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Selective synthesis of benzoquinones over Cu(II)-containing propylsalicylaldimine functionalized mesoporous solid catalysts†

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The major product, 2,3,5-trimethyl-1,4-benzophenone (TMB═O), was synthesised by an eco-friendly liquid-phase oxidation of 2,3,6-trimethylphenol (TMP-OH) over Cu(II)-containing propylsalicylaldimine (CSA) functionalized mesoporous solid catalysts, namely, CSASBA-15(0.2), CSASBA-15(0.1) and CSAMCM-41(0.2), synthesized using various amounts of copper in a simple post-grafting method using different mesoporous silica materials, *e.g.*, thick-silica walled SBA-15 and thin-silica walled MCM-41. The benzoquinones, *i.e.*, 2,6-disubstituted *p*-benzoquinones (DSBQs), were also synthesised by the slurry-phase oxidation of di/tri-substituted phenols using the prepared catalysts. A promising chemical treatment was used for the removal of extra-framework copper species from the active surface of CSASBA-15(0.2), and the catalytic activity of the recovered catalyst, *i.e.* green mesoporous CSASBA-15(0.2) or W-CSASBA-15(0.2), was evaluated. Various reaction parameters, oxidants and solvents were used in this catalytic oxidation. To confirm the catalytic stability, recyclability and hot-catalytic filtration experiments were performed. On the basis of all catalytic results, it is worth noting that the mesoporous CSASBA-15(0.2) is an outstanding and a promising heterogeneous catalyst for the selective synthesis of TMB═O and DSBQs, and produces 98% TMB═O selectivity with 100% TMP-OH conversion at 353 K for 40 min and 97–99% DSBQ selectivity with 98–100% di/tri-substituted phenols conversion at 330 K for 1–3 h. The green mesoporous catalyst has unprecedented catalytic activity compared with that of other CSA functionalized mesoporous solid catalysts.

1. Introduction

Trimethyl-1,4-benzoquinone (TMB═O) is synthesized by the multi-step oxidation of 2,3,6-trimethyl-phenol (TMP-OH) using traditional procedures, *i.e.*, sulfonation, oxidation and reduction.[1,2] To produce TMB═O, TMP-OH is sulfonated with sulfuric acid to produce 4-hydroxytrimethylbenzenesulfonic acid, which is then oxidized by manganese dioxide, as an inorganic metal-oxidant. The traditional method used for this oxidation system generates a great deal of solid and liquid wastes because of the use of sulfuric acid and stoichiometric solid oxidants. TMB═O is an important precursor in the synthesis of vitamin E, which is the best fat-soluble biological antioxidant.[3] The demand for vitamin E is more than 30 000 tons per year.

In a patent, the alkyl-substituted *p*-benzoquinone, which is a major product, is synthesized by the oxidation of alkyl-substituted phenols under an oxygen atmosphere (30 bar) using a stoichiometric amount of Cu(II) salt in dimethylformamide.[2] The yield of the corresponding *p*-benzoquinone was 80–87% at full conversion. BASF AG has prepared TMB═O with 98.5% yield using copper(II) halide as a catalyst in an alcohol/water two-phase medium.[4] The oxidation of TMP-OH to TMB═O is catalyzed over copper(II) chloride by applying co-catalysts, such as lithium chloride, magnesium chloride, and hydroxylamine hydrochloride.[4,5] But all the studies have many disadvantages technically. In some of the reports a high stoichiometric amount of catalyst is required for a complete and selective transformation from TMP-OH to TMB═O. In other cases, the co-catalysts, such as hydroxylamine hydrochloride, are partly consumed during the oxidation. In a homogeneous catalyst system, the main drawbacks, *e.g.*, separation, recycling, and product purification, are apparent after the reaction has completed. The main product can still be contaminated with traces of transition metals even though two solvent methods are used because of metal complexation by organics and subsequent extraction into the organic phase. In addition, the chlorine-contaminated by-products with a significant amount of copper-containing waste can be formed when high amounts of copper chloride are used as one of the catalytic materials. This catalytic system not only produces lots of chlo-

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rine- and copper-contaminated by-products with a main product but a special catalytic apparatus made with corrosion-resistant coatings might also be required.

For the production of TMB═O, several industrial routes are used for the oxidation of TMP-OH with manganese dioxide, nitric acid, or other toxic reagents as the catalysts but they are not eco-friendly.[6] As a challenging goal, eco-friendly catalytic methods are developed for selective oxidation of organic compounds.[7] For the synthesis of TMB═O, a few catalytic systems have been applied using ‘green’ and inexpensive oxidants, such as molecular oxygen and hydrogen peroxide (HP), over homogeneous catalysts such as Schiff-base cobalt complexes, ruthenium salts and heteropoly compounds.[7] These catalytic systems also remain problematic for catalyst separation, as the pure target products could be contaminated with hazardous transition metal compounds.

Recently, copper(II) chloride in the ionic liquid medium has been used as a catalyst to prepare TMB═O with 86% selectivity by an eco-friendly oxidation of TMP-OH with molecular oxygen, as an oxidant, and *n*-butanol, as a cosolvent.[8] In the modern industry, TMB═O is also produced in a catalytic process using molecular oxygen in the presence of copper chloride.[8] Kholdeeva and Zalomaeva explained clearly in a review that transition-metal supported catalysts are recently used in selective oxidation of phenols and methoxyarenes using environmentally benign oxidants.[8] The most efficient heterogeneous catalyst (a divanadium-substituted polyoxometalate supported on N-doped carbon nanotubes) for the synthesis of TMBQ has been recently reported by Evtushok *et al.*[8] Even though the above catalytic systems produce a better TMB═O selectivity, the best catalytic system with a highly active and an eco-friendly mesostructured copper(II) catalyst is greatly needed to achieve TMB═O selectivity. Therefore, to the best of our knowledge, for the selective synthesis of TMB═O by liquid-phase oxidation of TMP-OH and for the selective synthesis of DSBQs by oxidation of di/tri-substituted phenols, the mesoporous CSASBA-15 catalysts could not be successfully used so far.

Since 21st century, in both academia and industry, green catalytic technology has been significantly applied for the catalytic oxidation of phenols to their corresponding quinones in a halogen-free reaction system. In this study, for the selective synthesis of TMB═O, the green catalytic oxidation of TMP-OH using HP as a green oxidizing agent over CSA-SBA-15 catalysts under a variety of reaction conditions was conducted. The CSA-SBA-15 catalysts were also used for selective synthesis of DSBQs by the oxidation of di/tri-substituted phenols using HP as the green oxidising agent. The catalytic results obtained for the selective synthesis of TMB═O and DSBQs using all the CSA functionalized mesoporous silica catalysts were thoroughly correlated and compared.

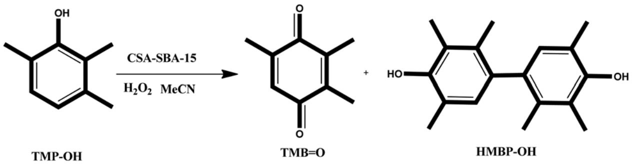
2. Results and discussion

Mesoporous CSASBA-15 catalysts, *i.e.* CSASBA-15(0.1) and CSASBA-15(0.2), which have the copper content of 0.097 wt% and 0.198 wt%, respectively, were synthesized by the post-synthetic grafting method using amino-functionalized SBA-15 (APTES-SBA-15), salicylaldehyde and copper(II) nitrate trihydrate. CSAMCM-41(0.2), which has the copper content of 0.192 wt%, was synthesized using the previously published procedure.[9,10] The results of elemental analysis of CSASBA-15 (0.2), which were obtained by using a ICP-AES and CHNS/O analyser, confirm that the molar ratios of N : Cu and C : Cu are ≈3.5 and 23.8, respectively.[9] The CSA functionalized mesoporous silica catalysts were extensively used in an eco-friendly oxidation of TMP-OH. Initially, the catalytic oxidation of TMP-OH was investigated using the reaction conditions listed in Table 1. In this catalytic reaction, TMB═O, as a major product, as well as 2,3,5-trimethylhydroquinone (TMHQ) and 2,2′,3,3′,5,5′-hexamethyl-4,4′-biphenol (HMBP-OH), as by-products, were formed, through a hydroxyl-radical oxidation mechanism, which is confirmed by the previous literature[11] as shown in Scheme 1. The order of the catalytic activities of the catalysts on the basis of TMB═O selectivity is as follows: CSASBA-15(0.2) > CSAMCM-41(0.2) > CSASBA-15(0.1). CSASBA-15(0.2) exhibits the best performance with 98% TMP-OH conversion and 95% TMB═O selectivity and has higher catalytic activity than other CSA functionalized mesoporous silica catalysts because huge amounts of Cu^{2+}-ions can be actively anchored on the inner pore walls of salicylaldimine functionalized SBA-15. It means that the numerous accessible active sites in CSASBA-15(0.2) can be effectively enhanced to the TMP-OH oxidation reaction while the Cu^{2+}-ions coordinated with a square planar structure in salicylaldimine functionalized SBA-15 produces high numbers of Lewis acid sites on the silica pore walls, as confirmed by acidity studies using Fourier-transform infrared (FTIR) pyridine spectroscopy for copper containing mesoporous silica catalysts.[12] The catalytic results obtained by CSASBA-15 catalysts show that the most of the Cu^{2+}-ions could be anchored to increase the active sites on the silica surface of inner pores as shown in Scheme 2 and can also be further confirmed by the results of inductively coupled-plasma atomic-emission spectroscopy (ICP-AES), FTIR, electron spin resonance (ESR) spectroscopy and ultraviolet-visible diffuse reflectance (UV–vis DRS) spectroscopy.[9] According to the literature,[13] we have explained in detail that the donor atoms of N and O on CSASBA-15(0.2) produce the steric and electronic effects to stabilise Cu^{2+} ions and increase the hydrophobicity, which plays an efficient catalytic role in increasing TMB═O selectivity and also achieving a square planar coordination with huge numbers of Cu^{2+}-ions in salicylaldimine functionalized SBA-15.[9] Moreover, in our study, the catalytic characterization results obtained by ICP-AES, X-ray diffraction (XRD), N_2-sorption isotherm analysis, FTIR, ESR and UV-vis DRS, as shown in Fig. S1–S5,† strongly support that CSASBA-15(0.2) has a higher catalytic activity than the other CSA functionalized mesoporous silica catalysts whereas CSAMCM-41(0.2) gives much lower TMB═O selectivity than CSASBA-15(0.2) due to the less number of Cu^{2+}-ions coordinated with a square planar structure. It is noteworthy that, compared to CSASBA-15(0.2), CSAMCM-41(0.2) has thinner mesopore walls, which could

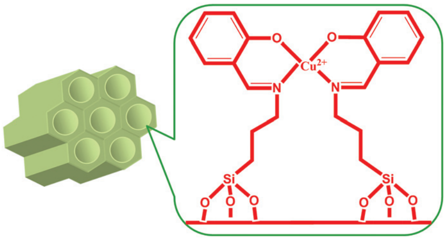
Table 1 Oxidations of TMP-OH over different CSASBA-15 catalysts[a]

Catalysts	Cu[b] (wt%)	Amounts of Cu in 50 mg (mmol)	TMP-OH conversion (%)	TMB=O selectivity (%)	TOF[g] (min^{-1})
CSASBA-15(0.1)	0.097	0.00076	45	39	147
CSASBA-15(0.2)	0.198	0.00155	100	95	162
CSASBA-15 (0.1)[c]	0.096	0.00075	46	40	152
CSASBA-15 (0.2)[c]	0.197	0.00155	100	96	161
CSAMCM-41(0.2)[d]	0.192	0.00151	90	85	149
SiSBA-15	—	—	10	3	—
W-CSASBA-15(0.2)[e]	0.197	0.00155	100	98	161
W-CSASBA-15(0.2)[f]	0.197	0.00155	100	98	107

[a] Reaction conditions: 50 mg of 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, 40 min. [b] The results are determined by ICP-AES. [c] The results were obtained in the 3rd run. [d] The catalyst was synthesized using the published procedure.[9,10] [e] The catalyst was washed before using in catalytic oxidation. [f] TMP-OH was added in three portions (3.33 mmol per 20 min) to the reaction mixture. [g] Turnover frequency (TOF) = (moles of substrate consumed)/(moles of active sites in the catalyst used × reaction time).



Scheme 1 Oxidation of TMP-OH.



Scheme 2 Structure of CSASBA-15.

not support to incorporate the high numbers of Cu^{2+}-ions.[9] The ICP-AES studies show that the silica pore walls of CSASBA-15(0.2) contain more Cu^{2+}-ions than the other CSASBA-15(0.1) and CSAMCM-41(0.2).[9] As reported in the literature,[14] the results of ^{29}Si magic-angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy show that the signal intensity of CSA functionalised mesoporous silica catalysts is much lower than that of siliceous SBA-15. This observation clearly supports the stabilization of the copper ions by the silanol groups (defect sites), and an additional point noted is that T^1 and T^2 peak signals further confirm that large numbers of CSA are functionalized within the inner surface of mesoporous silicas. The ESR and UV-vis DRS spectroscopy results (Fig. S4 and S5†) prove that the CSASBA-15(0.2) catalyst contains more Cu^{2+}-ions coordinated with a square planar structure than the other CSA functionalized mesoporous silica catalysts.[9] Additionally, the XRD (Fig. S1†) and N_2-sorption isotherm (Fig. S2†) results strongly indicate that the physicochemical parameters (*i.e.* unit cell size, pore size, surface area, pore volume, and wall thickness) of the CSASBA-15(0.2) catalyst contribute to increase its catalytic activity in this liquid-phase catalytic oxidation.[9] The structural and textural properties of the CSA functionalized mesoporous silica catalysts are listed in Table S1.† This reaction was also performed using SiSBA-15 synthesized using the previous procedure published by Selvaraj *et al.*[15] In this case, TMP-OH conversion (10%) with a trace amount of TMB=O selectivity (Table 1) can only be obtained by SiSBA-15. This catalytic result is highly recommended in that the high activity is possibly caused by CSA functionalized hexagonal mesoporous silica catalysts prepared with thick pore walls, which, is one of the main factors to increase catalytic activity and plays an important role in the production of TMB=O with higher selectivity.

Among the CSA functionalized mesoporous silica catalysts, CSASBA-15(0.2) and CSASBA-15(0.1) give the highest and lowest TMB=O selectivity, respectively. Therefore, we have taken the above two catalysts for reusability tests under the reaction conditions listed in Table 2. Initially, the CSASBA-15 catalysts used in the production of TMB=O usually cause lower product selectivity because the unreacted organic wastes screen the majority of active sites and create the sintering effect on the catalyst surface. Prior to reuse, we have regenerated the used CSASBA-15 catalysts by washing treatments. Initially, the used catalysts were reactivated by filtration from the reaction mixture, and then the catalysts were thoroughly washed with the corresponding solvents such as acetonitrile and dichloromethane for the complete removal of organics and unreacted TMP-OH molecules and dried using a vacuum oven at an ambient temperature. The recovered recyclable and active catalysts, *e.g.*, CSASBA-15(0.2) and CSASBA-15(0.1), were then reused for the reaction (Table 1). The recyclability experiments were performed for each run before initiation of the catalytic reaction. After two runs, the TMB=O selectivity of CSASBA-15(0.2) increases slightly from 98 to 100%; this is attributed to the complete removal of the extra-framework CuO nanoparticle species from the active surface of the catalyst resulting in the correct orientation of TMP-OH on the CSASBA-15(0.2) catalyst during oxidation. In the third run, the

TMP-OH conversion and TMB=O selectivity remain constant, as shown in Table 1, indicating that the active Cu^{2+} species could not be further leached from the mesoporous matrix; this is in good agreement with the ICP-AES results for filtrate solutions, which did not reveal any active Cu^{2+} species due to the steric and electronic effects increased by the donor atoms of N and O on CSASBA-15(0.2) as strongly indicated in the literature.[13] On the basis of our catalytic results, it is strongly confirmed that the TMB=O selectivity could not be highly achieved by CuO nanoparticles because its surface area is six-times lower compared to that of CSASBA-15(0.2).[11] The CSASBA-15(0.2) catalyst, before applying to the liquid-phase oxidation of TMP-OH, was washed more than four times using the solvents, acetonitrile and dichloromethane, to remove the non-framework CuO nanoparticles completely, and dried using a vacuum oven at an ambient temperature. Finally, the treated catalyst was used as a washed CSASBA-15(0.2) catalyst in this catalytic reaction. The catalytic activity of the recyclable CSASBA-15(0.2) catalyst, in the third run, is almost similarly obtained to CSASBA-15(0.2), as shown in Table 1. Based on this result, it is seen that the majority of active copper species on the surface of the CSASBA-15 catalyst could not be leached, as an irreversible manner. In addition, as a proof of the recyclability, the ICP-AES results also confirm the absence of copper species. After obtaining the results for the three runs over CSASBA-15(0.2), hot-catalyst filtration experiments were performed twice at 353 K for this oxidation reaction. In this case, the obtained catalytic results prove that the filtered solutions produce ~2–5% of TMB=O selectivity with 5–7% of TMP-OH conversion, which may be formed by HP. The above catalytic results confirm that the oxidation of TMP-OH occurs only on the surface of the green CSASBA-15(0.2) catalyst. Therefore, W-CSASBA-15(0.2) has an outstanding catalytic activity and leads to a green heterogeneous catalytic process.[16] It is obviously noted that the washing experiments confirm the complete removal of non-framework CuO nanoparticles on the surface of the catalyst, as the ICP-AES results show in Table S1,† and this catalytic result also closely matches that of the hot-catalyst filtrate solution of CSASBA-15(0.2). When the TMP-OH is added in three portions to the reaction, we have undoubtedly observed that the TMP-OH oxidation is 100% complete, as shown in Table 1. Moreover, the catalytic characterization results, such as XRD, N$_2$-sorption isotherm, and UV-vis DRS, prove that the structural and textural parameters, including the environment of the Cu^{2+} species coordinated to the surface of CSASBA-15(0.2) are maintained (Table S1†). The recycling results show that W-CSASBA-15(0.2) is unprecedented as a green catalyst among the metallosilicate mesoporous catalysts.[16]

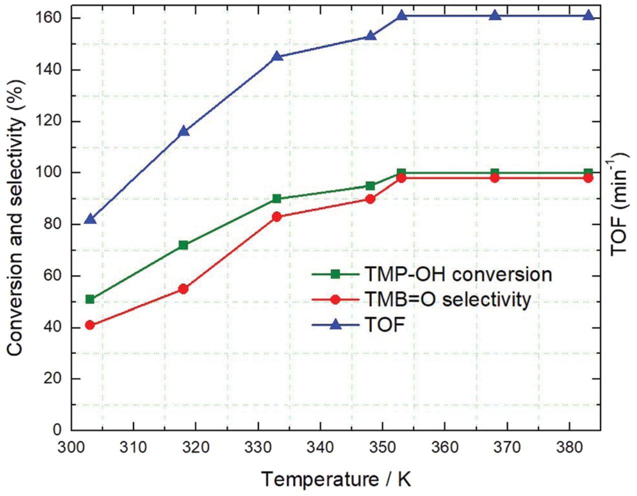


Fig. 1 Oxidations of TMP-OH at different temperatures over W-CSASBA-15(0.2). Reaction conditions: 50 mg of catalyst, 0.00155 mmol of Cu; 1 : 3 ratio of TMP-OH : HP (10 mmol TMP-OH, 30 mmol of HP); 15 mL of MeCN; reaction time, 40 min.

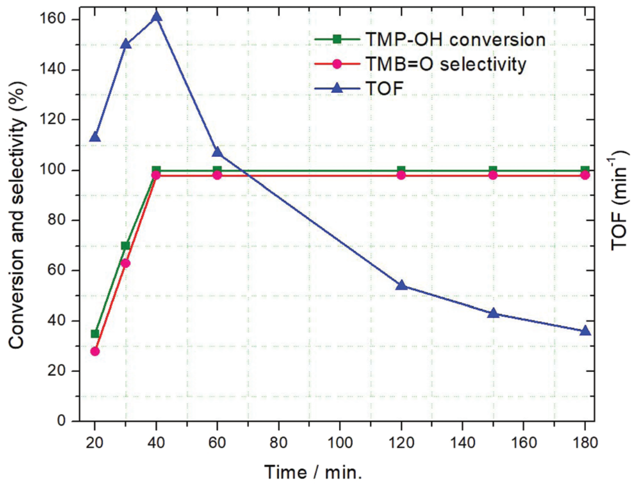


Fig. 2 Oxidations of TMP-OH at different times over W-CSASBA-15(0.2). Reaction conditions: 50 mg of catalyst, 0.00155 mmol of Cu; 1 : 3 ratio of TMP-OH : HP (10 mmol TMP-OH, 30 mmol of HP); 15 mL of MeCN; reaction temperature, 353 K.

The optimal reaction parameters, *i.e.* temperature, time, and reactant ratio, were investigated using W-CSASBA-15(0.2) because it is the most active catalyst of the CSA functionalized mesoporous silica catalysts. Oxidation of TMP-OH was carried out at different reaction temperatures and times under the reaction conditions listed correspondingly in Fig. 1 and 2. The rates of TMP-OH consumption and TMB=O formation increase on reaching 100% TMB=O selectivity when the reaction temperatures and times are increased from 303 to 353 K and 30 to 40 min, respectively. With a further increase in the temperature and time from 353 to 383 K and 40 to 180 min, respectively, the TMP-OH conversion and TMB=O selectivity could not be changed because TMB=O shows kinetic stability, as confirmed and reported in the literature.[17] Additionally, the TMHQ selectivity increases with decreasing temperature from 353 to 318 K and time from 40 to 30 min. The catalytic results obtained using different temperatures and times clearly show that the TMHQ selectivity increases with either decreasing temperature or time.[16,17] The TOF increases from 303 to 353 K.

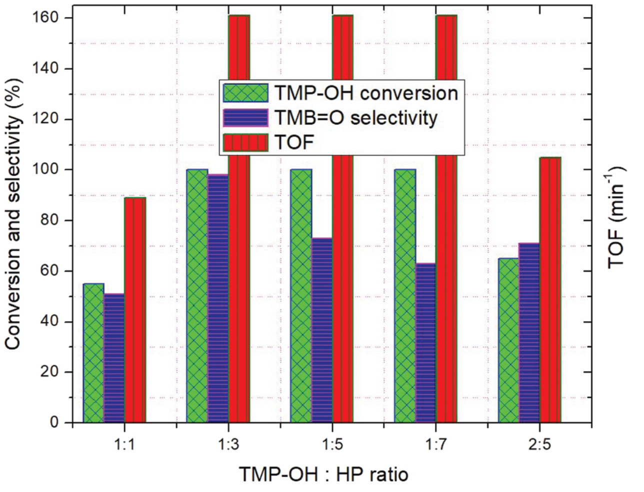


Fig. 3 Variations of TMP-OH to HP ratio over W-CSASBA-15(0.2). Reaction conditions: 50 mg of catalyst, 0.00155 mmol of Cu; 15 mL of MeCN; reaction temperature 353 K; reaction time, 40 min.

Table 2 Oxidations of TMP-OH by TBHP over W-CSASBA-15(0.2)[a]

Temperature (K)	Time (min)	TMP-OH conversion (%)	TMB=O selectivity (%)	TOF[g] (min^{-1})
298	30	31	42	67
333	30	79	50	170
353	30	88	57	189
353	40	91	78	98
353	180	97	69	35
353[b]	40	98	53	105
353[c]	180	99	45	35
333[d]	180	68	37	24
333[e]	180	53[f]	58	19

[a] Reaction conditions: 50 mg of W-CSASBA-15(0.2), 0.00155 mmol of Cu; 1 : 3 ratio of TMP-OH to TBHP (10 mmol TMP-OH; 30 mmol of TBHP); 15 ml of MeCN. [b] 1 : 6 ratio of TMP-OH to TBHP (10 mmol TMP-OH; 60 mmol of TBHP). [c] 1 : 8 ratio of TMP-OH to TBHP (10 mmol TMP-OH; 80 mmol of TBHP). [d] O_2 (excess) was used as an oxidizing agent. [e] 1,2,4-Trimethylbenzene was used instead of TMP-OH with urea hydrogen peroxide as the oxidizing agent and MeOH as the solvent. [f] Conversion of 1,2,4-trimethylbenzene. [g] Turnover frequency (TOF) = (moles of substrate consumed)/(moles of active sites in the catalyst used × reaction time).

Thereafter, the TOF is still sustained when temperature is increased from 353 to 383 K. It is noticeably found on the basis of catalytic results that the TMP-OH conversion as well as TMB=O selectivity could not be affected even when the reaction is conducted at a higher temperature (383 K). When this reaction is performed using a 1 : 3 ratio of TMP-OH to HP under the reaction conditions listed in Fig. 3, W-CSASBA-15(0.2) produces a higher TMB=O selectivity. The reaction rate ($\text{TOF} = 161\ \text{min}^{-1}$) for the ratio 1 : 3 is higher as compared to other ratios, 1 : 1 and 2 : 5, because there is no deactivation and no sintering effect caused, whereas the catalytic activity decreases in TMP-OH to HP ratios ranging from 1 : 1 to 2 : 5 because the byproducts, oxidative C–C coupling product (HMBP-OH) and dihydroxyarene product (TMHQ), could be formed by increasing the amounts of HP (TMP-OH to HP ratios, 1 : 5, 1 : 7). The diffusion rate of W-CSASBA-15(0.2) as well as TMP-OH conversion decreases for the ratios 1 : 1 and 2 : 5. The TMB=O selectivity could not be improved by these ratios because the active sites could be partially screened by unreacted organics deposited on the inner pore walls while the reactants in these ratios may not reach an equilibrium state. When this reaction is performed over W-CSASBA-15(0.2) using *tert*-butyl hydroperoxide (TBHP) as the oxidizing agent instead of HP at optimal temperatures, times, and reaction ratios listed in Table 2, the TMB=O selectivity gradually decreases compared with that using HP while the selectivity of by-products, HMBP-OH and TMHQ, can be increased. However, as shown in Table 2, the TMB=O selectivity decreases almost threefold when molecular oxygen is used as the oxidizing agent instead of HP under the same reaction conditions because HMBP-OH selectivity reached 63%. When pseudocumene is used instead of TMP-OH with urea hydrogen peroxide (UHP) as the oxidizing agent and MeOH as the solvent, the TMP-OH conversion and TMB=O selectivity significantly decrease with increasing selectivity of by-products, TMHQ and HMBP-OH, as shown in Table 2. These catalytic studies confirm that the water molecules of HP could not affect the catalytic activity of this system as reported in previous studies.[18] Comparing the catalytic results obtained over W-CSASBA-15(0.2) using different reaction parameters clearly confirms that the excellent TMP-OH oxidation is achieved *via* a reaction at 353 K for 40 min using a 1 : 3 ratio of TMP-OH to HP with a higher TMP-OH conversion as well as a higher TMB=O selectivity.

The liquid-phase oxidation of TMP-OH over W-CSASBA-15 (0.2) with the reaction parameters and with different solvents listed in Table 3 was performed to achieve 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 enable attack on the active sites to achieve higher TMP-OH conversion. The TMP-OH conversion (38%) and TMB=O selectivity (48%) decrease when this reaction is conducted, under similar reaction conditions, with 5 mL of MeCN, because large amounts of TMP-OH may be insoluble to react with HP. However, the conversion as well as selectivity is not majorly affected when the reaction is carried out using 30 mL of MeCN under the same reaction conditions, while other solvents were also used for this catalytic oxidation, as noted in Table 3. The order of the dielectric constants of the solvents is MeCN > MeOH > ethanol > AC=O > MeCOOH. All solvents could offer lower TMB=O selectivity than MeCN because of increasing by-product selectivity (TMHQ and HMBP-OH) as shown in Table 3. This is experimentally confirmed when the same solvents are used at either higher or lower reaction temperatures, as reported in the literature.[16,17] To confirm the effect of the solvent on the catalytic activity, the catalytic reaction is performed without a solvent at 353 K for 40 min; the TMP-OH conversion and TMB=O selectivity reach 15% and 19%, respectively. Additionally, the catalytic

Table 3 Oxidations of TMP-OH in different solvents over W-CSASBA-15(0.2)[a]

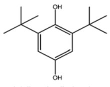
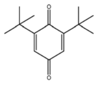
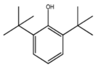
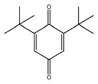
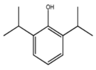
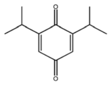
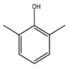
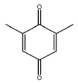
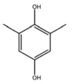
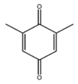
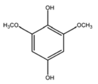
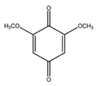
Temperature (K)	Solvent (15 ml)	Dielectric constant	TMP-OH conversion (%)	TMB=O selectivity (%)	TOF[d] (min^{-1})
353	MeCN	37.5	100	98	161
333	MeOH	33	85	73	137
330	AC=O	21	72	81	116
330	MeCOOH	6.2	37	52	60
353	MeCOOH	6.2	68	80	110
348	Ethanol	24.3	78	39	126
353	MeCN[b]	37.5	38	48	139
353	MeCN[c]	37.5	100	98	161
353	Solvent free	—	15	19	24

[a] Reaction conditions: 50 mg of W-CSASBA-15(0.2), 0.00155 mmol of Cu; 1 : 3 ratio of TMP-OH to HP (10 mmol TMP-OH; 30 mmol of HP); reaction time, 40 min. [b] 5 ml of solvent. [c] 30 ml of solvent. [d] Turnover frequency (TOF) = (moles of substrate consumed)/(moles of active sites in the catalyst used × reaction time).

results show that the TOF of this reaction for MeCN, used as a solvent, is higher than that of other solvents, because many solvents do not easily create complexes between the reactants and the active surface of the catalyst while they may block or screen the numerous active sites on the surface of the catalyst.[19,20] To achieve the highly selective synthesis of TMB=O, MeCN is found to be a beneficial solvent under these reaction conditions, as clearly shown by the above-mentioned catalytic results.

In organic synthetic chemistry, quinone derivatives play an important role in biosystems and are being used in the synthesis of vitamins.[1] To explore the advantages of a liquid phase catalytic system for the synthesis of quinone derivatives, the CSA functionalized mesoporous silica catalysts, *i.e.* CSASBA-15(0.2), recyclable CSASBA-15(0.2), and W-CSASBA-15(0.2), are used under the reaction conditions listed in Table 4. When the calcined CSASBA-15(0.2) catalyst is used to catalyse the oxidation of 2,6-di-*tert*-butylphenol (DTBP-OH) at 3 h (Table 4), excellent catalytic activity is obtained with a 100% di-*tert*-butyl-*p*-benzoquinone (DTBBQ=O) selectivity. A 1,4-diketone can be formed on the aromatic rings of *para*-substituted 2,6-di-*tert*-butylphenols (DTBP-OHs) during these oxidations, and we have clearly observed that the elimination groups can be easily eliminated from the *para* positions of DTBP-OHs, as experimentally confirmed elsewhere.[21] The alkyl groups, which are electron-donating, lead to form DSBQs. The higher DTBBQ=O selectivity is obtained at longer reaction times; however, at low reaction times (entries 2–4), the higher

Table 4 Oxidations of di/tri-substituted phenols over W-CSASBA-15(0.2)[a]

Entry	Time (h)	Substrate	Major product	Selectivity (%)	Conversion (%)
1[e]	2[b]	 2,6-di-*tert*-butylhydroquinone	 2,6-di-*tert*-butyl-*p*-benzoquinone	91	98
	2[c]			96	100
	2[d]			96	100
2	3[b]	 2,6-di-*tert*-butylphenol	 2,6-di-*tert*-butyl-*p*-benzoquinone	94	97
	3[c]			98	100
	3[d]			98	100
3	2[b]	 2,6-diisopropylphenol	 2,6-diisopropyl-*p*-benzoquinone	96	95
	2[c]			99	99
	2[d]			99	99
4	1[b]	 2,6-dimethylphenol	 2,6-dimethyl-*p*-benzoquinone	93	95
	1[c]			99	98
	1[d]			99	98
5[f]	1[b]	 2,6-dimethylhydroquinone	 2,6-dimethyl-*p*-benzoquinone	94	96
	1[c]			99	100
	1[d]			99	100
6[f]	1[b]	 2,6-dimethoxyhydroquinone	 2,6-dimethoxy-*p*-benzoquinone	93	94
	1[c]			97	98
	1[d]			97	98

[a] Reaction conditions: 50 mg of catalyst; 10 mmol of substrate; 30 mmol of HP; 10 ml of MeCN; reaction temperature, 330 K. [b] CSASBA-15(0.2), 0.00155 mmol of Cu. [c] W-CSASBA-15(0.2), 0.00155 mmol of Cu. [d] The results were obtained in the 3rd run. [e] 10 ml of hexane was used as a solvent. [f] The mixture of solvents (6 ml of dioxane : 4 ml of H_2O).

selectivities for 2,6-diisopropyl-*p*-benzoquinone (DIPBQ) and 2,6-dimethyl-*p*-benzoquinone (DMBQ) are obtained because of steric effects, which decrease in the order of *t*-butyl > isopropyl > methyl; a similar trend is previously reported.[21] The oxidations of 2,6-disubstituted hydroquinones at short reaction times show the excellent selectivities for DSBQs (entries 1, 5 and 6); however, 2,6-disubstituted hydroquinones cost approximately four times more than that of 2,6-disubstituted phenols. Moreover, the coupling products, *i.e.* 3,5,3′,5′-tetra-*tert*-butyldiphenoquinone (TTBDPQ), 3,5,3′,5′-tetraisopropyldiphenoquinone (TIPDPQ), 3,5,3′,5′-tetramethyldiphenoquinone (TMDPQ), and 3,5,3′,5′-tetramethoxydiphenoquinone (TMoDPQ), can be formed with lower selectivities (1–9%). W-CSASBA-15(0.2) produces larger amounts of DSBQs than CSASBA-15(0.2), as shown in Table 4, because the trace amounts of CuO nanoparticles, from the active surface of the catalyst, can be completely removed using washing treatments. Recyclable CSASBA-15(0.2) has a similar catalytic activity for these catalytic oxidations, as shown in Table 4. Hot-catalyst filtration experiments were also performed twice at specific temperatures and times (not shown in Table 4) during these oxidation reactions over CSASBA-15(0.2). The filtrate solutions contain very small amounts of the conversion product (2–7%), which may form *via* HP; this again confirms that excellent selective synthesis of DSBQs has been achieved on the surface of the W-CSASBA-15(0.2) catalyst resulting in a higher catalytic activity and providing further proof of its validity as a green heterogeneous process.[16,17,20] Overall, the results show that W-CSASBA-15(0.2) is a very active, recyclable, and unprecedented heterogeneous catalyst for the highly selective synthesis of DSBQs. Comparison of the results obtained here with those reported in the literature shows that the W-CSASBA-15 (0.2) catalyst has exceptional catalytic activity for the oxidation of DSBQs compared with that of other solid catalysts because it has thicker pore walls than CuMCM-41 and other mesoporous metallosilicate MCM-41 catalysts.[16,17,20]

3. Experimental

3.1. Materials

For the preparation of the CSA functionalized mesoporous silica catalysts, all chemicals, *i.e.* triblock copolymer poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) (Pluronic P123; molecular weight = 5800, $EO_{20}PO_{70}EO_{20}$), cetyltrimethylammonium bromide (CTMABr, $C_{16}H_{33}N(CH_3)_3Br$), sodium metasilicate (44–47% SiO_2), tetraethylorthosilicate (TEOS; 98%), sulphuric acid (99.99%), hydrochloric acid (HCl; 37%), aminopropyltriethoxysilane, salicylaldehyde, chloroform, dichloromethane, methanol and copper (II) nitrate trihydrate ($Cu(NO_3)_2{\cdot}3H_2O$), 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%), 2,6-diisopropylphenol (97%), 2,6-dimethylphenol (99%), 2,6-dimethylhydroquinone (>97%), 2,6-dimethoxyhydroquinone (>97%), 2,6-di-*tert*-butylhydroquinone, HP (30% in H_2O), TBHP (70% in H_2O), UHP (97%), MeCN (99.5%), AC═O (99.5%,), MeOH (99.8%), MeCOOH (99.7%), ethanol (≥99.5%), hexane (99%), and dioxane (>99%) were purchased from Sigma-Aldrich Inc. (USA), TCI (Japan), and BHZ (China) Chemical Inc. (China) and used as received without further purification.

3.2. Synthesis of SBA-15 and MCM-41

The well-ordered mesoporous SBA-15 molecular sieve material was synthesized using the pH-adjusting direct hydrothermal method according to the previous procedure published by Selvaraj and Kawi.[15] In a typical synthesis, 4 g of Pluronic P123 with 25 ml of water was stirred to obtain a clear solution. Thereafter, a required amount of dilute HCl solution was added, and the mixture solution was again stirred for another 1 h for the hydronium ions to be associated with the alkylene oxide units. Next, 9 g of TEOS was added, and the resulting mixture was stirred for 24 h at 313 K. The product was recovered by filtration, washed several times with water and dried overnight at 373 K. Finally, the obtained SBA-15 was calcined in air at 813 K for 6 h for the complete removal of the surfactant template. The mesoporous MCM-41(40) was alkaline-hydrothermally synthesized using cetyltrimethylammonium bromide (CTMABr) as the structuring agent according to a well-known synthetic procedure published by Selvaraj *et al.*[22]

3.3. Synthesis of CSASBA-15 and CSAMCM-41(0.2)

The mesoporous CSASBA-15 catalysts, CSASBA-15(0.1) and CSASBA-15(0.2), were synthesized by the post-grafting method, as shown in Scheme 1, using amino-functionalized SBA-15 (APTES-SBA-15) with appropriate amounts of salicylaldehyde and $Cu(NO_3)_2{\cdot}3H_2O$ according to the previous procedure published by Selvaraj *et al.*[9] In a typical synthesis of CSASBA-15 (0.2), one gram of SBA-15 was stirred with 1.8 g of aminopropyltriethoxysilane (3-APTES) in chloroform at room temperature for 15 h under an N_2 atmosphere. Thereafter, the stirred mixture was filtered and washed using the solvents such as chloroform and dichloromethane, and a white solid of APTES-SBA-15 was collected. APTES-SBA-15 was then refluxed with 5 g of salicylaldehyde in methanol (150 cm^3) for 4 h at 333 K. The yellowish solid was then collected by the filtration of the refluxed mixture. The obtained solid material was dried in a desiccator. Thereafter, 1.22 g of yellowish solid was stirred with 0.5 g of $Cu(NO_3)_2{\cdot}3H_2O$ solution (it was dissolved by the appropriate amount of methanol) at room temperature for 15 h. The formation of a green solid product was filtered and washed with methanol using Soxhlet. The obtained product was dried under vacuum and is designated as CSASBA-15 (0.2). This typical procedure was adopted for the preparation of thin-walled mesoporous CSAMCM-41(0.2).[9,10] Bulk amounts of catalysts, CSASBA-15(0.2), CSASBA-15(0.1) and CSAMCM-41(0.2), were synthesized using the above synthetic procedures for the selective synthesis of benzoquinones.

3.3. Investigation of catalytic stability

The mesoporous CSASBA-15 catalysts, *e.g.*, CSASBA-15(0.2) and CSASBA-15(0.1), used in oxidation reactions were regenerated by washing and drying at ambient temperature, as reported previously,[9] and the treated catalysts are denoted as recyclable CSASBA-15 catalysts, *i.e.* CSASBA-15(0.2) and CSASBA-15(0.1). Before application to the catalytic oxidation of TMP-OH, CSASBA-15(0.2) was simply washed several times using solvents, such as acetonitrile and dichloromethane, to improve the catalytic activity through the removal of any non-framework CuO nanoparticle species deposited on the active surfaces of the catalysts.[9]

3.4. Characterization

All the CSA functionalized mesoporous silica catalysts, including washed, and recyclable catalysts, were characterized using ICP-AES, a CHNS/O analyser, XRD, N_2-sorption isotherms, ^{29}Si MAS NMR spectroscopy, UV-vis DRS, field-emission scanning electron microscopy, and transmission electron microscopy, according to the published procedures.[9]

3.5. Oxidation of di-/tri-substituted phenols

For selective synthesis of benzoquinones, the liquid-phase oxidation of di-/tri-substituted phenols was carried out using various mesostructured CSA functionalized silica catalysts, recyclable catalysts and washed catalysts under vigorous stirring in a thermostated quartz-vessel reactor, as reported by Selvaraj.[16*k*] The details of the experimental procedure are shown in the ESI.†

4. Conclusions

Two-dimensional uniformly mesostructured CSASBA-15 catalysts have been successfully used in the preparation of benzoquinones by liquid-phase oxidation of di-/tri-substituted phenols. Washing studies confirm that the washed catalyst, W-CSASBA-15(0.2), recovered completely from the non-framework CuO nanoparticle species deposited on its surface has been successfully used in these oxidations to determine its catalytic activity. The recyclability and hot-catalytic filtration experiments for CSASBA-15(0.2) have been successfully performed. Recyclability studies of the oxidation reactions show that huge amounts of square planner Cu^{2+} species can be successfully incorporated to increase Lewis acid active sites on the silica surface of the CSASBA-15(0.2) catalyst. The results of the hot-catalyst filtrations in these oxidation reactions clearly confirm that the recyclable and W-CSASBA-15(0.2) catalysts are true heterogeneous catalysts. We clearly conclude on the basis of the catalytic results that the green mesoporous CSASBA-15 (0.2) is a highly active, recyclable, and environmentally friendly solid catalyst with an outstanding catalytic activity, among mesoporous metallosilicate catalysts.

Conflicts of interest

There are no conflicts to declare.

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