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1. Introduction

Quinone derivatives synthesized for the preparation of vitamins are of general interest in organic synthetic chemistry and play an important role in biosystems.¹ 2,3,5-Trimethyl-1,4-benzoquinone (TMB=O) is a key intermediate in the production of vitamin E,¹ which is the best fat-soluble biological antioxidant.¹ The demand for vitamin E is more than 30 000 tons per year.

The industrial synthesis of vitamin E involves the production of TMB=O via the oxidation of 2,3,6-trimethylphenol (TMP-OH) with molecular oxygen (or air) over the copper(n)chloride (CuCl₂) catalyst in various solvents, including twophase systems. This catalytic system affords a higher yield of TMB=O (>95%).² However, after completion of the catalytic reaction, this homogeneous catalyst system has well-known drawbacks related to its separation, recycling and product purification. Although the use of two-phase solvent systems partially solves these problems, the product can still be contaminated with traces of transition metals because of metal complexation by organics and subsequent extraction into the organic phase. In addition, the formation of

Highly active and green mesostructured titanosilicate catalysts synthesized for selective synthesis of benzoquinones†

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Two-dimensional hexagonal thick-walled mesoporous titanosilicate catalysts synthesized using various amounts of titanium were used for the synthesis of 2,3,5-trimethyl-1,4-benzoguinone (TMB=O) by liquid-phase oxidation of 2,3,6-trimethylphenol (TMP-OH). These catalysts were also used for the oxidation of di-/tri-substituted phenols to produce 2,6-disubstituted p-benzoquinones (DSBQs). A promising chemical treatment method, for the preparation of green mesoporous TiSBA-15(6) or Washed TiSBA-15(6), was used for removal of non-framework TiO₂ nanoparticle species from the active surface, and the catalytic activity of the recovered mesoporous TiSBA-15(6) catalyst has been evaluated. To confirm the green aspects, recyclability and hot-catalytic filtration experiments were performed. Based on the experimental results, it was found that the green mesoporous TiSBA-15(6) is a highly active, recyclable, and promising heterogeneous catalyst for the selective synthesis of TMB=O and DSBQs and produces >99% TMB=O selectivity with 100% TMP-OH conversion at 353 K for 60 min and 90-100% DSBQs selectivity with 83-99% phenol conversion at 330 K for 1-5 h.

> chlorine-containing by-products can occur and a significant amount of copper-containing waste is produced when using high concentrations of CuCl₂. In this catalytic system, a special apparatus containing corrosion-resistant coatings might be required. Moreover, the environmentally unfriendly stoichiometric oxidation of TMP-OH with manganese dioxide (MnO₂), nitric acid (HNO₃), or other toxic reagents was previously the main industrial route for the production of TMB=0.³ Since 1983, the development of eco-friendly catalytic methods for selective oxidation of organic compounds has been a challenging goal.⁴ Many catalytic systems for the oxidation of TMP-OH to TMB=O have been developed using 'clean' and inexpensive oxidants, such as molecular oxygen and hydrogen peroxide, over homogenous catalysts such as cobalt-Schiff base complexes, ruthenium salts, and heteropoly compounds.⁴ These catalytic systems still remain problematic for catalyst separation, and, therefore, the pure target products could not be completely recovered from hazardous transition metal compounds.

> Since 2000, various titanium-containing silicate catalysts such as Ti-MMM, Ti-MCM-41, and TiO₂-SiO₂ have been used for TMP-OH oxidation with aqueous hydrogen peroxide (H₂O₂; HP), as the oxidant, for the synthesis of TMB=O with yields of 80-98%.⁵ However, these catalysts (*i.e.* Ti-MMM, Ti-MCM-41, and TiO₂-SiO₂ aerogels) have low hydrolytic stabilities because of their thin walls, and the activity of the catalysts decreases dramatically after the first catalytic run.⁵ In response to these problems, a few hydrothermally stable

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catalysts have been efficiently used to achieve a higher yield of TMB=O.⁶ Recently, mesoporous titanium-silicate catalysts synthesised by evaporation-induced self-assembly (EISA) produce a higher TMB=O selectivity due to the increase of the catalytic activity by the highly dispersed dimeric and/or oligomeric Ti species, and this catalytic activity is similar to that of Ti/Ti-MMM-2, which is synthesised using the titanocene dichloride precursor by the post-grafting method.^{6a,b}

Hydrothermally stable and thick-walled mesoporous titanosilicates (Ti-MMM-2 synthesised by the hydrothermal method, and TiSBA-15 synthesized using the pH-adjusting direct hydrothermal (pH-aDH) method) have been extensively used in the synthesis of vitamin K_3 *via* liquid-phase oxidation of 2-methyl-1-naphthol.^{7,8} However, to the best of our knowledge, there have been no reports on the successful use of two-dimensional hexagonal thick-walled mesostructured TiSBA-15 synthesized with rich Ti-species for the selective synthesis of TMB=O via liquid-phase oxidation of TMP-OH nor for the selective synthesis of 2,6-disubstituted phenols.

During the 21st century, green catalytic technology for the catalytic oxidation of phenols to their corresponding quinones in halogen-free reaction systems has become a central issue in both academia and industry. In our study, TMB==O has been synthesized by catalytic oxidation of TMP–OH over mesoporous TiSBA-15 catalysts, and the selective synthesis of TMB==O has been conducted under a variety of reaction conditions. The thick-walled mesostructured TiSBA-15 catalysts have also been used for the synthesis of DSBQs by liquid-phase oxidation of di-/tri-substituted phenols using HP as the green oxidizing agent. The catalytic results for the selective synthesis of TMB==O and DSBQs using the mesostructured TiSBA-15 catalysts synthesised with various amounts of titanium have been correlated and compared.

2. Results and discussion

2.1. Catalytic oxidation of TMP-OH with different TiSBA-15 catalysts

Calcined mesoporous titanosilicate catalysts, *i.e.* TiSBA-15(6), TiSBA-15(15), TiSBA-15(20), TiSBA-15(30), and TiSBA-15(60), which have $n_{\rm Si}/n_{\rm Ti}$ values of 6, 15, 20, 30, and 60, respectively, were synthesized using the pH-aDH method.⁸ Ti-MCM-41(40), which has a $n_{\rm Si}/n_{\rm Ti}$ value of 40, was synthesized using a basic hydrothermal method.⁹ The synthesized mesoporous catalysts were extensively used in the liquid-phase oxidation of TMP-OH (Scheme 1). Initially, the catalytic oxidation of TMP-OH was investigated, using the reaction conditions listed in Table 1,



Scheme 1 Oxidation of TMP-OH.

through the formation of 2,3,5-trimethylcyclohexa-2,5dienone radicals by a one-electron oxidation mechanism, which was first suggested by Kholdeeva's group.^{5,6} In the catalytic oxidation of TMP-OH, the TiSBA-15 catalysts produce TMB=O, as a major product, as well as a C-C coupling dimer, 2,2',3,3',5,5'-hexamethyl-4,4'-biphenol (HMBP-OH) and a C-O coupling dimer, 2,3,6-trimethyl-4-(2,3,6-trimethylphenoxy)phenol (TMPP-OH), as by-products. The order of the catalytic activities of the catalysts with regards to TMB=O selectivity is as follows: TiSBA-15(6) > TiSBA-15(15) > TiSBA-15(20) > TiMCM-41(40) > TiSBA-15(30) > TiSBA-15(60). TiSBA-15(6) exhibits the best performance with 99% TMP-OH conversion and 97% TMB=O selectivity; its productivity is higher than those of the other titanosilicate catalysts due to its higher content of active titanium species on the inner pore walls of SBA-15. Because the active titanium species on the inner surfaces of the pore walls form the Lewis acid sites, which can be confirmed by Fourier-transform infrared (FTIR) spectroscopy with ammonia as a probe molecule,^{6e} this results in many accessible active sites.⁵⁻¹⁰ However, Trukhan et al.^{10a} reported that the mesoporous TiSBA-15 catalyst synthesized using sodium silicate solution as the silica source by a direct acetic hydrothermal method produces only 77% TMB=O selectivity because sodium silicate solution is not favoured to homogenously distribute the high amounts of active titanium species on the surface of silica pore walls and does not significantly improve the structural properties of TiSBA-15 because the sodium ions increase the basicity of the synthesis gel. Moreover, the TiSBA-15 catalyst synthesised using TEOS by the pH-aDH method has higher structural and textural properties as compared to that synthesised using sodium silicate solution.^{8,10a} In our study, the results of inductively coupled plasma-atomic emission spectroscopy (ICP-AES), X-ray diffraction (XRD), N₂-sorption isotherm analysis, and ultraviolet-visible diffuse reflectance spectroscopy (UV-vis DRS) strongly support that TiSBA-15(6) has higher catalytic activity compared to the other mesoporous titanosilicate catalysts. The ICP-AES studies show that the silica pore walls of TiSBA-15(6) contain more titanium species compared to the other TiSBA-15 catalysts.8 In addition, ²⁹Si magic-angle spinning nuclear magnetic resonance (MAS-NMR) spectroscopy (Fig. S1[†]) results show that the relative signal intensity ratio (Q3/Q4 = 0.48) of TiSBA-15(6) is much lower than that (Q3/Q4 = 0.8) of siliceous SBA-15.⁷ This observation clearly supports the stabilization of the active titanium species by the silanol groups (defect sites), with huge amounts of Si-O-Ti formation. The UV-vis DRS spectroscopy results (Fig. S2[†]) prove that the calcined TiSBA-15(6) catalyst contains more titanium hydroxyl moieties (=Ti-OH) on the inner surface of silica pore walls compared to the other TiSBA-15 catalysts. As Kholdeeva's group reported,^{6c} UV-vis DRS results further confirm that the high amounts of titanium hydroxyl moieties can form 5-coordinated doubly bridged hydroxo-Ti species (double site Ti active centre), as shown in Scheme 2. Apparently, the large amounts of 5-coordinated Ti species on the surface of SBA-15 generate its hydrophilic nature, which is highly favourable to produce a higher

Table 1 Oxidations of TMP-OH over different TiSBA-15 catalysts^a

	$n_{\rm si}/n_{\rm tri}$ ratio				Top
Catalysts	Gel	Calcined ^b	conversion (%)	selectivity (%)	(\min^{-1})
TiSBA-15(6)	6	18.9	99	97	3.0
TiSBA-15(15)	15	33.4	71	68	3.8
TiSBA-15(20)	20	42.0	60	57	4.0
TiSBA-15(30)	30	59.4	49	45	4.7
TiSBA-15(60)	60	88.6	35	33	4.9
TiMCM-41 (40)	40	42.0	55	52	3.7
TiSBA-15 $(6)^c$	_	21.4	100	97	3.4
$TiSBA-15(6)^d$	_	21.4	100	100	3.4
TiSBA-15 $(60)^c$	_	88.6	35	32	4.9
SiSBA-15	_		10	3	_
Washed TiSBA-15(6)	_	21.4	100	>99	3.4
Washed TiSBA-15(6) ^e	_	21.4	100	100	3.4

^{*a*} Reaction conditions: 50 mg of the catalyst; 1:3 ratio of TMP–OH to HP (10 mmol TMP–OH; 30 mmol of HP); 15 mL of MeCN; reaction temperature, 353 K; reaction time, 60 min. ^{*b*} The results of n_{Si}/n_{Ti} ratios in the products are determined by ICP-AES. ^{*c*} The results were obtained after the 4th run. ^{*d*} The results were obtained after the 7th run. ^{*e*} TMP–OH was added to the reaction mixture by three portions (3.33 mmol per 20 min). ^{*f*} TOF = (moles of TMP–OH consumed)/(moles of Ti in the catalyst used × reaction time), determined from the initial rates of TMP–OH consumption.



Scheme 2 Structure of titanium active sites bonded on the surface of mesoporous silica.

TMB=O selectivity.^{6c} In addition, the results of N₂-sorption isotherm (Fig. S3[†]) and XRD (Fig. S4[†]) strongly indicate that the physicochemical parameters (i.e. unit cell size, pore size, surface area, pore volume, and wall thickness) of the TiSBA-15(6) catalyst contribute to the improvement of its catalytic activity in this liquid-phase catalytic oxidation.8 The elemental compositions and the structural and textural properties of the TiSBA-15 catalysts are listed in Table S1.[†] Compared to the catalytic performance of various wall-natured mesoporous catalysts with similar amounts of titanium, the TiSBA-15(20) catalyst has higher catalytic activity compared to the Ti-MCM-41(40) catalyst due to thicker pore walls.9,10b The similar catalytic activity is reported for mesoporous Ti-MMM-2.6b,c The above catalytic results show that the thick pore walls of mesoporous titanosilicate catalysts improve hydrolytic stabilities and catalytic activities.8

The turnover frequency (TOF) of TiSBA-15 catalysts used in the oxidation of TMP–OH was evaluated from the initial rates of TMP–OH consumption. Although the TOF of TiSBA-15(6) is much lower than that of other TiSBA-15 catalysts (Table 1), the thick-walled TiSBA-15(6) produces higher TMP–OH conversion (99%) and TMB=O selectivity (97%) compared to other TiSBA-15 catalysts (Table 1). Based on the experimental results, it was found that TiSBA-15(6) has higher Ti(IV) dimers compared to other TiSBA-15 catalysts, and the Ti(IV) dimers are connected to the surface of silica pore walls through OH bridges, as confirmed by UV-DRS.^{6b,c} Therefore, the 5-coordinated doubly bridged hydroxo–Ti species and some related forms are responsible to achieve high TMB=O selectivity. Moreover, the presence of the "double site Ti active centre" is required to ensure fast oxidation of key intermediates like phenoxyl radicals, thus preventing the formation of dimeric by-products (HMBP-OH and TMPP-OH). As shown in Table S2,† the similar catalytic activity for mesoporous Ti/Ti-MMM-2 was found by Kholdeeva's group.^{6b} With increasing TMB=O selectivity, the density of Ti species increases but the TOF decreases from TiSBA-15(60) to TiSBA-15(6). Hence, the high Ti density does possibly improve the thick-walled pore walls and is the key parameter to be carefully controlled in order to obtain active and highly selective catalysts for TMP-OH oxidation.^{6b} This reaction was also performed using SiSBA-15 synthesized by the pH-aDH method. In this case, only 10% TMP-OH conversion with very low TMB=O selectivity is observed (Table 1), indicating that the higher catalytic activity is only obtained when the active titanium species are incorporated into SBA-15. The catalytic activities show that the hexagonal mesoporous TiSBA-15(6) catalyst with thick pore walls plays an important role in the production of TMB=O with a higher TMB=O selectivity.^{6b}

2.2. Performance of recyclable and Washed TiSBA-15(6)

Among the two-dimensional mesostructured titanosilicate catalysts, TiSBA-15(6) and TiSBA-15(60) produce the highest and lowest TMB=O selectivity, respectively. Therefore, we have investigated the reusability of TiSBA-15(6) and TiSBA-15(60) under the reaction conditions listed in Table 1 to determine their catalytic stabilities. Initially, the used TiSBA-15 catalysts usually afford lower product selectivity because most of the active sites are screened by unreacted organics, which create the sintering effect on the catalyst surface; accordingly, the catalysts have been regenerated by washing and calcination before reuse. The used TiSBA-15 catalysts were washed four times with acetone (AC=O) and dried at 393 K overnight.

Finally, the catalysts were calcined at 773 K for 6 h in air to completely remove the organics and unreacted TMP-OH molecules. The recovered recyclable and active catalysts, i.e. TiSBA-15(6) and TiSBA-15(60), were reused for this catalytic reaction (Table 1). The recyclability experiments were also performed for each run before initiation of the catalytic reaction. A decrease of TMB=O selectivity from the first run to the third run is observed for TiSBA-15(6) and after the 4th run, the selectivity increases from 97 to 100%, and the rate of reaction (TOF) stabilizes. It is worth noting from the catalytic results that the non-framework and inactive TiO₂ nanoparticles, which cause the screening effect on the active sites of the catalyst, are completely removed. Moreover, the TMP-OH conversion and TMB=O selectivity remain constant from the 4th run to the 7th run, as shown in Table 1, indicating that the leaching of active titanium species from the mesoporous matrix is not further observed; this is in good agreement with the ICP-AES results for the filtrate solutions, in which the absence of active titanium species is found. Our catalytic results clearly show that the non-framework TiO2 nanoparticles could not be further enhanced to achieve higher TMB=O selectivity because the surface area of TiSBA-15(6) is three times higher than that of TiO₂ nanoparticles.^{5,6,8} Before using TiSBA-15(6) for the oxidation of TMP-OH, the catalyst was washed more than four times with acetone and dried at 393 K overnight. Finally the treated catalyst was calcined at 773 K for 6 h in air to completely remove the non-framework TiO₂ nanoparticles generating "Washed TiSBA-15(6)", which was used in this reaction as the green mesoporous TiSBA-15(6) catalyst to determine its catalytic stability. The catalytic activity of Washed TiSBA-15(6) is nearly the same as that of the recyclable TiSBA-15(6) catalyst used in the 7th run, as shown in Table 1. Moreover, the thick-walled silica mesopore improves stability and prevents deactivation.6a-c The UV-DRS spectra at the 250-270 nm region (Fig. S2[†]) show that both catalysts, *i.e.* recyclable TiSBA-15(6) used in the 7th run and Washed TiSBA-15(6), have the same amounts of active titanium species, as confirmed by ICP-AES. These catalytic results prove that the active titanium species could not further leach from the surface of the SBA-15 matrix. Additionally, ICP-AES analysis confirms the absence of titanium species. After obtaining the results for the three runs, hot-catalyst filtration experiments were performed twice at 353 K during the oxidation of TMP-OH over calcined TiSBA-15(6). In this case, the filtrate solutions contain a very small amount of the conversion product (~7%), which may have formed by HP; this confirms that the oxidation of TMP-OH occurs only on the surface of the green TiSBA-15(6) catalyst. Therefore, Washed TiSBA-15(6) has a higher catalytic activity and results in a green heterogeneous catalytic process.^{6,11} Moreover, the ICP-AES results shown in Table S1[†] clearly confirm that the few non-framework TiO₂ nanoparticles were completely removed by the washing treatments; similar results were also observed for hot-catalyst filtrate solution of TiSBA-15(6). Moreover, 100% completion of this catalytic reaction is achieved when the TMP-OH is added in three

portions, as shown in Table 1. Furthermore, the XRD, N_2 -sorption isotherm, and UV-vis DRS results prove that the structural and textural parameters, including the "double site Ti active centre" coordinated to the surface of Washed TiSBA-15(6), are maintained (Table S1).† As shown in Table S2,† the catalytic activity of Washed TiSBA-15(6) is very close to that of the mesoporous titanium–silicate catalyst.^{6a} The recycling results show that Washed TiSBA-15(6) is unprecedented as a green catalyst among the calcined mesoporous titanosilicate catalysts.

2.3. Effect of reaction parameters

The Washed TiSBA-15(6) catalyst is the most active catalyst among all of the calcined TiSBA-15 catalysts and used to determine the optimal reaction parameters, *i.e.* temperature, time, and reactant ratio. TMP-OH was oxidized at different reaction temperatures and for different durations under the reaction conditions listed in Fig. 1 and 2. When the reaction temperatures and times are correspondingly increased from 303 to 353 K for 20 to 60 min, a high TMP-OH consumption as well as high TMB=O formation is observed with 100% TMB=O selectivity. With further increasing the temperatures from 353 to 378 K, the TMP-OH conversion as well as TMB=O selectivity does not change, but the selectivities for the by-products, HMBP-OH and TMPP-OH, increase with decreasing temperature from 353 to 318 K because the Lewis acid sites on the surface of the catalyst favour the formation of HMBP-OH and TMPP-OH under these reaction conditions. The catalytic results obtained using different temperatures clearly show that the selectivity for the by-products increases with decreasing temperature.^{6c} The TOF increases with increasing temperature from 303 K to 353 K. After that,



Fig. 1 Oxidations of TMP-OH at different temperatures over Washed TiSBA-15(6). Reaction conditions: 50 mg of the catalyst; 1:3 ratio of TMP-OH : HP (10 mmol TMP-OH, 30 mmol of HP); 15 mL of MeCN; reaction time, 60 min.

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Fig. 2 Oxidations of TMP–OH for different times over Washed TiSBA-15(6). Reaction conditions: 50 mg of the catalyst; 1:3 ratio of TMP–OH : HP (10 mmol TMP–OH, 30 mmol of HP); 15 mL of MeCN; reaction temperature, 353 K.



Fig. 3 Various ratios of TMP-OH:HP over Washed TiSBA-15(6). Reaction conditions: 50 mg of the catalyst; 10 mL of MeCN; reaction temperature, 353 K; reaction time, 60 min.

Table 2 Oxidations of TMP-OH by TBHP over Washed TiSBA-15(6)^a

the TOF is still maintained (Fig. 1) when the temperature increases from 353 K to 383 K. It is worth noting from the results that the TMP-OH conversion as well as TMB=O selectivity is not affected even when the reaction is carried out with a higher reaction temperature (383 K). When this liquidphase catalytic reaction is performed using a 1:3 ratio of TMP-OH to HP under the reaction conditions listed in Fig. 3, Washed TiSBA-15(6) gives a higher TMB=O selectivity, and the reaction rate (TOF = 3.4 min⁻¹) for the ratio of 1:3 is higher as compared to other ratios because there is no deactivation. When the amounts of HP (TMP-OH to HP ratios, 1:2, 1:5 and 1:7) are increased, the conversion as well as selectivity is much lower than that of 1:3 ratio of TMP-OH to HP, due to the formation of by-products HMBP-OH and TMPP-OH (Fig. 3). The diffusion rate of Washed TiSBA-15(6) as well as TMP-H conversion decreases for ratios 1:1 and 2:5. The TMB=O selectivity does not also improve because the active sites may be partially screened by unreacted organics deposited on the inner pore walls. When this reaction is performed over Washed TiSBA-15(6) using tert-butyl hydroperoxide (TBHP) as the oxidizing agent instead of HP at the optimal temperatures, times, and reaction ratios listed in Table 2, the TMB=O selectivity gradually decreases due to increasing selectivity for HMBP-OH and TMPP-OH. However, as shown in Table 2, the TMB=O selectivity decreases almost threefold when molecular oxygen (10 bar) is used as the oxidizing agent instead of HP under the same reaction conditions because the active titanium species may be inactive in molecular oxygen. When pseudocumene is used instead of TMP-OH with urea hydrogen peroxide (UHP) as the oxidizing agent and MeOH as the solvent for longer reaction times (Table 2), the TMB=O selectivity decreases significantly but the selectivity for HMBP-OH increases. In addition, a very small quantity of the 2,3,5trimethylhydroquinone by-product is formed.^{10c,12} From this evidence, we found that the catalytic activity is not affected by the water molecules of HP while the water molecules lead the catalytic activity in this system.¹³ Comparing the catalytic results obtained over Washed TiSBA-15(6) using different reaction parameters, it is found that the excellent TMB=O selectivity is achieved via a reaction at 353 K for 60 min using a 1:3 ratio of TMP-OH to HP.

Temperature (K)	Time (min)	TMP-OH conversion (%)	TMB=O selectivity (%)	TOF^{f} (min ⁻¹)
298	30	35	32	2.4
333	30	44	39	3.0
353	30	46	42	3.1
353	60	95	81	3.2
353 ^b	60	96	78	3.3
333 ^c	60	25	31	0.8
333 ^d	180	55 ^e	61	0.6

^{*a*} Reaction conditions: 50 mg of Washed TiSBA-15(6); 1:3 ratio of TMP–OH to TBHP (10 mmol DTBP–OH; 30 mmol of TBHP); 15 mL of MeCN. ^{*b*} 1:6 ratio of TBP–OH to TBHP (10 mmol DTBP–OH; 60 mmol of TBHP). ^{*c*} O₂ (10 bar) was used as the oxidizing agent. ^{*d*} 1,2,4-Trimethylbenzene was used instead of TMP–OH with urea hydrogen peroxide as the oxidizing agent and MeOH as the solvent. ^{*e*} Conversion of 1,2,4-trimethylbenzene. ^{*f*} TOF = (moles of TMP–OH consumed)/(moles of Ti in the catalyst used × reaction time), determined from the initial rates of TMP–OH consumption.

2.4. Effect of solvents

The liquid-phase oxidation of TMP-OH was performed using a variety of solvents, i.e. AC=O, acetonitrile (MeCN), methanol (MeOH), acetic acid (MeCOOH), ethanol, acetic anhydride (AC₂O), and nitromethane over Washed TiSBA-15(6), under the reaction conditions listed in Table 3 to achieve a higher TMB=O selectivity. MeCN is a common polar aprotic solvent that can form complexes on the catalyst surface at ambient temperature (353 K) and preferentially enables attack on the active sites to achieve maximum TMP-OH conversion. When this reaction is carried out with 5 mL of MeCN under similar reaction conditions, the TMP-OH conversion (48%) and TMB=O selectivity (54%) decrease because the large amount of TMP-OH may not completely dissolve to react with HP. However, the conversion and selectivity were unaffected when the reaction was carried out using 30 mL of MeCN under the same conditions. When pseudocumene is used instead of TMP-OH with acetic anhydride (AC₂O) as the solvent, the formation of TMB=O is obtained with 78% selectivity. Almost a similar result is confirmed when TMP-OH was catalyzed with MeCOOH as the solvent at 353 K; however, the HMBP-OH selectivity in MeCOOH at 330 K is higher than that in AC₂O. Nitromethane is a slightly viscous and highly polar solvent and yields 83% TMP-OH conversion with 90% TMB=O selectivity. But, under the same reaction conditions, the TMB=O selectivity is 70% in nitromethane and 89% in MeCN when 2,3,5-trimethlyphenol is used instead of TMP-OH; it is eventually found that nitromethane has a much lower ability to attack the active sites compared to MeCN. Compared to all of the solvents tested, ethanol affords the lowest TMB=O selectivity.¹⁴ Although MeOH affords a high TMB=O selectivity, it is highly toxic and environmentally unsustainable. The order of the dielectric constants of the solvents is nitromethane > $MeCN > MeOH > ethanol > AC=O > AC_2O > MeCOOH.$ All of the solvents, i.e. MeOH, MeCOOH, AC=O, AC2O, and nitromethane, afford lower TMB=O selectivity compared to

Table 3 Oxidations of TMP-OH in different solvents over Washed TiSBA-15(6)^a

MeCN, as shown in Table 3. This is confirmed experimentally when the same solvents were used at either higher or lower reaction temperatures, as reported in the literature.^{5,6,13} To confirm the effect of the solvent on the catalytic activity, the catalytic reaction is performed without a solvent at 353 K for 60 min, in which low TMP–OH conversion (21%) and low TMB=O selectivity (28%) are obtained. A comparison of the catalytic activities obtained with different solvents shows that unsuitable solvents could not show high catalytic activities, could not easily form complexes between the reactants and the active surface of the catalyst, and may block most of the active sites on the catalyst surface.^{8,11,15,16} MeCN is, therefore, found to be the best solvent under these reaction conditions for the highly selective synthesis of TMB=O.

2.5. Selective synthesis of DSBQs

To explore the scope and limitations of this liquid-phase catalytic system, the mesoporous titanosilicate catalysts, i.e. calcined TiSBA-15(6), recyclable TiSBA-15(6), and Washed TiSBA-15(6), were used for the heterogeneous catalytic oxidation of di-/tri-substituted phenols under the reaction conditions listed in Table 4. When the calcined TiSBA-15(6) catalyst is used to catalyse the oxidations of para-substituted 2,6-di-tertbutylphenols (DTBP-OHs) such as 2,6-di-tert-butyl-4-methoxyphenol (DTPB-OCH₃) and 3,5-di-*tert*-butyl-4-hydroxybenzyl acetate, the formation of di-tert-butyl-p-benzoquinone (DTBBQ=O) with higher selectivity is observed after 5 h when the elimination group is eliminated from the para position (Table 4, entries 1 and 2). However, the catalyst is used to catalyse the oxidation of DTBP-OH for 3 h (Table 4) and gives the excellent catalytic activity with 100% DTBBQ=O selectivity. 1,4-Diketones are easily generated on the aromatic rings during these oxidations, and the elimination groups are easily eliminated from the para positions of DTBP-OHs, as experimentally confirmed elsewhere.¹⁷ The formation of DSBQs depends on alkyl groups, which are electron-donating.

Temperature (K)	Solvent (15 ml)	Dielectric constant	TMP-OH conversion (%)	TMB=O selectivity (%)	$\operatorname{TOF}^{h}(\min^{-1})$
353	MeCN	37.5	100	>99	3.4
333	MeOH	33	91	95	3.1
330	AC=O	21	81	87	2.7
330	MeCOOH	6.2	43	53	1.4
353	MeCOOH	6.2	75	83	2.5
348	Ethanol	24.3	84	45	2.8
353	MeCN ^b	37.5	48	54	1.6
353	MeCN ^c	37.5	100	100	3.4
333	Ac_2O^d	21.0	70^e	78	2.3
353	Solvent free	_	21	28	0.7
353	Nitromethane ^f	39.4	61^g	70	2.1
353	MeCN ^f	37.5	90 ^g	89	3.1
353	Nitromethane	39.4	83	90	2.8

^{*a*} Reaction conditions: 50 mg of Washed TiSBA-15(6); 1:3 ratio of TMP-OH to HP (10 mmol TMP-OH; 30 mmol of HP); reaction time, 60 min. ^{*b*} 5 ml of the solvent. ^{*c*} 30 ml of the solvent. ^{*d*} 1,2,4-Trimetylbenzene was used instead of TMP-OH. ^{*e*} Conversion of 1,2,4-trimetylbenzene. ^{*f*} 2,3,5-Trimethylphenol was used instead of TMP-OH. ^{*g*} Conversion of 2,3,5-trimethylphenol. ^{*h*} TOF = (moles of TMP-OH consumed)/(moles of Ti in the catalyst used × reaction time), determined from the initial rates of TMP-OH consumption.

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Entry	Time (h)	Substrate	Major product	Selectivity (%)	Conversion (%)	TOF^g (h^{-1})
1	5^b 5^c 5^d	OH	kj.k	96 98 98	90 94 94	33 38 38
2	5^b 5^c 5^d	OCH ₉ 2,6-di-ferr-buty1-4-methoxyphenol	2.6-di-ferf-buryt-p-benzoquinone	85 90 90	78 83 83	28 34 34
3 ^e	2^b 2^c 2^d	GH ₂ OCOCH ₃ 3.5-di- <i>terr</i> -buty1-4-hydroxybenty1 acetate	2,6-di-rerr-bury-p-benzaquinone	99 100 100	97 99 99	89 101 101
4	3^b 3^c 3^d	CH 2,6-di-ferr-butylhydroquinone	2,6-di-fert-buty-ty-benzoquinone	99 100 100	95 99 99	57 68 68
5	2^b 2^c 2^d	2.6-di-ferri-buty (phenol	2,6-di-rerr-buty-p-benzaquinone	98 100 100	93 97 97	84 99 99
6	$1^b \\ 1^c \\ 1^d$	2.6-discopropylphenol	2,6-diisoprops1-p-benzoquinone	98 100 100	94 97 97	170 198 198
7 ^f	$1^b \\ 1^c \\ 1^d$	2.6-dimethylphenol	2.6-dimethyl-p-benzequinone	97 100 100	95 98 98	171 200 200
8 ^f	$1^b_1^c_1^d_1^d$	CH 2.6-dimethy/thydroquinone H ₄ CO H ₄ CO CO H ₁ CO H ₁ CO H ₁	2.6-dimethyl-p-benzoquinone	98 100 100	96 99 99	173 203 203
		ÓH 2,6-dimethoxyhydroquinone	0 2,6-dimethoxy-p-benzoquinone			

Table 4 Oxidations of di/tri-substituted phenols over calcined, recyclable, and Washed TiSBA-15(6)⁴

^{*a*} Reaction conditions: 50 mg of the catalyst; 10 mmol of the substrate; 30 mmol of HP; 10 mL of MeCN; reaction temperature, 330 K. ^{*b*} Calcined TiSBA-15(6). ^{*c*} Washed TiSBA-15(6). ^{*d*} The results were obtained after the 7th run, using recyclable TiSBA-15(6). ^{*e*} 10 mL of hexane was used as the solvent. ^{*f*} A mixture of solvents (6 mL of dioxane : 4 mL of H₂O). ^{*g*} TOF = (moles of substrate consumed)/(moles of Ti in the catalyst used × reaction time), determined from the initial rates of TMP–OH consumption.

At longer reaction times, a higher DTBBQ=O selectivity is obtained; however, higher selectivities for 2,6-diisopropyl-*p*benzoquinone (DIPBQ) and 2,6-dimethyl-*p*-benzoquinone (DMBQ) are obtained at low reaction times (Table 4, entries 4–6) because of steric effects, which decrease in the order *t*-butyl > isopropyl > methyl; a similar trend was previously reported.¹⁷ At short reaction times, the oxidations of 2,6-disubstituted hydroquinones show the excellent selectivities for DSBQs (Table 4, entries 3, 7, and 8); however, 2,6-disubstituted hydroquinones cost approximately four times higher than 2,6-disubstituted phenols. Moreover, the coupling products, *i.e.* TTBDPQ, 3,5,3',5'-tetraisopropyldiphenoquinone (TIPDPQ), 3,5,3',5'-tetramethyldiphenoquinone (TMDPQ), and 3,5,3',5'-tetramethoxydiphenoquinone (TMoDPQ), are formed with lower selectivities (1–16%). Washed TiSBA-15(6) forms larger amounts of DSBQs compared to calcined TiSBA-15(6), as shown in Table 4, because the small number of TiO₂ nanoparticles deposited on the catalyst surface can be completely removed. Recyclable TiSBA-15(6) has also the similar catalytic activity, as shown in Table 4. The TOF values for recyclable TiSBA-15(6) and Washed TiSBA-15(6) are higher than that for calcined TiSBA-15(6). Hot-catalyst filtration experiments were also performed twice at specific temperatures and times (not shown in Table 4) during these oxidation reactions over calcined TiSBA-15(6). The filtrate solutions contain very small amounts of the conversion product (2-7%), which may be formed *via* HP oxidation; this again confirms that the Washed TiSBA-15(6) catalyst achieves, through a green heterogeneous process, a higher catalytic activity for the selective synthesis of DSBQs.^{5,6,11,16} Overall, the results show that Washed TiSBA-15(6) is a very active, recyclable, and unprecedented heterogeneous catalyst for the highly selective synthesis of DSBQs. A comparison of the results obtained here with those reported in the literature shows that the Washed TiSBA-15(6) catalyst has exceptional catalytic activity for the oxidation of DSBQs compared to other solid catalysts.

2.6. Mechanism of TMP-OH oxidation

Generally, the oxidation of di-/tri-substituted phenols with a suitable oxidizing agent and a perfect miscible solvent proceeds by a one-electron oxidation mechanism, which was first suggested by Kholdeeva's group.^{5,6,19} Accordingly, we have proposed a hypothetical reaction pathway for liquid-phase oxidation of TMP-OH by H_2O_2 in the presence of MeCN catalyzed with Washed TiSBA-15(6) catalysts at 353 K for 60 min, as shown in Scheme 3. Initially, the 5-coordinated doubly bridged hydroxo–Ti species (double site Ti active centre), as

confirmed by UV-vis DRS and ²⁹Si MAS NMR, interact with H_2O_2 to afford a titanium peroxide complex (1). Concurrently, TMP-OH reacts with the titanium peroxide complex to form the 2,3,5-trimethylcyclohexa-2,5-dienone radical (2 and 3), which reacts with another titanium peroxide complex (4) to give 2,3,5-trimethyl-4-hydroxycyclohexa-2,5-dienone with a titanium-oxo radical complex (Ti-O radicals). 2,3,5-Trimethyl-4-hydroxycyclohexa-2,5-dienone rearranges with titanium-oxo radicals to produce the desired product, *i.e.* TMB=O (Scheme 3), with the regeneration of the "double site Ti active centre" (1a). In addition, the reaction mechanism is significantly dependent on the nature of the catalyst. Based on the previously published literature and our results obtained from several oxidation reactions in other studies,^{5,6,10,16b,18-20} it is evident that a homolytic mechanism most likely operates in the oxidation of alkane, alkyl aromatics, and di-/tri-substituted phenols.

3. Experimental

3.1. Materials

For the preparation of mesoporous titanosilicate catalysts, all chemicals, *i.e.* triblock copolymer poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) (Pluronic



Scheme 3 Proposed reaction pathway of TMP-OH oxidation over Washed TiSBA-15(6).

P123; molecular weight = 5800, $EO_{20}PO_{70}EO_{20}$), tetraethylorthosilicate (TEOS; 98%), hydrochloric acid (HCl; 37%), and titanium isopropoxide (TIP; 99.9%), were purchased from Aldrich Chemical Inc. and used as received without further purification. Deionized water was used throughout the syntheses. For the selective synthesis of p-benzoquinones, all chemicals, *i.e.* TMP-OH (≥97%), 2,3,5-trimethylphenol (99%), pseudocumene (98%), DTBP-OH (99%), DTBP-OCH₃ (97%), 2,6-diisopropylphenol (97%), 2,6-dimethylphenol (99%), 2,6-dimethylhydroquinone (>97%), 2,6-dimethoxyhydroquinone (>97%), 2,6-di-tert-butylhydroquinone, HP (30% in H₂O), TBHP (70% in H₂O), UHP (97%), MeCN (99.5%), AC=O (99.5%), MeOH (99.8%), MeCOOH (99.7%), ethanol (≥99.5%), acetic anhydride (\geq 98%), nitromethane (\geq 95%), hexane (99%), and dioxane (>99%), were purchased from Sigma-Aldrich Inc. (USA), TCI (Japan), and ABI Chem (Germany) and used as received without further purification.

3.2. Synthesis of TiSBA-15 and Ti-MCM-41

The as-synthesized mesostructured TiSBA-15 catalysts with $n_{\rm Si}/n_{\rm Ti}$ ratios of 6, 15, 20, 30, and 60 were synthesized using a gel with a TEOS/TIP/Pluronic P123/HCl/H₂O molar composition of 1:0.0167–0.167:0.016:0.43:127 using the pH-aDH method, based on a previously published procedure.⁸ The samples were calcined at 813 K in air for 6 h for complete removal of the template. The calcined mesoporous samples with $n_{\rm Si}/n_{\rm Ti}$ ratios of 6, 15, 20, 30, and 60 were denoted as TiSBA-15(6), TiSBA-15(15), TiSBA-15(20), TiSBA-15(30), and TiSBA-15(60), respectively. The mesoporous Ti-MCM-41(40) catalyst with a $n_{\rm Si}/n_{\rm Ti}$ ratio of 40 was hydrothermally synthesized using cetyltrimethylammonium bromide (CTMABr) as the structuring agent with a gel with a SiO₂/TIP/CTMABr/H₂O molar ratio of 1:0.025:0.25:100, based on a previously published procedure.⁹

3.3. Investigation of catalytic stability

The used mesoporous titanosilicate catalysts such as TiSBA-15(6) and TiSBA-15(60) were regenerated by washing and calcination, as reported previously,⁸ and the treated catalysts were denoted as recyclable catalysts, *i.e.* TiSBA-15(6) and TiSBA-15(60). TiSBA-15(6) was simply washed several times with acetone for the removal of non-framework TiO₂ nanoparticle species deposited on the surface of silica pore walls and further treated, based on the published procedure,⁸ to generate Washed TiSBA-15 or green mesoporous TiSBA-15(6), which was used for the catalytic oxidation of TMP–OH at different optimal parameters.

3.4. Characterization

The calcined, recyclable, and Washed TiSBA-15 mesoporous catalysts were characterized using ICP-AES, XRD, N₂-sorption isotherm analysis, ²⁹Si MAS NMR spectroscopy, UV-vis DRS, field-emission scanning electron microscopy, and transmission electron microscopy, based on published procedures.⁸ The mesoporous Ti-MCM-41(40) catalyst was characterized

Catalysis Science & Technology

using ICP-AES, XRD, N₂-sorption isotherm analysis, and UV-vis DRS, based on published procedures.⁹

3.5. Oxidation of TMP-OH

The liquid-phase oxidation of TMP-OH to TMB=O was performed under vigorous stirring in a thermostated quartzvessel reactor. In a typical experimental procedure, 50 mg of TiSBA-15(6) was placed in the reactor with 10 mmol of TMP-OH and 15 mL of MeCN as the solvent. The mixture was stirred constantly while the temperature was slowly raised to 353 K. After reaching 353 K, 30 mmol of HP was carefully added to the reaction mixture through a septum and the mixture was continuously refluxed for 60 min under atmospheric pressure. After completion of the reaction, the products were collected through the recovery of TiSBA-15(6). To find the best catalyst, various mesostructured TiSBA-15 catalysts were used for the oxidation of TMP-OH under similar reaction conditions. Various reaction parameters, i.e. the time, temperature, and stoichiometric ratio of the reactants (TMP-OH to HP ratios), were studied to determine the optimal reaction conditions for Washed TiSBA-15(6). The oxidation of TMP-OH was also performed with different oxidants, i.e. HP, TBHP, UHP, and molecular oxygen (O₂). In the production of TMB=O, two substrates, i.e. pseudocumene and 2,3,5-trimethylphenol, were used instead of TMP-OH. To identify the best solvent for TiSBA-15(6) reactions, various solvents, i.e. MeCN, MeOH, AC=O, MeCOOH, ethanol, acetic anhydride, and nitromethane, were used for the selective synthesis of TMB=O.

The organic products collected after completion of the reaction were extracted from the resulting mixture using diethyl ether, cooled to room temperature, and compared with the authentic samples by gas chromatography (GC; Chromosorb WHP 80/100) using a flame ionization detector. The products were further confirmed using a combined gas chromatography-mass spectrometry system (GC-MS; Hewlett G1800A).

Furthermore, using various mesostructured titanosilicate catalysts *i.e.* calcined TiSBA-15(6), recyclable TiSBA-15(6), and Washed TiSBA-15(6), liquid-phase oxidations of di-/tri-substituted phenols were performed in a vigorously stirred thermostated glass-vessel reactor at a specific temperature for a specific period of time in the presence of HP as the green oxidizing agent. After completion of the reaction, the organic products were extracted from the resulting mixture using non-chlorinated solvents (diethyl ether/ethyl acetate/hexane). All of the crude products were compared with authentic samples by GC and confirmed *via* GC-MS. The C-C coupling products in the reaction mixture were identified by ¹H NMR spectroscopy after separating the used catalyst.

The recyclable mesoporous titanosilicate catalysts, *i.e.* TiSBA-15(6) and TiSBA-15(60), were reused (50 mg of the catalyst) for liquid-phase oxidations of di-/tri-substituted phenols to determine their catalytic stabilities. The Washed TiSBA-15(6) catalyst (50 g of the catalyst) was used in these

reactions to determine its catalytic activity. After completion of each catalytic reaction, the catalyst was filtered and analysed by ICP-AES to determine the percentage of titanium, and the conversions of phenols and the selectivities for DSBQs were calculated using standard formulas after GC and GC-MS analyses. The spectral data for the C–C coupling products are as follows:

(i) HMBP–OH. ¹H NMR (400 MHz, CDCl₃): δ 1.92 (s, 6H, CH₃), 2.20 (s, 6H, CH₃), 2.21 (s, 6H, CH₃), 6.71 (s, 2H, aromatic H₆).

(ii) TTBDPQ. ¹H NMR (400 MHz, CDCl₃): δ 7.72 (s, 4H), 1.36 (s, 36H).

(iii) TIPDPQ. ¹H NMR (400 MHz, CDCl₃): δ 7.54 (s, 4H),
3.02 (septet, *J* = 7.2 Hz, 4H), 1.2 (d, *J* = 7.2 Hz, 24H).

(iv) TMDPQ. ¹H NMR (400 MHz, CDCl₃): δ 7.73 (s, 4H), 2.15 (s, 12H).

(v) TMoDPQ. ¹H NMR (400 MHz, *d*-DMSO): δ 8.3 (s, 4H), 3.71 (s, 12H).

4. Conclusions

Two-dimensional uniformly mesostructured TiSBA-15 catalysts have been successfully used for the selective synthesis of TMB=O by liquid-phase oxidation of TMP-OH and further used in the syntheses of DSBQs via liquid-phase oxidations of di-/tri-substituted phenols. Washing studies show that the green mesoporous TiSBA-15(6) catalyst has been completely recovered with the removal of the non-framework TiO₂ nanoparticle species and successfully used in these oxidations to determine its catalytic activity. The catalytic stabilities of the TiSBA-15 catalysts have been confirmed by the experimental results of recyclability and hot-catalytic filtration experiments. Recyclability studies of the oxidation reactions show that many active titanium species are successfully incorporated into SBA-15 for improving the catalytic activity. The results of the hot-catalyst filtrations clearly show that the recyclable and Washed TiSBA-15(6) catalysts are excellent heterogeneous catalysts in these oxidation reactions. Based on the catalytic results, the green mesoporous TiSBA-15(6) is found to be a highly active, recyclable, and environmentally friendly solid catalyst with unprecedented catalytic activity among the calcined mesoporous titanosilicate catalysts.

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