DOI: 10.1002/adsc.200900109

# Highly Selective Oxidation of Alkylphenols to Benzoquinones with Hydrogen Peroxide over Silica-Supported Titanium Catalysts: Titanium Cluster Site *versus* Titanium Single Site

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Received: February 17, 2009; Published online: July 27, 2009

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.200900109.

**Abstract:** Titanium-silica catalysts have been prepared by supporting titanium(IV) precursors with different nuclearity {mononuclear titanocene dichloride $Ti(Cp)_2Cl_2$, dinuclear titanium diethyl tartrate and the tetranuclear titanium peroxo complex $(NH_4)_8[Ti_4(C_6H_4O_7)_4(O_2)_4]\cdot 8H_2O$} onto the surface of silica materials with different textural characteristics. The supported catalysts have been explored as highly active and reusable catalysts for the oxidation of 2,3,6-trimethylphenol (TMP) and 2,6-dimethylphenol (DMP) to 2,3,5-trimethyl-1,4-benzoquinone (TMBQ, vitamin E key intermediate) and 2,6-dimethyl-1,4-benzoquinone (DMBQ), respectively, using aqueous hydrogen peroxide as green oxidant. Catalysts prepared by grafting mononuclear $Ti(Cp)_2Cl_2$ revealed a strong dependence of the product selectivity on the surface concentration of titanium active centers. Mesoporous materials with titanium surface concentration in the range of 0.6–1.0 Ti/nm$^2$ were identified as optimal catalysts for the transformation of alkylphenols to benzoquinones. Catalysts having $<0.6$ Ti/nm$^2$ produced a mixture of benzoquinones and dimeric by-products. Conversely, when di-/tetranuclear titanium precursors were employed for the catalyst preparation, a diminution of the titanium surface concentration had no impact on the benzoquinone selectivity, which was typically as high as 96–99%. DR-UV spectroscopic studies revealed that the catalysts capable of producing alkylbenzoquinones with nearly quantitative yields possess titanium dimers and/or subnanometer-size clusters homogeneously distributed on a silica surface. On the contrary, catalysts with isolated titanium sites give a considerable amount of dimeric by-products. This is the first example which clearly demonstrates the advantages of titanium cluster-site catalysts over titanium single-site catalysts in hydrogen peroxide-based selective oxidation reaction.

**Keywords:** alkylphenols; heterogeneous catalysis; hydrogen peroxide; quinones; selective oxidation; titanium-silica catalysts

## Introduction

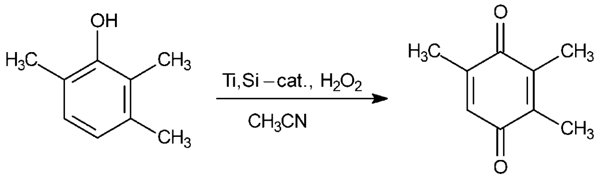
The selective catalytic oxidation of organic compounds with environmentally benign, cheap and readily available oxidants is the most economic and ecological route to a wide variety of valuable oxygen-containing products and intermediates.[1] In past decades, the replacement of stoichiometric and homogeneous processes by environmentally friendly ones, which would employ heterogeneous catalysts and clean oxidants, such as $O_2$ and $H_2O_2$, has become a widely accepted strategy in fine chemicals synthesis.[2] However, progress in this direction is obstructed by the limited availability of efficient and stable heterogeneous catalysts for selective oxidations in the liquid phase.[3] Much attention was focused on the elaboration of different approaches, leading to spatially well-separated active sites, uniform in composition and distribution, on the surface, in the framework or within the cages of inorganic solids – the so-called heterogeneous single-site catalysts.[4] Such catalysts are expected to combine the main advantages of homogeneous (activity and selectivity) and heterogeneous catalysts (simplicity of recovering and recycling). The key strategies for their design involve insertion of an active center into an inert matrix by grafting, framework substitution, tethering, encapsulation, intercalation, and some other techniques.[4,5]

The remarkable properties of Ti,Si catalysts in selective oxidations with clean oxidants, such as $H_2O_2$ and *t*-BuOOH, are well-documented.[4,5a,6] Mesoporous titanium silicates possess active Ti centers accessible to large molecules (>1 nm kinetic diameter), which makes them attractive for catalytic applications in the transformation of bulky and richly functionalized fine chemicals. So far, the most studied reaction catalyzed by mesoporous Ti,Si catalysts was the epoxidation of alkenes.[6,7] The selective oxidation of phenols is a less investigated topic although quinones with different functional groups are powerful intermediates in the production of fine chemicals, including the synthesis of vitamins E and K, coenzyme Q, and other valuable products.[2,8]

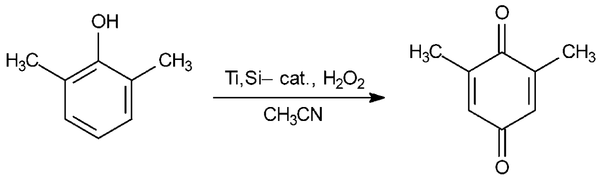
Pinnavaia and co-workers revealed that bulky 2,6-di-*tert*-butylphenol (DTBP) can be selectively oxidized to a mixture of the corresponding benzoquinone and diphenoquinone using aqueous $H_2O_2$ as oxidant and mesoporous Ti-HMS as catalyst.[9] Catalysts prepared by post-synthesis methodology *via* grafting titanium precursors on to the surface of MCM-41, KIT-1 and MCM-48 were also found to be active in the liquid phase oxidation of DTBP with aqueous $H_2O_2$.[10] However, the question about the ratio between the monomeric and dimeric quinone products was not addressed, and the factors governing the product selectivity were not studied.

In 2000, some of us found that oxidation of 2,3,6-trimethylphenol (TMP) to 2,3,5-trimethyl-1,4-benzoquinone (TMBQ, a key intermediate in the synthesis of vitamin E) can be accomplished with the yield of 75–80% using aqueous $H_2O_2$ as oxidant and mesostructured titanium silicate Ti-MMM as catalyst.[11] Similar results were obtained over Ti-MCM-41[12] and later, over hydrothermally stable Ti-MMM-2.[13] Surprisingly, $TiO_2$-$SiO_2$ aerogels appeared to be even more selective catalysts for TMP oxidation, yields of the target quinone as high as 95–98% being attained.[14] In 2003, Tuel and Hubert-Pfalzgraf claimed high selectivities (98%) to TMBQ obtained using nanometric monodispersed titanium oxide particles supported on mesostructured silicates, SBA-15, MCM-41 and HMS.[15] Recently, we found that some catalysts prepared by grafting titanium(IV) onto commercial mesoporous silica produce TMBQ with a nearly quantitative yield.[16] A correlation between TMBQ selectivity and Ti surface concentration has been noted during the analysis of the data on TMP oxidation acquired over various titanium silicate catalysts.[17]

In this paper, we report the synthesis of titanium-silica catalysts by supporting titanium precursors with different nuclearity onto the surface of ordered and non-ordered silica supports, their characterization and systematic study of their catalytic performance in $H_2O_2$-based oxidation of two representative alkylsubstituted phenols, TMP and DMP.



TMP TMBQ



DMP DMBQ

We discuss the crucial factors that govern the reaction selectivity, address the question on the structure/selectivity relationships, and suggest a reaction mechanism. Special attention is paid to the issue of catalyst reusability, which is crucial for heterogeneous liquid phase oxidation processes.

## Results and Discussion

### Catalyst Synthesis and Characterization

The supports used in this work were commercial non-ordered silicas from different suppliers and mesostructured materials MCM-41 and Ti-MMM-2 prepared by hydrothermal synthesis. The textural properties of the supports are presented in Table 1 along with the data on the concentration of OH groups on the surface acquired by TGA method. The size of mesopores spanned in the range of 2.6 to 16.0 nm. The concentration of OH groups on the surface covered the range of 2.9–5.1 OH per square nanometer (Table 1). In accord with literature,[13,18] low angle XRD patterns of MCM-41 and Ti-MMM-2 exhibited a sharp primary (100) reflex as well as less intensive higher order (110) and (200) diffraction reflexes, in-

**Table 1.** Textural and surface properties of the silica supports.

| Support | BET surface area $S$ [$m^2 g^{-1}$] | Pore volume $V$ [$cm^3 g^{-1}$] | Mean pore diameter $D$ [nm] | OH/nm$^2$[a] |
|---|---|---|---|---|
| Davicat | 295 | 1.48 | 16.0 | 5.10 |
| Davisil A | 291 | 1.28 | 13.7 | 4.74 |
| Davisil C | 529 | 0.88 | 5.4 | 3.87 |
| Nippon–Kasei | 679 | 0.66 | 3.8 | 3.10 |
| MCM-41 | 972 | 0.65 | 2.6 | 2.90 |
| Ti-MMM-2 | 976 | 0.54 | 3.1 | n.d.[b] |

[a] From TGA data, considering that 1 molecule of $H_2O$ forms from 2 OH groups.
[b] Not determined.

dicating that the materials have an ordered hexagonal structure of mesopore channels.

The use of post-synthesis techniques displays some advantages with respect to a conventional direct synthesis of in-framework or in-matrix titanium silicates. In particular, the amount of Ti sites loaded onto a support can be easily tuned, and a wide series of catalysts with variable surface Ti concentrations can be obtained. The textural and surface properties of some representative Ti/SiO$_2$ catalysts, prepared using the mononuclear precursor Ti(Cp)$_2$Cl$_2$, with high Ti loadings are presented in Table 2. The specific surface area, pore volume and mean mesopore diameter had some tendency to decrease after the grafting procedure, as already reported.[7f,15]

It is evident that the surface density of Ti atoms should increase with increasing Ti loading and/or decreasing surface area of the support. The Ti surface concentration is roughly estimated from the specific surface area of the support and Ti content (determined by elemental analysis), and some values are given in Table 2. Note that for grafted titanium catalysts, the preparation method excludes the occlusion of Ti species in the bulk (within the walls) of the silica solid, which justifies the correctness of such estimations.

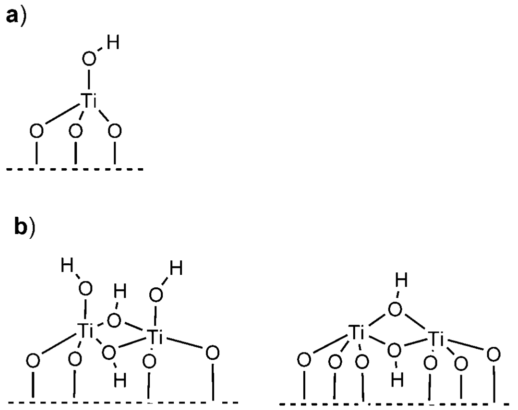
Using the grafting methodology, we managed to achieve a high Ti concentration (1.1 Ti/nm$^2$) on the surface of Davicat silica. On the contrary, we were not able to introduce by grafting more than 0.5 Ti/nm$^2$ into MCM-41 channels. Note that both values are much less than the value of 5.5 Ti/nm$^2$ for the surface Ti density of an anatase 010 plane or the value of *ca.* 4 Ti/nm$^2$ estimated as experimental monolayer dispersion of surface titanium oxide species on SiO$_2$.[19] In terms of silica-supported titanium species, the loading of 3 Ti/nm$^2$ was estimated by Srinivasan et al. to be the upper limit for dispersed titania on silica, which corresponds to monolayer coverage.[20] However, the authors could not achieve Ti loading greater than 1 atom Ti/nm$^2$ on the high surface area silicas using room temperature impregnation with Ti(IV) isopropoxide.[20] In fact, maximal loadings around 1.4 Ti/nm$^2$ are widely accepted as the upper limit in the case of the mesoporous Merck silica functionalized with titanium isopropoxide.[21]

The surface density of hydroxy groups (OH/nm$^2$) in the catalysts obtained by grafting Ti(Cp)$_2$Cl$_2$ was estimated by TGA, and the values are summarized in Table 2. The hydroxy density of Ti-containing catalysts is lower than that of the initial supports (Table 2 *vs.* Table 1). However, the Ti-grafted catalysts showed a higher concentration of hydroxy groups than expected, if the grafting reaction led only to isolated TiOH species tripodally bound to three SiOH moieties of the silica support (Scheme 1 a). This allowed us to suggest that dimers or higher oligomers (clusters) containing OH bridges and similar to the di(poly)nuclear

**Table 2.** Textural and surface properties of grafted Ti/silica catalysts.

| Catalyst (wt% Ti) | BET surface area $S$ [$m^2 g^{-1}$] | Pore volume $V$ [$cm^3 g^{-1}$] | Mean pore diameter $D$ [nm] | Ti/nm$^2$[a] | OH/nm$^2$[b] |
|---|---|---|---|---|---|
| Ti/SiO$_2$ Davicat (1.93) | 286 | 1.46 | 15.4 | 0.82 | 3.58 |
| Ti/SiO$_2$ Davisil A (2.19) | 301 | 1.26 | 12.8 | 0.94 | 2.78 |
| Ti/SiO$_2$ Davisil C (3.13) | 479 | 0.80 | 4.9 | 0.74 | 2.64 |
| Ti/SiO$_2$ Nippon–Kasei (3.63) | 592 | 0.50 | 3.3 | 0.70 | 2.02 |
| Ti/MCM-41 (3.87) | 922 | 0.63 | 2.6 | 0.50 | 2.01 |
| Ti/Ti-MMM-2 (6.13) | 548 | 0.25 | 3.0 | 0.95 | n.d.[c] |

[a] Estimated based on BET surface area of the support and Ti content.
[b] From TGA data, considering that 1 molecule of $H_2O$ forms from 2 OH groups.
[c] Not determined.



**Scheme 1.** **a**) Isolated Ti single-site species and **b**) possible dinuclear Ti species supported on silica surface.

species, supposed earlier by Marchese et al.,[22] are present in the samples of the grafted catalysts with high Ti surface concentrations (Scheme 1 b).

The presence of such species was confirmed by DR-UV spectroscopy, which is a useful and available technique to characterize the local geometry and bonding environment of the titanium ions. It is widely accepted in the literature that catalysts containing site-isolated Ti atoms show a ligand-to-metal charge transfer band with a maximum centered in the range of 208–230 nm.[6,22,23] The position of the maximum depends on the coordination number of Ti(IV) and reveals a red-shift upon interaction with $H_2O$ and other coordinating molecules due to expansion of the titanium coordination sphere.[23] A shift of the maximum to wavelengths $\geq$230 nm is usually attributed to the formation of Ti–O–Ti connectivities.[22,23] However, as noted by Gao and Wachs,[23c] it is often not easy to distinguish whether a change in the position of DR-UV band is related to the alteration in the coordination number of Ti(IV) or in the nature of ligands.

DR-UV spectra of MCM-41-grafted titanium catalysts are shown in Figure 1 a. One can see that catalysts with Ti loading $\leq$2 wt% exhibit a rather narrow band with a maximum at 212 nm, which is typical of isolated titanium sites, presumably, in tetrahedral coordination.[6a,23] The increase in Ti loading to 3.9 wt% leads to the broadening and red-shift of the DR-UV band (Figure 1 a). When 2 wt% of Ti was grafted onto the non-ordered Nippon–Kasei silica (a support with a lower surface area than MCM-41; see Table 1), a sample with a higher Ti surface density was evidently produced, compared to the Ti/MCM-41 sample with the same Ti loading. This was manifested in the DR-UV spectrum (Figure 1 b) which showed a broad band centered around 240 nm. As mentioned above, the band broadening and shifting to wavelengths $\geq$230 nm 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.[23] Although the nature of Ti in such catalysts is not completely understood, most of authors attribute broad bands centered at 240–250 nm to dimeric and/or small oligomeric (clustered) titanium species.[22,23] Further band shifting to 260–290 nm is usually interpreted in the literature as yn indication of a gradual increase in the degree of oligomerization of Ti atoms and formation of subnanometric titanium oxide clusters.[15,23c,24] Note that DR-UV spectra of all the samples with high Ti surface concentration (0.60–

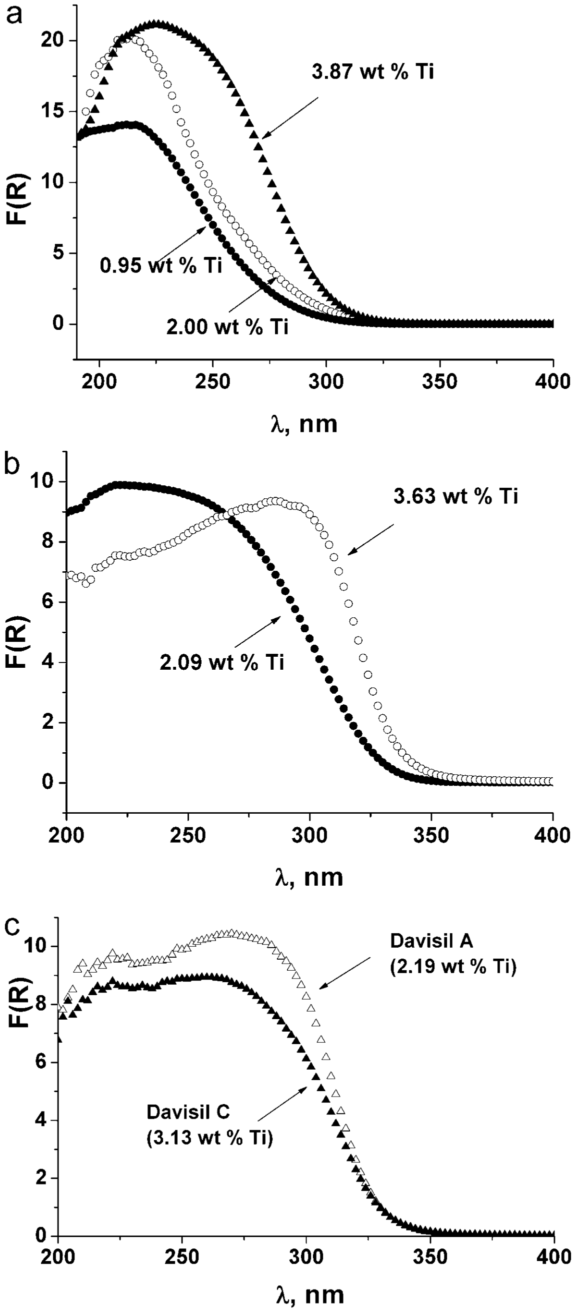


**Figure 1.** DR-UV spectra of Ti catalysts prepared by grafting $Ti(Cp)_2Cl_2$ on **a**) MCM-41, **b**) Nippon-Kasei silica and **c**) Davisil silicas.

1.0 Ti/nm$^2$) reveal the characteristic broad band in the range of 260–290 nm (Figure 1a–c). Some authors attributed such bands to highly hydrated six-coordinated isolated Ti species.[6d] However, the red-shift of the band that we and other authors observed with increasing Ti content in the sample strongly supports that the broad feature is mainly due to associated rather than isolated Ti species. Note that the band at 215–220 nm, corresponding to isolated Ti sites, can also be distinguished in the DR-UV spectra of the catalysts with high Ti concentration (Figure 1a–c). Its intensity is a bit higher for the ordered catalysts than for the non-ordered ones, but generally it is rather low compared to the broad feature centered at 260–290 nm. Therefore, we may conclude that a clusterized state of Ti predominates on the surface of the grafted $Ti/SiO_2$ catalysts with Ti density in the range of 0.60–1.0 Ti/nm$^2$.

DR-UV spectra of $Ti_4/SiO_2$ and $Ti_2/SiO_2$ catalysts prepared using $(NH_4)_8[Ti_4(C_6H_4O_7)_4(O_2)_4]\cdot 8H_2O$ and titanium diethyl tartrate complex, respectively, are shown in Figure 2. Even for catalysts with a rather low Ti loading (about 1 wt% of Ti), the spectra are very similar to those of $Ti/SiO_2$ catalysts with high Ti content (Figure 1b and c) and show a broad absorption band centered around 250–280 nm, suggesting the presence of titanium dimers/oligomers. Again, the DRS-UV band shifted to longer wavelengths with increasing Ti loading in the samples, indicating a further condensation of Ti species on the silica surface.

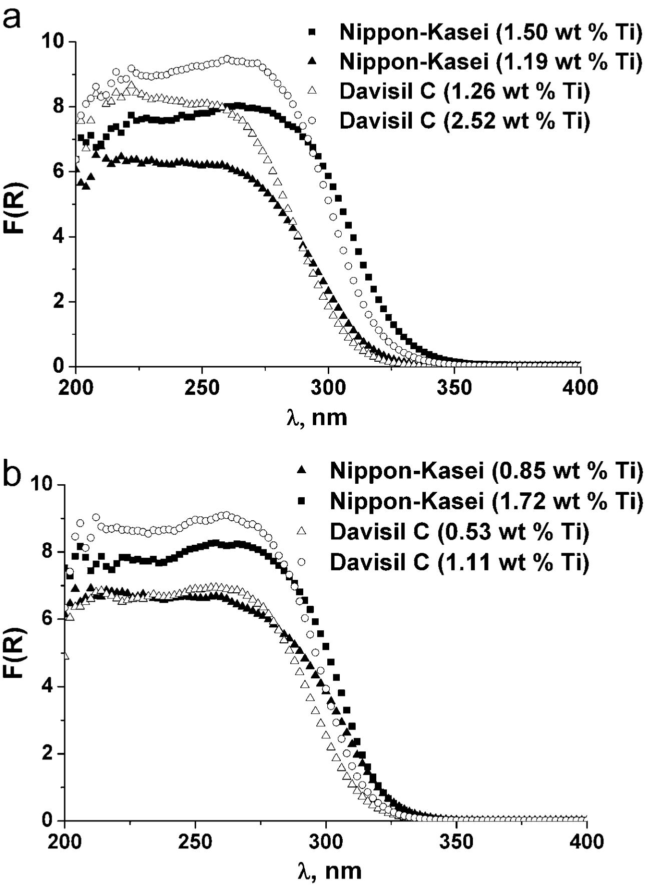


**Figure 2.** DR-UV spectra of Ti catalysts prepared using **a**) $(NH_4)_8[Ti_4(C_6H_4O_7)_4(O_2)_4]\cdot 8H_2O$ and **b**) diethyl tartrate Ti(IV) complex.

Importantly, the DR-UV band edge in the spectra of all supported titanium catalysts here described was always observed below 350 nm. Stein and co-workers estimated titania cluster diameters of 1.2–1.6 nm (30–70 $TiO_2$ units) for a UV band edge of 355 nm.[24b] Given in mind this estimation and the position of the DR-UV band edge in our catalysts, we may suggest that the number of Ti atoms in the clusters formed on the silica surface at high Ti loadings is, at least, lower than 30 and the size of the clusters, most likely, does not exceed 1 nm.

Raman spectroscopy is one of the most sensitive techniques, which enables detection of early stages of the emergence of $TiO_2$ anatase microcrystallites in titanium silicates.[6a,23c,24,25] We used Raman spectroscopy to check the presence of $TiO_2$ extra-phase species in the supported Ti-catalysts obtained in this work. No band at 140–145 cm$^{-1}$ characteristic of anatase was found (Figure 1 S in the Supporting Information), thus pointing out that titanium species are well dispersed and no $TiO_2$ microcrystallites formed on the silica surface.

## Catalytic Oxidation

The results of the catalytic tests performed for the oxidation of TMP with 30% $H_2O_2$ over the catalysts prepared by grafting $Ti(Cp)_2Cl_2$ onto various silica supports are summarized in Table 3. One can see that practically for all catalysts TMP conversion was close to 100% when a 75% molar excess of $H_2O_2$ with respect to the stoichiometric ratio (2:1 for TMP conversion to TMBQ) was employed. Previously, some of us found that the use of a lower $H_2O_2$/TMP ratio results in uncompleted TMP conversion because unproductive decomposition of the oxidant occurs along with its consumption in the phenol oxidation reaction. As a result, $H_2O_2$ efficiency in the TMP oxidation was moderate (*ca.* 56%) over Ti single-site catalysts like Ti-MMM-2.[13,17] Surprisingly, we revealed that $H_2O_2$ efficiency can be improved using grafted $Ti/SiO_2$ catalysts. Thus 95% TMP conversion and 94% TMBQ yield were achieved with only 25% excess of $H_2O_2$ (that is 76% $H_2O_2$ efficiency) over $Ti/SiO_2$ Davicat (1.93 wt% Ti) catalyst.

The MCM-41-supported catalysts with Ti content $\leq 2$ wt% Ti (entries 8 and 9 in Table 3), which possess isolated Ti centers according to their DR-UV spectra (see Figure 1a), revealed the highest activity expressed as TOF values (2.7 min$^{-1}$). This is close to the

**Table 3.** TMP oxidation with $H_2O_2$ over titanocene-derived grafted $Ti/SiO_2$ catalysts.[a]

| Entry | Catalyst | Ti loading [wt%] | TMP conversion [%] | TMBQ selectivity [%] | TOF[b] [$min^{-1}$] |
|---|---|---|---|---|---|
| 1 | $Ti/SiO_2$ Davicat | 0.92 | 100 | 79 | 2.0 |
| 2 | $Ti/SiO_2$ Davicat | 1.93 | 100 | 97 | 1.9 |
| 3 | $Ti/SiO_2$ Davicat | 2.50 | 95 | 95 | 1.4 |
| 4 | $Ti/SiO_2$ Nippon–Kasei | 2.09 | 97 | 91 | 1.4 |
| 5 | $Ti/SiO_2$ Nippon–Kasei | 3.63 | 100 | 99 | 1.4 |
| 6 | $Ti/SiO_2$ Davisil A | 2.19 | 100 | 98 | 2.1 |
| 7 | $Ti/SiO_2$ Davisil C | 3.13 | 100 | 99 | 1.8 |
| 8 | Ti/MCM-41 | 0.95 | 97 | 47 | 2.7 |
| 9 | Ti/MCM-41 | 2.00 | 98 | 77 | 2.7 |
| 10 | Ti/MCM-41 | 3.87 | 99 | 89 | 2.0 |
| 11 | Ti-MMM-2[c] | 1.89 | 100 | 76 | 3.0 |
| 12 | Ti/Ti-MMM-2 | 6.13 | 99 | 96 | 1.9 |

[a] *Reaction conditions:* TMP, 0.1 M; catalyst, 0.006 mmol of Ti, $H_2O_2$, 0.35 M, $CH_3CN$ 1 mL, 80 °C, 30 min.

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

[c] Mesostructured Ti-MMM-2 catalyst prepared by hydrothermal synthesis, given for comparison with Ti/Ti-MMM-2.

activity found for the Ti-MMM-2 catalyst (entry 11) prepared by hydrothermal synthesis, which enclosed mostly isolated Ti atoms in the framework.[13] The constant activity of the Ti/MCM-41 samples with 0.95 and 2.0 wt% of Ti implies that all the Ti centers remain accessible for reactants and have the same nature. In turn, the activity of the catalysts containing Ti dimers/clusters (those showing DRS-UV absorption maxima at 240–290 nm) is a bit lower compared to the catalysts with isolated Ti atoms. Such a trend is evident if we compare the TOF values of samples with different Ti loadings on the same silica support. Indeed, the activities within the $Ti/SiO_2$ Davicat and Ti/MCM-41 series decrease after Ti loading reaches a certain level (Table 3; entries 1 through 3 and 8 through 10). This might be explained either by some gradual reduction of the number of accessible Ti sites in the supported clusters and/or by changes in the active site nature (e.g., altering coordination number of Ti(IV) from 4 in a single site to 5 in a dimer, etc.).

Earlier, we found a very low activity for microporous TS-1 in the title reaction.[13] From the TOF values given in Table 3, it is clearly seen that even a large increase in mesopore diameter from 2.6 nm (Ti/MCM-41) to 15.4 nm ($Ti/SiO_2$ Davicat) does not affect markedly the reaction rate. Therefore, internal diffusion limitations do not play a primary role in TMP oxidation over catalysts with mesopores larger than 2.6 nm. In addition, the structure ordering has no pronounced effect on the catalytic activity in this reaction, as one can judge comparing the data given in Table 3 for the catalysts with comparable Ti surface concentrations.

It is worth noting that selectivity to TMBQ, in general, does not correlate with catalytic activity (Table 3). While the activity is high for catalysts having isolated Ti sites (*ca.* 0.3 Ti atoms/$nm^2$), their selectivity is rather moderate and usually does not exceed 75–80%. Moreover, it decreases with further decreasing surface Ti density and reaches only 47% for Ti/MCM-41 with 0.12 Ti/$nm^2$ (entry 8). Figure 3 shows TMBQ selectivity as a function of Ti surface concentration. Excellent selectivity (95–99%) is typically observed for catalysts having Ti densities in the range of 0.6–1.0 Ti/$nm^2$, which corresponds to clusterized Ti centers as indicated by the DRS-UV study. An additional increase in titanium concentration leads to a decrease in TMBQ selectivity (Figure 3), most likely, due to further aggregation of titanium clusters, which finally produces $TiO_2$-like extra-phase species. The maximal selectivity, close to 100%, is achieved around 0.7 Ti/$nm^2$. Importantly, introducing an additional amount of titanium by grafting $Ti(Cp)_2Cl_2$ onto the surface of the Ti-MMM-2 in-

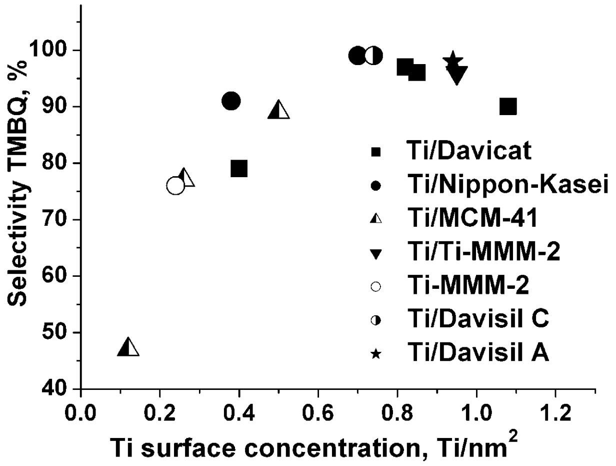


**Figure 3.** TMBQ selectivity *versus* Ti surface concentration in the silica-grafted Ti catalysts. Reaction conditions as in Table 3.

matrix catalyst (hence passing from 1.89 to 6.13 wt% Ti, that is 0.25 and 0.95 Ti/nm$^2$) results in a significant increase of the quinone selectivity from 76 to 96%.

It is evident from the data in Table 3 and Figure 3 that no considerable effect of the nature of the mesoporous silica support on the reaction selectivity was found for a wide series of Ti/SiO$_2$ catalysts. In fact, the bell-shaped curve presented in Figure 3 is valid for any sort of the grafted titanium catalyst, notwithstanding the morphology, the shape, the order, the pore size or the specific surface area of the mesoporous material. Hence, the surface Ti density is the key parameter to be carefully controlled in order to obtain an active and highly selective catalyst for TMP oxidation.

In order to extend these observations to other substituted phenols, we studied the oxidation of DMP too and found a similar dependence of the quinone selectivity on the surface Ti density, as we recorded for TMP oxidation. The results are shown in Table 4. As one can see, the selectivity to DMBQ achieved 97% over the Ti/SiO$_2$ Davicat sample having an optimal Ti density (0.82 Ti/nm$^2$). The selectivity was lower (86%) for Ti/MCM-41 (0.5 Ti/nm$^2$) and it reduced further and attained only 69% for the catalyst having 0.12 Ti/nm$^2$, the main by-product being 2,2′,6,6′-tetramethyl-4,4′-diphenoquinone.

## Active Site and Reaction Mechanism

The structure-selectivity relationships established in this work allowed us to suggest that Ti dimers or small oligomers (clusters) are the active species responsible for the highly selective transformation of alkylphenols to alkylbenzoquinones. To verify this hypothesis, we intentionally prepared and investigated the catalysts using dinuclear and tetranuclear titanium complexes. With such precursors, the proximity of the Ti sites and the formation of surface polynuclear species should be enhanced with respect to the use of mononuclear precursors.

The catalytic performances of the Ti$_4$/SiO$_2$ and Ti$_2$/SiO$_2$ catalysts (Table 5 and Table 6, respectively) were very similar to the catalytic performance of the Ti/SiO$_2$ catalysts with optimal Ti surface density (0.6–

**Table 4.** DMP oxidation with H$_2$O$_2$ over grafted Ti/SiO$_2$ catalysts.[a]

| Catalyst | Ti loading [wt%] | DMP conversion [%] | DMBQ selectivity [%] | TOF[b] [min$^{-1}$] |
|---|---|---|---|---|
| Ti/SiO$_2$ Davicat | 1.93 | 93 | 97 | 1.6 |
| Ti/MCM-41 | 3.87 | 90 | 86 | 1.7 |
| Ti/MCM-41 | 0.95 | 90 | 69 | 1.9 |

[a] Reaction conditions as in Table 3, with the only difference that DMP was used instead of TMP.

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

**Table 5.** TMP oxidation with H$_2$O$_2$ over Ti$_4$/SiO$_2$ catalysts obtained using (NH$_4$)$_8$[Ti$_4$(C$_6$H$_4$O$_7$)$_4$(O$_2$)$_4$]·8 H$_2$O.[a]

| Catalyst | Ti loading [wt%] | TMP conversion [%] | TMBQ selectivity [%] | TOF[b] [min$^{-1}$] |
|---|---|---|---|---|
| Ti$_4$/SiO$_2$ Nippon–Kasei | 1.19 | 96 | 99 | 1.6 |
| Ti$_4$/SiO$_2$ Nippon–Kasei | 1.50 | 95 | 99 | 1.5 |
| Ti$_4$/SiO$_2$ Davisil C | 1.26 | 99 | 96 | 2.0 |

[a] Reaction conditions as in Table 3.

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

**Table 6.** TMP oxidation with H$_2$O$_2$ over Ti$_2$/SiO$_2$-catalysts obtained using Ti diethyltartrate complex.[a]

| Catalyst | Ti loading [wt%] | TMP conversion [%] | TMBQ selectivity [%] | TOF[b] [min$^{-1}$] |
|---|---|---|---|---|
| Ti$_2$/SiO$_2$ Nippon–Kasei | 0.85 | 97 | 96 | 1.5 |
| Ti$_2$/SiO$_2$ Nippon–Kasei | 1.72 | 98 | 98 | 1.7 |
| Ti$_2$/SiO$_2$ Davisil C | 0.53 | 100 | 97 | 1.9 |
| Ti$_2$/SiO$_2$ Davisil C | 1.11 | 95 | 99 | 1.9 |

[a] Reaction conditions as in Table 3.

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

1.0 Ti/nm$^2$). First, comparable TOF values were observed for the $Ti_4/SiO_2$, $Ti_2/SiO_2$ and $Ti/SiO_2$ catalysts, thus pointing out a similar nature of the active centers in all these catalysts. Secondly, both TMP conversion and selectivity to TMBQ were very high ($>95\%$) over the $Ti_4/SiO_2$ and $Ti_2/SiO_2$ catalysts. In particular, excellent selectivity (98–99%) was achieved even with low Ti loading, such as 1.19% $Ti_4/SiO_2$ Nippon–Kasei or 1.72% $Ti_2/SiO_2$ Nippon–Kasei, to be compared with the inferior performance of 2.09% $Ti/SiO_2$ Nippon–Kasei (Table 3; entry 4). So, in sharp contrast with $Ti/SiO_2$ catalysts, no decrease in TMBQ selectivity was observed with decreasing Ti loading when dinuclear or tetranuclear Ti precursors were used for the catalyst preparation.

All these results strongly support the hypothesis that the catalytic site necessary for the efficient and selective 4-electron oxidation of alkylphenols into alkylbenzoquinones does enclose, at least, two Ti atoms. The formation of doubly hydroxo-bridged Ti dimers and higher oligomers upon grafting $Ti(Cp)_2Cl_2$ onto silica support was suggested by Marchese and co-workers.[22] The formation of dinuclear Ti species in silica-grafted Ti catalysts and high activity of dimeric Ti species (both homogeneous and supported) in alkene epoxidation were reported by a few authors.[26] Recently, the efficiency of a binuclear Ti(IV) dihydroxide site in catalyzing the epoxidation of olefins with hydrogen peroxide was demonstrated by Panas et al. using density functional theory calculations.[26e] Nevertheless, the majority of researchers still view isolated Ti species as the species responsible for high yields of epoxides. The latter point of view is, likely, valid for reactions which proceed *via* heterolytic oxygen atom transfer mechanisms (alkene epoxidation, hydroxylation of aromatics), but it certainly cannot be applied to alkylphenol oxidation, the reaction which has been established to occur through a homolytic mechanism.[27] The results obtained in this work clearly demonstrate the advantage of polynuclear Ti sites over Ti single sites in the oxidation of alkylphenols to alkylbenzoquinones with hydrogen peroxide.

It has been reported that as far as the Ti content increases, Brønsted acid sites appear and their relative concentration increases with the amount of titanium in the materials.[6] This implies that Ti dimers and oligomers formed on the catalyst surface are connected through OH bridges. Unfortunately, the modern level of spectroscopic techniques does not allow one to distinguish unequivocally between Ti dimers and small oligomers (e.g., tetramers) and to determine the structure of the polynuclear Ti species which operate in our catalytic system. Meanwhile, some suggestions might be made based on the following experiments.

First, we found that a proper catalyst pre-treatment is extremely important to achieve high yields of quinone. The effects of different pre-treatments on both the state of Ti in the grafted catalyst and the TMP oxidation process are shown in Figure 4. It is clearly seen that exposure of the preliminary calcined catalyst to humid air resulted in a red shift of the DR-UV band, indicating increasing amount of 6-coordinated Ti species upon adsorption of water. In turn, subsequent catalyst evacuation led to a blue shift and enhancing intensity of the 215 nm feature, thus pointing out the increase of isolated and/or tetrahedrally-coordinated Ti species.[23] Importantly, both treatments resulted in decreasing selectivity to TMBQ compared to the freshly calcined catalyst (Figure 4). Therefore, we may conclude that only calcination gives rise to the formation of optimal active sites on the silica surface, which most likely includes 5-coordinated (unsaturated) hydroxo-bridged Ti dimers/clusters similar to those shown in Scheme 1 b.

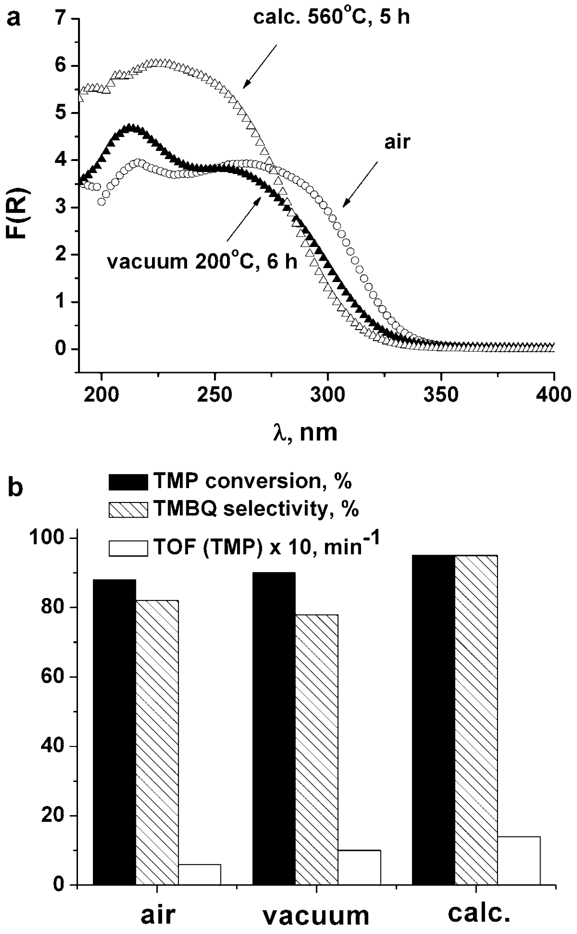


**Figure 4.** The effect of different treatments on the DR-UV spectrum **a**) and catalytic performance **b**) of $Ti/SiO_2$ (Davicat, 1.93 wt% Ti).

This conclusion is also supported by the unusual effect of water on the TMP oxidation rate in the presence of the grafted Ti catalysts. Indeed, we found that the reaction rate increases with decreasing water concentration in the reaction medium (Figure 5). This is

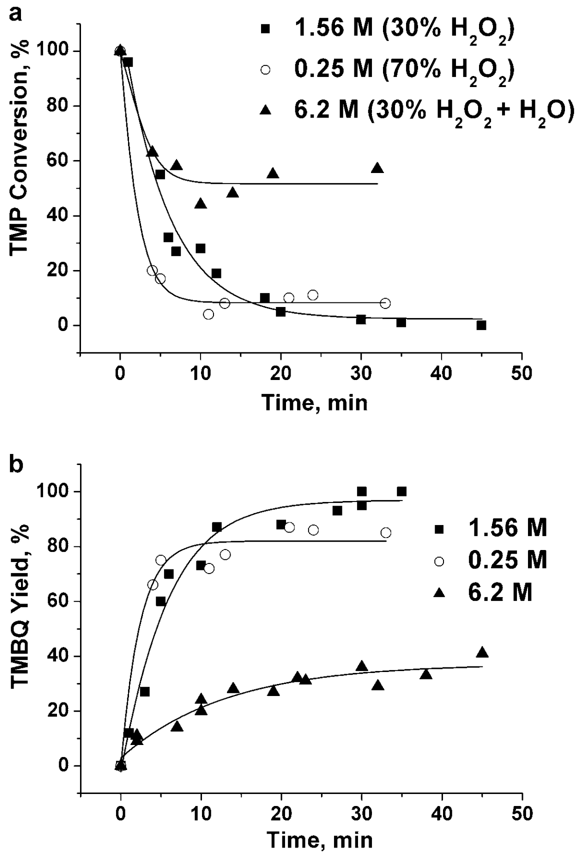
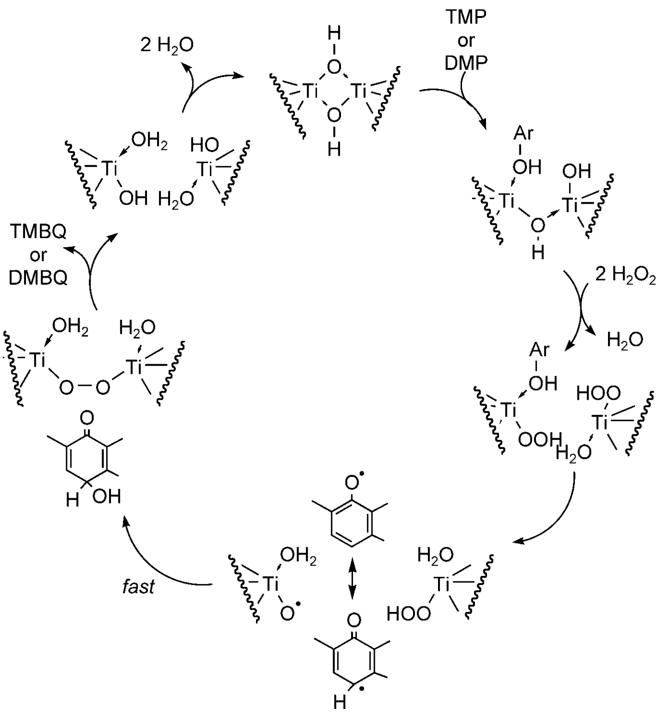


**Figure 5.** The effect of water concentration on TMP consumption **a**) and TMBQ accumulation **b**) rates over Ti/$SiO_2$ (Davicat, Ti 1.97 wt%; reaction conditions as in Table 3).

not a typical behaviour for Ti,Si catalysts.[28] It has been found that water addition to a reaction solvent accelerated the catalytic oxidation of phenol with hydrogen peroxide over TS-1.[28a] For $TiO_2$-$SiO_2$ aerogels, some of us observed a bell-shape dependence of the reaction rate on the amount of water in the catalytic system.[28b] The initial increase of the oxidation rate is usually explained by the necessity to hydrolyze the Ti–O–Si bond to produce Ti–OH, which easily reacts with $H_2O_2$ with the formation of an active hydroperoxo titanium species. The different performance that we observed for the grafted Ti catalysts is caused, most likely, by the specificity of the preparation method.[4] Since the formation of more than three Si–O–Ti linkages to the mesoporous walls would be sterically difficult to achieve, each Ti is expected to have at least one Ti–OH group resulting from the conversion of the remaining $\eta^5$-cyclopentadienyl-Ti group into Ti–OH group during calcination. Hence, these catalysts have already Ti–OH species on the catalyst surface to accomplish the reaction with $H_2O_2$, and the adsorption of water results in expansion of Ti coordination sphere, which is indicated by the DRS-UV study (see Figure 4). This process leads to reduction of the TMP oxidation rate because water and phenol compete for the adsorption site. Hence, unsaturation of the coordination sites of titanium and the presence of TiOH groups are crucial for the catalyst efficiency in the title reaction.

To get a deeper insight into the reaction mechanism over clusterized Ti centers, we performed a careful analysis of the TMP oxidation by-products. Under the reaction conditions shown in Table 3, the main identified by-products were the C–C and C–O coupling dimers, 2,2′,3,3′,5,5′-hexamethyl-4,4′-biphenol and 2,3,6-trimethyl-4-(2,3,6-trimethyl)phenoxyphenol. When we increased the concentrations of reactants keeping the molar ratios constant, the selectivity to TMBQ decreased markedly (see Table S1 in the Supporting Information) and some other by-products (Scheme S1 in the Supporting Information), also consistent with a homolytic oxidation mechanism, were found. Additionally, the formation of phenoxyl radicals during TMP oxidation over the Ti/$SiO_2$ catalyst was confirmed by EPR techniques using the spin-trap agent, 3,5-dibromo-4-nitrosobenzene-sulfonic acid (DBNBS) (Figure S2 in the Supporting Information). The observed EPR spectrum was very close to the EPR spectra of DBNBS adducts with TMP phenoxyl radicals acquired earlier for $TiO_2$-$SiO_2$ aerogel.[27]

All these facts collectively corroborate a homolytic mechanism for alkylphenol oxidation to quinone, which is tentatively shown in Scheme 2. A dinuclear active site may undergo chemisorption of two $H_2O_2$ molecules and ensure a close proximity of two TiOOH species. Provided TMP concentration is kept



**Scheme 2.** Tentative mechanism of alkylphenol oxidation with $H_2O_2$ over a dimeric Ti site.

low enough and the $H_2O_2$ concentration is oppositely kept high (these are exactly the conditions which favour TMBQ formation[11]), one phenol molecule can be adsorbed by the reactive center that involves two adjacent hydroperoxo titanium groups. Interaction with the first TiOOH group produces a phenoxyl radical which is oxidized immediately by the second TiOOH, giving rise to an intermediate quinol product, which is, in turn, oxidized rapidly to the final quinone. As a consequence, recombination of phenoxyl radicals leading to the undesired C–C and C–O dimeric by-products is minimized or, in the best cases, suppressed over the dimeric Ti site, while the yield of the target quinone is enhanced compared to a single Ti site.

## Catalyst Stability and Re-usability

The question about the stability of a heterogeneous catalyst is crucial for liquid phase oxidations.[2,3] Thus, chemical analysis of the mother liquor after reaction of DTBP oxidation over grafted Ti-MCM-48 showed that about 1.6% of Ti had been leached.[10b] It is a matter of common observation that monopodal titanium species are more prone to be leached and hence the use of a support with higher silanol density increases the stability of the catalyst. Elemental analysis data confirmed that no titanium leaching from the $Ti/SiO_2$, $Ti_2/SiO_2$ and $Ti_4/SiO_2$ catalysts occurs under the conditions used for TMP oxidation. Following the methodology suggested by Sheldon et al.,[3a] we found neither TMP conversion nor TMBQ accumulation in the filtrate after fast hot catalyst filtration at about 40% TMP conversion (Figure S3 in the Supporting Information), which proved a true heterogeneous nature of catalysis over $Ti/SiO_2$.

To assess the propensity of the materials to be recovered and reused, the $Ti/SiO_2$, $Ti_2/SiO_2$ and $Ti_4/SiO_2$ catalysts were recycled in several consecutive catalytic runs. We found that the $Ti/SiO_2$ catalysts with a higher Ti concentration are more stable to deactivation than the catalysts with a lower Ti loading (Figure 6). The recycling behaviour of the $Ti_2/SiO_2$ and $Ti_4/SiO_2$ catalysts was similar to that of $Ti/SiO_2$ with high Ti surface density (Figure S4 in the Supporting Information). The catalyst re-usability can be further improved by using more concentrated $H_2O_2$. Figure 7 demonstrates that with 70% $H_2O_2$, the optimal $Ti/SiO_2$ catalyst can be used repeatedly for at least four catalytic runs without a loss in both activity and selectivity. Therefore, the grafted Ti catalysts revealed one more advantage in comparison with in-matrix Ti,Si catalysts, for which the TMP oxidation rate decreased significantly when concentrated $H_2O_2$ was employed and, as a result, no complete substrate conversion could be achieved.[6f,11]

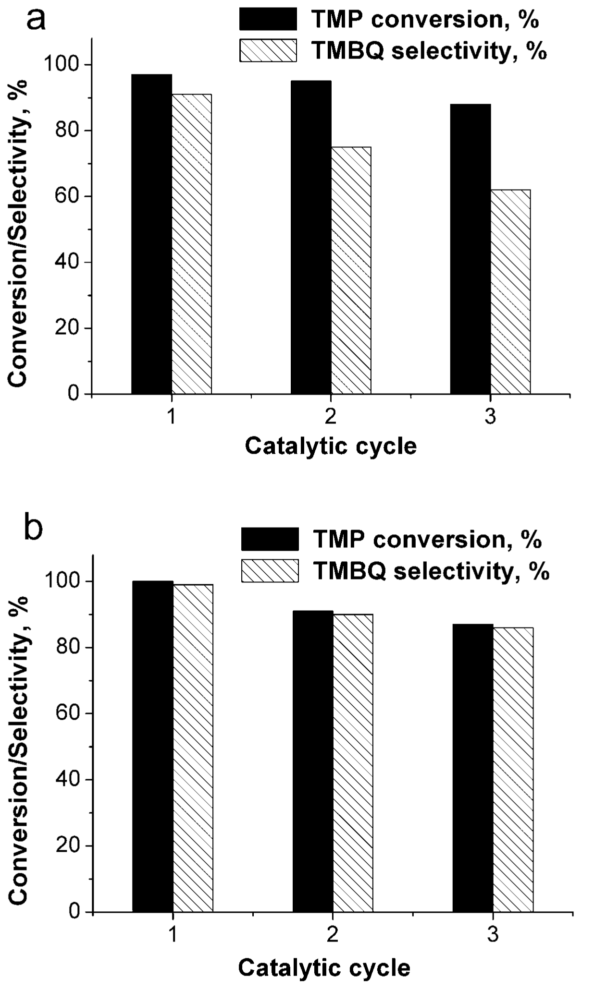


**Figure 6.** Catalyst recycling in TMP oxidation with 30% $H_2O_2$ over $Ti/SiO_2$ (Nippon–Kasei): **a**) Ti 2.09 wt% and **b**) Ti 3.63 wt%.

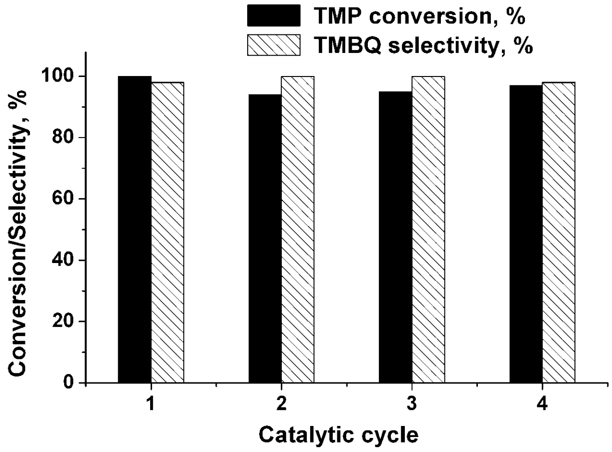


**Figure 7.** Catalyst recycling in TMP oxidation with 70% $H_2O_2$ (0.5 M) over $Ti/SiO_2$ (Nippon–Kasei, Ti 3.63 wt%).

## Conclusions

The investigation of the relationships between composition, structure and selectivity of the grafted titanium-silica catalysts in alkylphenol oxidation to benzoquinones with hydrogen peroxide revealed an outstanding performance of the mesoporous solids with Ti surface concentration in the range of 0.6–1.0 Ti/nm$^2$. Using such catalysts, TMBQ (vitamin E precursor) and other benzoquinones can be obtained with nearly quantitative yields. The DRS-UV study identified dimers and/or subnanometer-size clusters homogeneously distributed on a silica surface as the optimal catalytic sites for this reaction.

The silica-supported Ti catalysts intentionally prepared to obtain Ti dimers and/or clusters *via* immobilization of peroxocitrate or tartrate di/tetranuclear Ti precursors displayed excellent properties in terms of selectivity to quinones regardless of Ti loading, thus confirming the superior performance of clusterized Ti sites with respect to isolated Ti single sites. This phenomenon can be explained by the particularly favourable interaction between the phenolic substrate and (at least) two contiguous Ti hydroperoxo groups, as indicated by the suggested oxidation mechanism.

Yet, the results of this study show that the catalysts with di-/polynuclear Ti active sites have advantages of a better $H_2O_2$ efficiency and improved re-usability in alkylphenol oxidation compared to single-site Ti catalysts.

Finally, the bell-shaped curve displaying the dependence of the selectivity on surface Ti density obtained in this work can be used as a predictive tool for the preparation of catalysts with optimized performance for the oxidation of substituted phenols to related quinones with hydrogen peroxide. Using this curve, one can evaluate the optimal amount of Ti precursor necessary for grafting onto the surface of silica with known textural properties.

## Experimental Section

### Reagents and Catalysts

2,3,6-Trimethylphenol (TMP) and 2,6-dimethylphenol (DMP) were purchased from Fluka and used without additional purification. Reference 2,2′,3,3′,5,5′-hexamethyl-4,4′-biphenol (BP) was prepared as described elsewhere.[29] The tetranuclear ammonium citratoperoxotitanate(IV) complex, $(NH_4)_8[Ti_4(C_6H_4O_7)_4(O_2)_4]\cdot 8H_2O$, was synthesized according to the literature protocol.[30] Dinuclear titanium diethyl tartrate complex was prepared from L-(+)diethyl tartrate (Aldrich) and Ti(O-*i*-Pr)$_4$ (Fluka) taken in equimolar amounts following the protocol proposed by Sharpless et al.[31] Hydrogen peroxide (*ca.* 30%) was determined iodometrically prior to use. Acetonitrile was dried and stored over activated 4 Å molecular sieves. All other reactants were obtained commercially and used without further purification.

Commercial amorphous silica supports, herein mentioned as $SiO_2$ Davicat, $SiO_2$ Davisil and $SiO_2$ Nippon–Kasei, were received directly from the suppliers (Grace Davison and Nippon–Kasei). Nippon–Kasei silica was used without any further pre-treatment. Davicat and Davisil silicas were washed in 1 M aqueous $HNO_3$, thoroughly rinsed and dried in oven prior to use. MCM-41 was prepared using cetyltrimethylammonium bromide (CTAB) as surfactant following the literature procedure.[18]

Ti/SiO$_2$ catalysts were synthesized by supporting a titanium precursor onto the surface of various silicas. Titanocene dichloride $Ti(Cp)_2Cl_2$, dinuclear titanium diethyl tartrate complex [Ti(tartrate)(*i*-PrO)$_2$]$_2$ and peroxo complex $(NH_4)_8[Ti_4(citrate)_4(O_2)_4]\cdot 8H_2O$ were used to prepare catalysts hereinafter referred to as Ti/SiO$_2$, Ti$_2$/SiO$_2$ and Ti$_4$/SiO$_2$, respectively. Grafting of $Ti(Cp)_2Cl_2$ was accomplished by adapting the method developed by Maschmeyer, et al.[4a,7f] Ti$_2$/SiO$_2$ catalysts were prepared as follows. Nippon–Kasei and Davisil C silicas were pre-treated at 300 °C for 1 h in open air and 1 h under vacuum, then cooled down under vacuum. A solution of an equimolar mixture of L-(+)-diethyl tartrate and Ti(O-*i*-Pr)$_4$ in anhydrous dichloromethane was added to the pre-treated silica under argon atmosphere using standard Schlenk techniques. The suspension was maintained under stirring for 3 h and then the solvent was removed by evaporation under reduced pressure and dried under vacuum overnight. The samples were calcined at 550 °C for 3 h under oxygen flow (100 mL min$^{-1}$). Ti$_4$/SiO$_2$ catalysts were prepared by impregnation at the rotary evaporator from aqueous solution of the complex $(NH_4)_8[Ti_4(citrate)_4(O_2)_4]\cdot 8H_2O$ onto the Nippon–Kasei and Davisil C pre-treated silicas. The impregnated samples were calcined at 550 °C for 3 h under an oxygen flow. Ti-MMM-2 was prepared by hydrothermal synthesis under moderately acidic conditions following a slightly modified procedure described earlier.[13] All the catalysts were calcined at 560 °C for 5 h in air directly prior to use in catalytic tests or before physical measurements. The catalysts were characterized by elemental analysis, N$_2$ adsorption, thermogravimetric analysis (TGA) and DRS-UV measurements.

### General Procedure for Catalytic Oxidation of Alkylphenols

Catalytic oxidations with $H_2O_2$ were performed under vigorous stirring (500 rpm) in thermostated glass vessels. The rate of phenol substrate consumption remained constant when the stirring rate varied in the range of 200–1000 rpm, indicating no external diffusion limitation. Typically, the reactions were initiated by adding 0.35 mmol $H_2O_2$ to a mixture, containing 0.1 mmol of TMP (or DMP), 8–28 mg of Ti catalyst (to introduce 0.006 mmol of Ti), internal standard (biphenyl), and 1 mL of a solvent (anhydrous $CH_3CN$). The reaction time was 15–40 min. Samples of the reaction mixture were withdrawn periodically during the reaction by a syringe through a septum. Each experiment was reproduced 4–6 times.

The oxidation products were identified by GC-MS and $^1$H NMR (see the Supporting Information). The TMBQ and DMBQ yields as well as TMP and DMP conversions were quantified by GC using internal standard (diphenyl). Turnover frequency values (TOF) were determined from the initial rates of substrate consumption. In order to isolate quinone product, the reaction mixture was diluted with water followed by extraction with $CH_2Cl_2$. After concentration under vacuum, pure TMBQ (or DMBQ) was isolated by preparative thin-layer chromatography on silica gel using gradient elution with hexane and hexane/ethyl acetate. $^1$H NMR spectra of the isolated quinone products were identical to those of the authentic samples.

### Instrumentation

Gas chromatographic analyses were performed using a gas chromatograph "Tsvet-500" equipped with a flame ionization detector and a quartz capillary column (30 × 0.25) filled with Supelco MDN-5S. GC-MS analyses were carried out using a gas chromatograph Agilent 6890 (quartz capillary column 30 m × 0.25 mm/HP-5ms) equipped with a quadrupole mass-selective detector Agilent MSD 5973. $^1$H NMR spectra of the reaction products were recorded on an AM 250 Bruker spectrometer. Nitrogen adsorption measurements were carried out at 77 K using an ASAP-2400 instrument (Micromeritics) instrument within the partial pressure range $10^{-6}$–1.0. Before measurements, the samples were degassed at 90 °C during 48 h. Thermogravimetric analysis (TGA) was performed using a Perkin-Elmer Pyris apparatus. The analyses were run under an oxygen flow (25 mL min$^{-1}$) in the temperature range between 50 °C and 1000 °C. DRS-UV measurements were performed on a Shimadzu UV-VIS 2501PC spectrophotometer. Raman spectra were recorded on a RFS 100/S Bruker spectrometer with 1064 nm excitation line of an Nd-YAG laser operating at a power of 100 mW. EPR spectra were recorded at room temperature using a Bruker ER-200D spectrometer. Experiments in the presence of the spin trap DBNBS were carried out as described previously.[27]

## Acknowledgements

*The authors are grateful to V. A. Rogov for GC-MS analyses, O. V. Zalomaeva for EPR, and E. Gavrilova for TGA measurements. OAK thanks CNR for the Short Term Mobility Program grants (Nos. 30212, year 2006 and 50558, year 2007).*

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