig. 1 shows DR-UV spectra typical of the grafted titanium catalysts containing about 2 wt.% of Ti. The spectrum of Ti–MMM-2 is also given. One can see that the DR-UV spectrum of Ti grafted onto high surface area MCM-41 (Ti/D-2) and the spectrum of Ti–MMM-2 are close to each other and show a rather narrow DR-UV band with a maximum at 210–212 nm indicating the presence of isolated titanium sites, presumably, in tetrahedral coordination [23,24]. Ti/D-1 and TiO_2–SiO_2 aerogel have DR-UV spectra similar to those of Ti/D-2 and Ti–MMM-2, with the only difference that the aerogel shows a second maximum at 225, which disappears after evacuation, most likely, due to transformation of octahedral Ti(IV) to tetrahedral one. Importantly, these catalysts (Ti/D-1, Ti/D-2, Ti–MMM-2 and TiO_2–SiO_2 aerogel) display the highest catalytic activities, as evidenced by the TOF values in Table 2.

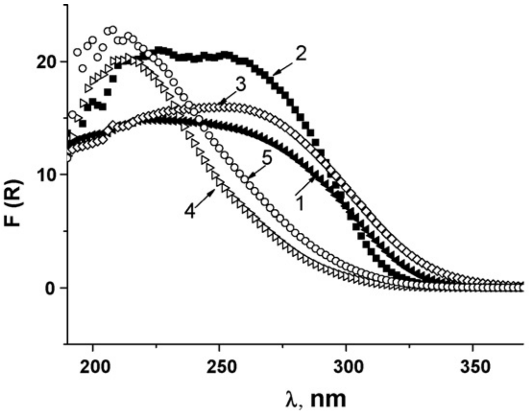


Fig. 1. DR-UV spectra of grafted Ti,Si-catalysts: (1) Ti/B, (2) Ti/A-2, (3) Ti/C and (4) Ti/D-2 and DR-UV spectrum of Ti–MMM-2 (5).

The DR-UV spectra of Ti grafted onto non-ordered silicas with a lower surface area compared to MCM-41 and MMM-2 and, therefore, with a higher Ti surface concentration are different and reveal a new broad band centred around 240–250 nm (Fig. 1; Table 2). According to the literature, the maximum broadening and shift to longer wavelengths may indicate both an increase of the coordination number of Ti and the presence of species having at least one Ti atom in the second coordination sphere [11,21,22,25]. Although the state of Ti in such catalysts is not fully understood and is currently under debate, many authors attributed the bands at 240–250 nm to dimeric and/or small oligomeric (clustered) titanium species [16,21,25,26]. Significantly, the activity of catalysts containing this type of catalytic centres (we denote it further as “double site Ti” to distinguish from “single site Ti”) is a bit lower compared to the catalysts containing mostly isolated Ti atoms. Such trend is clearly seen if we compare different samples of Ti-catalysts obtained *via* grafting on the same support. Indeed, the activity of both Ti/A and Ti/D series decreases with increasing Ti loading which leads to the formation of Ti–O–Ti bonds.

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

Catalyst (Ti, wt.%)	TMP conversion (%)	TMBQ selectivity (%)	TOF (TMP)[b] (min^{-1})	DRS-UV maximum (nm)
Ti/A-1 (0.92)	100	79	2.2	215, 252[c]
Ti/A-2 (1.97)	100	96 (100)[d]	2.0	252[e]
Ti/A-3 (2.50)	95	95	1.4	255[e]
Ti/B (2.09)	97	91	1.2	240[e]
Ti/C (1.78)	85	47	1.0	256[e]
Ti/D-1 (0.95)	97	47	2.7	212
Ti/D-2 (2.00)	98	77	2.7	212
Ti/D-3 (3.87)	99	89	2.0	226
Ti–MMM-2 (1.89)	100	76	3.0	210
TiO_2–SiO_2 aerogel (1.70)	100	82	3.1	215, 225
TiO_2–SiO_2 xerogel[f] (1.44)	71[g]	96	0.5	216
Ti-SBA-15[h] (2.05)	52[i]	69	0.1	250, 320
Sil–Ti/A-2[j] (1.73)	51	95	0.5	255[k]

[a] Reaction conditions: TMP, 0.1 M; H_2O_2, 0.35 M; catalyst, 0.006 mmol of Ti; MeCN, 1 mL, 80 °C, 20–30 min.

[b] TOF (TMP) = (moles of TMP consumed)/(moles of Ti) × (time), determined from the initial rates of TMP consumption.

[c] Shoulder.

[d] The catalyst amount was increased twice.

[e] Broad maximum.

[f] Both micro and mesopores are present in this catalyst (average pore diameter 2.3 nm); the data are taken from Ref. [9,10].

[g] After 100 min.

[h] TiO_2-like species are present in this catalyst; the data are taken from Ref. [27].

[i] After 4 h.

[j] Silylated catalyst: $S = 260\ m^2\ g^{-1}$; $V = 1.21\ cm^3\ g^{-1}$; $D = 14$ nm.

[k] From Ref. [30].

Earlier, Trukhan et al. showed that hydrothermal synthesis of Ti–SBA-15 under moderately acidic conditions (pH 3) leads to catalysts containing a considerable amount of TiO_2-like oligomerized species, which are manifested by a strong absorption at 290–330 nm in DR-UV spectra as well as reveal characteristic XANES and Raman spectra [27]. Such catalysts possess a low catalytic activity in H_2O_2-based TMP oxidation because of poor accessibility of Ti centres, as has been confirmed by FT-IR study using CO as a probe molecule [28]. Indeed, one can see from the data presented in Table 2 that the Ti–SBA-15 sample is more than one order of magnitude less active compared to the other, TiO_2-free catalysts.

Textural properties are also crucial for the activity because the catalytic site must be accessible for reactants. Fig. 2 shows the activity of different catalysts containing isolated and, therefore, well accessible Ti centres (this state corresponds to Ti surface concentration <0.3 Ti/nm^2) *versus* the average pore size, *D*. One can see that a very little difference in the activity is observed for the aerogel and Ti–MMM-2, the pores of which differ significantly (13.2 and 3.1 nm, respectively). This allows us to suggest that no diffusion limitation occurs for TMP oxidation within mesopores larger than 3 nm. On the contrary, Ti/MCM-41 ($D = 2.5$ nm after titanocene-grafting methodology) seems to be on the boundary, where diffusion limitation starts to manifest. Then, the activity becomes practically negligible for microporous TS-1 [11,27]. Earlier, it was found that TiO_2–SiO_2 xerogels, which comprise both meso- and micropores, reveal a significant decrease of the catalytic activity compared to entirely mesoporous Ti,Si-catalysts [8–10]. Furthermore, incomplete conversion of TMP was achieved over TiO_2–SiO_2 xerogels, as one can judge from the example given in Table 2.

Another important factor governing the catalytic activity is surface hydrophilicity, which ensures optimal conditions for the reagents adsorption. After silylation, the catalyst activity dramatically decreases (Table 2), most likely, because a hydrophobic environment around Ti sites hinders the approach of a polar substrate, as the TMP molecule, as well as of a polar oxidant, as H_2O_2. In this case, the specific activity of the catalyst is, therefore, diminished by the unfavourable adsorption of the reactants. On the contrary, when less hydrophilic substrates are oxidised, as cyclohexene or limonene, the same kind of silylated Ti/SiO_2 catalyst shows higher specific activities compared to non-silylated ones [29,30]. Meanwhile, hydrophilic non-silylated Ti,Si-catalysts should be calcined prior to use in order to remove water and other adsorbed molecules from the surface, otherwise their activity declines significantly. In fact, addition of MeOH to the reaction mixture strongly reduces the reaction rate [31], most likely, because alcohol competes with TMP for the adsorption sites.

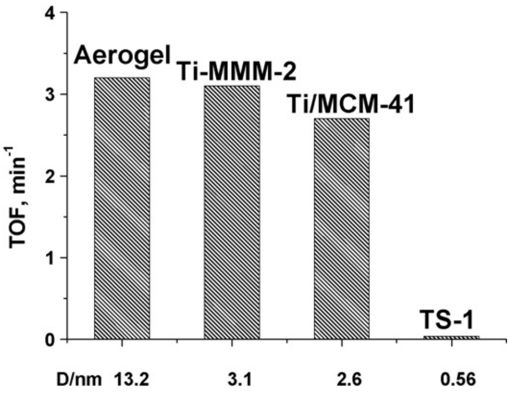


Fig. 2. The effect of pore size on the activity of Ti single site catalysts in TMP oxidation. The data for TS-1 were taken from Ref. [27].

Finally, the critical parameter that governs the reaction rate is the catalyst surface acidity. The FT-IR study with adsorption of CO revealed that surface hydroxyl groups of mesoporous titanium-silicates possess weak Brønsted acidity, slightly higher to that of pure silicate and close to that of TS-1 [28]. This weak acidity is extremely important for the catalytic activity. Many authors (and also some of us) observed that traces of Na (K) or basic additives strongly deactivate titanium-silicates, both micro- and mesoporous ones, in H_2O_2-based oxidation processes [11,20,22,31,32]. That is also true for oxidation of TMP [31]. With regard to this, Clerici suggested first [32] that Brønsted acidity is crucial for the formation of active titanium hydroperoxo species TiOOH *via* the following reaction:

$$\mathrm{Ti{-}OH} + H_2O_2 \rightleftarrows \mathrm{Ti{-}OOH} + H_2O.$$

3.2. Factors affecting TMBQ selectivity

In our previous studies [6,9], we found that the reaction conditions have a strong impact on the selectivity of TMBQ formation over Ti,Si-catalysts. The selectivity increases with increasing oxidant to substrate molar ratio and also with rising temperature. A crucial factor is the phenol to Ti molar ratio, the selectivity being enhanced with decreasing this parameter. Thus, TMBQ selectivity over Ti/A-2 was improved from 96–100% when the catalyst amount was enlarged twice (Table 2). Yet, a stepwise addition of TMP to the reaction mixture also led to the selectivity enhancement, while stepwise addition of the oxidant produced an opposite effect [6]. The solvent nature appeared to be important not only for the activity, but also for the selectivity. In alcoholic medium the selectivity is lower compared to acetonitrile, which seems to be the best solvent for the TMP oxidation.

Under the same, optimal reaction conditions, TMBQ selectivity differs significantly for different Ti,Si-catalysts. What are the critical characteristics of a catalyst, which ensure high selectivity? Our first important observation was that the selectivity, in general, does not correlate with the catalyst activity (see Table 2). Testing a variety of Ti,Si-catalysts in TMP oxidation, we found a correlation between the TMBQ selectivity and the surface concentration of Ti. For TiO_2-free catalysts, this latter parameter can be roughly estimated from the specific surface area of the catalyst and its Ti content. In fact, it is worth noting that in the case of Ti-catalysts obtained by grafting titanocene precursors onto the silica surface, no Ti species should be occluded or ‘buried’ in the bulk of the solid. Likewise, the openwork structure of aerogels and the thin silicate walls of Ti–MMM-2 (ca. 1 nm [15]) should allow a good exposition of the Ti centres and their accessibility to the reagents.

The peculiar trend of TMBQ selectivity as a function of Ti surface concentration is shown in Fig. 3. While the activity is higher for catalysts having isolated Ti sites (<0.3 Ti atoms/nm^2), the selectivity over such catalysts is rather moderate and usually does not exceed 75–82%. Moreover, it decreases with further decreasing Ti surface concentration and is only 47% for Ti/D-1 (0.12 Ti atoms/nm^2). On the contrary, the highest selectivity (95–97%) is typically observed for catalysts having 0.7–1.0 Ti/nm^2 (the case of the Ti/A and aerogel catalysts in Fig. 3). Importantly, further increase in titanium concentration leads to decreasing TMBQ selectivity, most likely, due to aggregation of titanium atoms into TiO_2-like species. Interestingly, the correlation shown in Fig. 3 is true only for porous catalysts. When Ti was grafted onto non-porous aerosil (0.85 Ti/nm^2), the selectivity to TMBQ was just 47%. The reasons for that are not completely understood yet and need further investigation. Although Ti,Si-catalysts of different nature fit well the curve shown in Fig. 3, some effects of the silica support on the TMBQ selectivity

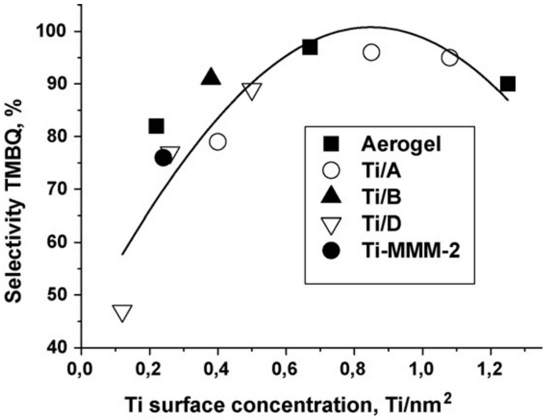


Fig. 3. The effect of Ti surface concentration in the catalyst on TMBQ selectivity. The data for aerogel samples with 0.67 and 1.25 Ti/nm^2 were taken from Ref. [9].

cannot be ruled out. The study of such effects is still in progress in our groups.

The H_2O_2 efficiency in TMP oxidation over Ti,Si-catalysts is moderate (about 60%) because some unproductive decomposition of the oxidant takes place. That is why a 3.5 molar excess of H_2O_2 with respect to TMP is required to reach 100% TMP conversion, while the reaction stoichiometry is 2:1 for TMP conversion to TMBQ. The use of lower H_2O_2/TMP ratio results in uncompleted TMP conversion.

To deepen our understanding of the factors which favour TMBQ formation, we studied in detail the mechanism of the TMP oxidation with H_2O_2 over Ti,Si-catalysts [33]. First, a detailed study of by-products revealed the formation of two dimeric products, specifically the C–C and C–O coupling dimers, indicating one-electron oxidation mechanism that involves the formation of phenoxyl radicals. As an example, TMP oxidation over Ti–MMM-2 produced 76% of TMBQ, 9% of 2,2′,3,3′,5,5′-hexamethyl-4,4′-biphenol and 15% of 2,3,6-trimethyl-4-(2,3,6-trimethyl)phenoxyphenol. The formation of phenoxyl radicals during TMP oxidation process was detected by EPR techniques using a spin-trap agent, 3,5-dibromo-4-nitrosobenzene-sulfonic acid (DBNBS). In fact, two types of adducts were identified [33]. The first one is formed upon interaction of the spin trap with the carbon atom of the phenoxyl radical, while the second adduct derives from the interaction of DBNBS with the oxygen atom. Thus, the results of the EPR study are in good agreement with the composition of the by-products. Importantly, the addition of the spin trap caused a pronounced inhibitory effect on the rate of both TMP consumption and TMBQ formation, so as the selectivity to TMBQ remained unchanged. This implies that both the target product, TMBQ, and dimeric by-products derive from the same radical intermediate, namely ArO$^\bullet$, which forms in the first step of a homolytic oxidation process.

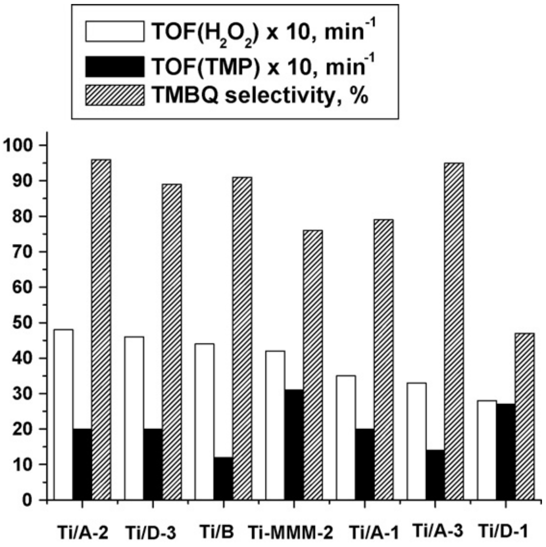
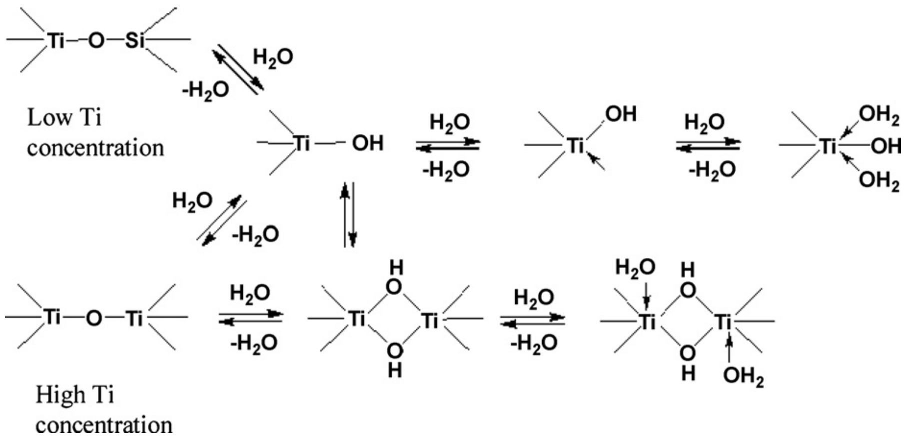
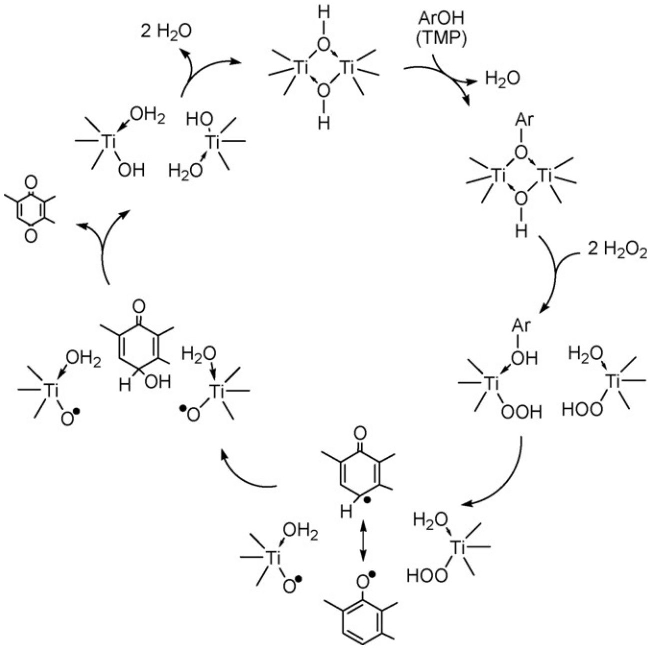


Fig. 4. TMP oxidation and H_2O_2 decomposition over Ti,Si-catalysts.

Several lines of evidence are consistent with a mechanism involving TMP chemisorption on Ti centre rather than a mechanism that involves TMP interaction with OH$^\bullet$ radicals produced during H_2O_2 decomposition over a Ti,Si-catalyst. First, neither TMP oxidation rate nor TMBQ yield correlate with the rate of H_2O_2 decomposition (Fig. 4). Secondly, the phenol binding to Ti centre was confirmed by the DRS-UV–vis measurements [33]. Third, the kinetic study revealed a fractional reaction order (between 0 and 1) in TMP, and thus also points out the reaction mechanism involving TMP coordination at the active Ti centre [31]. Based on all these facts collectively, we suggested recently a general mechanism of TMP oxidation over a single site Ti catalyst [33]. However, this mechanism could not explain the observed relationship between TMBQ selectivity and Ti surface concentration. This prompted us to suppose a mechanism that implicates a participation of a "double site" Ti active centre. Indeed, when two titanium atoms are located close to each other (the case of 0.7–1.0 Ti/nm^2), the formation of Ti dimers is very likely. Based on general Ti chemistry we may



Scheme 1. Possible forms of Ti species on the surface of Ti,Si-catalysts.



Scheme 2. Hypothesized mechanism of TMP oxidation to TMBQ over a "double site" Ti catalyst.

suppose the existence of at least three dimeric forms with different coordination state of Ti (Scheme 1). Evacuation would favour the formation of 4-coordinated Ti, while exposure to humid air would result in the appearance of saturated octahedral forms. Apparently, 5-coordinated Ti most likely exists in calcined samples of hydrophilic mesoporous Ti catalysts. It is very likely that 5-coordinated doubly bridged hydroxo species or some related forms are responsible for the high selectivity of TMBQ formation. This hypothesis is corroborated by the fact that both evacuation and long-term exposure to air produce a decrease in the selectivity of the reaction. For a "double site" Ti active centre, a favourable situation is possible when one coordinated phenol molecule is located in a close proximity to two TiOOH species (Scheme 2), provided the concentration of TMP is kept low, while H_2O_2 concentration is kept high (these are exactly the conditions required for high TMBQ yield). In this case, the phenoxyl radical oxidation by the second TiOOH group would lead to the formation of an intermediate quinol product, which is then easily oxidised to the desired quinone (TMBQ). If the proximity condition is satisfied, such process occurs faster than the recombination reaction, according to which the phenoxyl radical meets another radical, giving rise to the undesired C–C and C–O coupling dimers. However, further spectroscopic and mechanistic studies are needed to clarify the nature of the active Ti "double" site and to verify the reaction scheme.

4. Conclusions

Based on the analysis of the whole results acquired so far on TMP oxidation with H_2O_2 over Ti,Si-catalysts, we can now formulate the practical guidelines for reaching 100% selectivity to TMBQ in this reaction. The optimal reaction conditions are (1) use of poorly coordinating solvent (MeCN) to assist TMP sorption on Ti site; (2) high temperature (80 °C); (3) low TMP concentration (not higher than 0.1 M); (4) high H_2O_2/TMP molar ratio (ca. 3.5) and (5) low TMP/Ti ratio ($<$10–20). All these conditions are required to favour TMP oxidation to TMBQ and to suppress the radical coupling.

The optimal (i.e. both active and selective) Ti,Si-catalyst should possess mesoporosity (no micropores) and high dispersion of Ti (no TiO_2-like aggregates) to provide accessibility of the active sites. The catalyst surface should be hydrophilic enough to assist TMP and H_2O_2 sorption. The catalyst should possess some weak Brønsted acidity as well (no alkali metal ions) to promote the formation of active titanium hydroperoxo species. The catalyst should have an optimal Ti surface concentration (0.7–1.0 Ti/nm^2) to favour the formation of Ti "double" or, probably, small oligomeric (clustered) sites that appear to play a key role in the highly selective TMP oxidation to TMBQ. The "double" sites are the ideal catalytic centres to achieve a fast consecutive "double" monoelectronic transfer from TMP and thus to block out the route leading to phenoxyl radical coupling. The simple and affordable post-synthesis methodology of grafting titanium onto the surface of commercial mesoporous silica allows designing catalysts, which fulfil at best these requirements and thus can be viewed as promising candidates for the clean and sustainable synthesis of TMBQ. With optimal catalyst under optimal reaction conditions TMBQ yield does attain 100%.

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