Catalysis Today 158 (2010) 377–384

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Highly selective synthesis of vitamin K_3 over mesostructured titanium catalysts

M. Selvaraj[a,*], M. Kandaswamy[b], D.W. Park[a], C.S. Ha[c]

[a] *School of Chemical and Biomolecular Engineering, Pusan National University, Busan 609735, Republic of Korea*
[b] *Department of Inorganic Chemistry, University of Madras, Chennai 600025, India*
[c] *Department of Polymer Science & Engineering, Pusan National University, Busan 609735, Republic of Korea*

ARTICLE INFO

Article history:
Available online 9 June 2010

Keywords:
pH-adjusting direct hydrothermal method
TiSBA-15
2M1N-OH oxidation
Catalytic stability
2M1N-OH conversion
Vitamin K_3 selectivity

ABSTRACT

Mesoporous TiSBA-15 catalysts have been synthesized using Pluronic P123 as a structuring agent under pH-adjusting direct hydrothermal (pH-aDH) method. The mesoporous TiSBA-15 catalysts characterized by sophisticated instrumental techniques via. ICP-AES, XRD, N_2 adsorption, FE-SEM, TEM, UV–vis DRS and ^{29}Si MAS NMR show their two-dimensional mesostructures with tetrahedral titanium on the silica surface. The highly ordered TiSBA-15 catalysts have been used in the liquid-phase oxidation of 2-methyl-1-naphthol (2M1N-OH) with hydrogen peroxide (H_2O_2, 30%), for the synthesis of vitamin K_3 (2-methyl-1,4-naphthoquinone). The recyclable TiSBA-15 catalysts have also been reused to find their catalytic activities. The influences of various reaction parameters such as temperature, time, ratios of reactant (2M1N-OH: H_2O_2) have been then investigated in this catalytic reaction for the highly selective synthesis of vitamin K_3. In addition, the liquid-phase oxidation of 2M1N-OH has been carried out with different solvents to find the best solvent with a good catalytic activity. Based on the all catalytic studies, TiSBA-15(6) catalyst is found to be a highly active and eco-friendly heterogeneous catalyst for the selective synthesis of vitamin K_3. Furthermore, TiSBA-15(6) catalyst has higher 2M1N-OH conversion (100%) and vitamin K_3 selectivity (93.2%) than other TiSBA-15 and TiMCM-41(40).

1. Introduction

Quinone derivatives are useful intermediates in the production of 'bio-activity fine chemicals' [1]. For example, vitamin K_3 (2-methyl-1,4-naphthoquinone or menadione) is synthesized by the oxidation of 2-methylnapthalene (MN) over CrO_3 in sulfuric acid [2,3], and it is widely used as a blood coagulating agent and is a key intermediate in the preparation of other vitamins such as vitamin K_1 (phylloquinone), vitamin K_2 (menaquinone), vitamin K_3 and vitamin K_4 (acetomenaphthone). Ever since the vitamin K_3 is found to be more active than vitamin K_1 and vitamin K_2 as antihemorrhagic agent [2], many methods have been described to bring about the controlled oxidation of MN using various oxidizing agents in the presence of catalyst [4–7]. In a well-known industrial process, MN is oxidized by CrO_3 in sulfuric acid to give vitamin K_3 with a yield of 30–60% [2,3]. However, in this stoichiometric oxidation about 18 kg of inorganic waste is produced for the synthesis of 1 kg of the target product and there is a necessary treatment for the removal of inorganic waste from the target product. No wonder this process is often cited as an example of a "dirty" fine chemical industry process [2,3,8].

The development of clean catalytic methods for the production of vitamin K_3 has received increasing attention over the last two decades. The vitamin K_3 is synthesized by the oxidation of MN with hydrogen peroxide (H_2O_2) or *tert*-butyl hydroperoxide (TBHP) over different catalysts [9–15]. Although the catalytic systems are good in the oxidation of MN, they have several drawbacks, as the yield of vitamin K_3 synthesized by the catalytic systems is ~40–60%. Moreover, several catalysts used in the catalytic systems become homogeneous as a result of leaching of the active species from a solid catalyst during the oxidation process. The catalytic systems cause the well-known problems with catalyst separation and inevitably lead to contamination of the product with traces of hazardous transition metals.

The development of cleaner, catalytic methods for the synthesis of vitamin K_3 is therefore a challenging goal. Several catalytic procedures based on the oxidation of MN are reported [11–18]. In general, the selectivity of vitamin K_3 is moderate due to formation of numerous side-products, the main one being isomeric 6-methyl-1,4-naphthoquinone (6-MNQ). Recently, 2-methyl-1-naphthol (2M1N-OH) instead of MN as a substrate is thus used for the synthesis of vitamin K_3 with a high selectivity. Moreover, this catalytic system mostly avoids the formation of some byproducts such as 6-MNQ and oxidation products of methyl group [19,20]. In addition, Mo–V-phosphoric Keggin heteropoly acids can also be used as reversibly acting oxidants to convert 2M1N-OH to vitamin K_3 with yield of up to 80–85% [21]. However, the excess

---

[*] Corresponding author. Tel.: +82 51 510 2397; fax: +82 51 512 8563.
E-mail address: chems@pnu.edu (M. Selvaraj).

0920-5861/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2010.04.041

V-containing compounds used in the oxidation of 2M1N-OH are ruled out as an environmentally benign route for the synthesis of vitamin K_3. The development of a 2M1N-OH oxidation process using an atom-efficient, clean oxidizing agent and a highly active heterogeneous catalyst remains a challenge.

A new mesoporous SBA-15 material is prepared using Pluronic P123 triblock copolymer as the structuring agent under strong acidic hydrothermal condition [22], and under the similar condition the introduction of more heteroatomic species into SBA-15 is very difficult because the formation of metal-oxo species in the mesoporous materials is much less. To overcome this problem, the high amounts of metal species such as Al, Fe, Ga, Ti, Mn, Sn and Nb, are successfully substituted/incorporated into SBA-15 under different direct hydrothermal methods [23–33]. Generally, a better hydrothermal stability of mesoporous material is an important factor for the catalytic studies. In this way, when the mesoporous MSBA-15 (where M stands for transition metal species) is compared with MMCM-41, it has more hydrothermal stability than MMCM-41, because, the MSBA-15 has thicker silica pore walls than MMCM-41 [30–34].

Several microporous and mesoporous titanium and iron silicates, including TS-1, Ti-Beta, Fe-Beta, Ti-MCM-41 and some others can be used in MN oxidation with 30% H_2O_2. The vitamin K_3 with selectivity of 35–63% obtains at 10–28% of MN conversion [12,16]. Recently, TiMMM-2 catalyst is extensively used in the synthesis of vitamin K_3 by the oxidation of 2M1N-OH [19,20]. However, to the best of our knowledge, the liquid-phase oxidation of 2M1N-OH using TiSBA-15 catalysts synthesized by pH-adjusting direct hydrothermal (pH-aDH) method has not been clearly reported with a higher vitamin K_3 selectivity, in the open literature so far.

Herein we report the selective synthesis of vitamin K_3 by the oxidation of 2M1N-OH with H_2O_2 over TiSBA-15 catalysts synthesized with different concentrations of titanium species by pH-aDH method. To find the mesoporous nature with the environments of titanium species coordinated on the silica surface of pore walls, the TiSBA-15 catalysts have been characterized by ICP-AES, XRD, N_2 adsorption, SEM, TEM, UV–vis DRS and ^{29}Si MAS NMR. The calcined TiSBA-15 catalysts have been used in the liquid-phase oxidation of 2M1N-OH for the synthesis of vitamin K_3. To prepare the highly selective synthesis of vitamin K_3, the oxidation of 2M1N-OH has been carried out with different reaction parameters such as temperature, time and reactant ratios. The catalytic activity of TiSBA-15 has also been investigated with different solvents. For the investigation of catalytic stabilities, the recyclable TiSBA-15 catalysts have also been reused. The catalytic results of the mesoporous catalysts used for the oxidation of 2M1N-OH have been correlated and compared for the selective synthesis of vitamin K_3.

2. Experimental

2.1. Materials

For the syntheses of Ti-containing mesoporous silica catalysts viz., TiSBA-15 and TiMCM-41, all chemicals viz., 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 (99%), tetraethylorthosilicate (98%, TEOS), hydrochloric acid (37%, HCl) and titanium(IV) isopropoxide (99.9%, TIP) were purchased from Sigma–Aldrich Chemical Inc. All the chemicals were used as received without further purification. Millipore water was used in all experiments.

For the synthesis of vitamin K_3, all chemicals viz., 2-methyl-1-naphthol (98%, 2M1N-OH), hydrogen peroxide (30% H_2O_2), acetonitrile (MeCN), ethyl acetate (EtAc), acetic acid (AcOH), methanol (MeOH) and ethanol (EtOH), were also purchased from Sigma–Aldrich Chemical Inc. and used as received without further purification.

2.2. Synthesis of TiSBA-15 catalysts

The mesoporous TiSBA-15 catalysts with $n_{Si}/n_{Ti} = 6$, 15, 20, 30 and 60 in gel, were synthesized using pH-aDH method. In a typical synthesis of TiSBA-15, 4 g of Pluronic P123 was stirred with 25 ml water to get a clear solution. In order to adjust the pH of this solution above 1.8, an aqueous HCl solution with n_{H_2O}/n_{HCl} ratio of 295 (75 ml of 0.25 M HCl solution) was added to the solution, and the mixture solution was again stirred for another 1 h. Then, 9 g of TEOS together with the required amount of TIP solution ($n_{Si}/n_{Ti} = 6$, 15, 20, 30 and 60) was added to the solution mixture, yielding a gel-like solution with pH > 2. The resulting mixture was again stirred for 24 h at 313 K before it was transferred into an autoclave to be hydrothermally treated at 373 K for 24 h. After hydrothermal process, the solid products were recovered by filtration, washed several times by water, and dried overnight at 373 K. The molar composition of the synthesis gel was 1 TEOS/0.0167–0.167 TIP/0.016 P123/0.43 HCl/127 H_2O. Finally, the samples were calcined at 813 K in air for 6 h for complete removal of the template. The calcined samples are denoted as TiSBA-15(6), TiSBA-15(15), TiSBA-15(20), TiSBA-15(30) and TiSBA-15(60).

2.3. Synthesis of TiMCM-41(40)

Mesoporous TiMCM-41 catalyst with a ratio of $n_{Si}/n_{Ti} = 40$, was synthesized using cetyltrimethylammonium bromide as the structuring agent with a molar ratio, 1 SiO_2/0.025 TIP/0.25 CTMABr/100 H_2O under basic direct hydrothermal method according to the previous published procedure [35]. The calcined catalyst is denoted as TiMCM-41(40). The catalysts were characterized using ICP-AES, XRD, N_2 adsorption, FTIR and UV–vis DRS according to the published procedure [35].

2.4. Characterization

The elemental composition of the resultant solid products was analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES, PerkinElmer, Optima 3000). The small-angle X-ray diffraction (XRD) patterns were recorded under ambient conditions on a Shimadzu XRD-6000 with Cu Kα radiation. The X-ray tube was operated at 40 kV and 30 mA while the diffractograms were recorded in the 2θ range of 0.6–10° with a 2θ step size of 0.01 and a step time of 10 s. Nitrogen adsorption/desorption measurements were conducted using Quantachrome Autosorb-1 by N_2 physisorption at 77 K. All catalytic samples were outgassed for 3 h at 523 K under vacuum ($p < 10^{-5}$ mbar) in the degas port of the sorption analyzer. The Brunauer–Emmett–Teller (BET) specific surface areas of the catalytic samples were calculated in the range of relative pressures between 0.05 and 0.35. The pore size distributions were calculated from the adsorption branch of the isotherm using the thermodynamics-based Barrett–Joyner–Halenda (BJH) method. The total pore volume was determined from the adsorption branch of the N_2 isotherm. Ultraviolet (UV)–vis diffuse reflectance (DR) spectra of TiSBA-15 catalysts were recorded at room temperature with a PerkinElmer Lambda 950 equipped with diffuse reflectance attachment, with $BaSO_4$ as the reference. ^{29}Si magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopic studies for calcined TiSBA-15 catalysts were carried out with a resonance frequency of 79.5 MHz for ^{29}Si on a Bruker DRX-400 spectrometer. Tetraethyl orthosilicate ($\delta = 82.4$ ppm from TMS) was used as the reference compound for ^{29}Si. Field-emission scanning electron microscopy (FE-SEM) images were obtained with

Table 1
Structural and textural parameters of calcined TiSBA-15 catalysts.

Catalysts	n_{H_2O}/n_{HCl} (molar ratio)	n_{Si}/n_{Ti}		a_o (Å)	A_{BET} (m^2/g)	V_p (cm^3/g)	d_p (Å)	$T_w = a_0 - d_p$ (Å)
		Gel	Product[a]					
SiSBA-15	40	–	–	118.2	908	1.07	87.4	30.8
TiSBA-15(6)	295	6	18.9	125.0	950	1.09	87.8	37.2
TiSBA-15(15)	295	15	33.4	122.0	990	1.09	88.0	34.0
TiSBA-15(20)	295	20	42.0	121.6	1015	1.09	88.0	33.6
TiSBA-15(30)	295	30	59.4	119.1	970	1.08	87.8	31.3
TiSBA-15(60)	295	50	88.6	118.8	915	1.07	87.6	31.2
TiSBA-15(6)[b]	–	–	21.4	124.0	960	1.10	87.8	36.2
TiSBA-15(60)[b]	–	–	88.6	118.7	918	1.10	87.6	31.1
TiMCM-41(40)[c]	–	40	42.0	48.6	1081	0.80	30.9	17.7
TiMCM-41(40)[b]	–	–	44.6	48.0	1001	0.80	30.9	17.1

a_o, unit cell parameter; A_{BET}, specific surface area; V_p, pore volume; d_p, pore diameter; and T_w, wall thickness.

[a] n_{Si}/n_{Ti} ratios in the products were determined by ICP-AES.

[b] The recyclable catalysts were used for three runs on the oxidation of 2M1N-OH.

[c] The catalyst was synthesized under basic direct hydrothermal method.

a HITACHI S-4800 microscope at an accelerating voltage of 5.0 kV. Transmission electron microscopy (TEM) images were collected on a JEOL 2010 electron microscope operated at an acceleration voltage of 200 kV.

2.5. *Oxidation of 2-methyl-1-naphthol*

Oxidation of 2M1N-OH to vitamin K_3 was carried out under vigorous stirring in a thermostatted glass vessel reactor at different temperatures. In a typical experimental procedure, 3 mg of TiSBA-15(6) catalyst and 0.03 mmol of 2M1N-OH dissolved in 5 ml of acetonitrile (MeCN) were taken in the reactor. After that, the reaction mixture was stirred under constant stirring, and subsequently the reaction temperature was slowly raised to 358 K and 0.15 mmol of H_2O_2 was carefully added through the septum to the reactant mixture and refluxed for 40 min. After completion of the reaction, the TiSBA-15(6) catalyst was filtered, and the products were collected. The oxidation of 2M1N-OH was conducted with different Ti-containing mesoporous silica catalysts. To find an optimal condition in the presence of TiSBA-15(6), the catalytic reaction was further carried out with different reaction parameters such as time, temperature, stoichiometric molar ratios of reactants (2M1N-OH-to-H_2O_2). For the identification of a better solvent, the oxidation of 2M1N-OH was carried out with different solvents like MeCN, EtAc, AcOH, MeOH and EtOH.

The preliminary oxidation product was analyzed with authentic sample using gas chromatograph (GC) using a VF5-MS capillary column coupled with a flame ionization detector (FID). Additionally, the product was further confirmed using a HP-5MS capillary column by gas chromatograph–mass spectroscopy using the Hewlett-Packard model 6890 gas chromatograph combined Hewlett-Packard 5973 mass spectroscopy (GC–MS), and ^{1}H nuclear magnetic resonance (NMR, Bruker 800). The coupling/overoxidation byproducts were also confirmed by GC–MS and ^{1}H NMR.

2.6. *Experimental procedures of catalytic stabilities*

The mesoporous Ti-containing silica catalysts viz., TiSBA-15(6), TiSBA-15(60) and TiMCM-41(40) were reused in the oxidation of 2M1N-OH to find their stabilities. In a typical experimental procedure, the TiSBA-15(6) catalyst used in a catalytic run was separated from the reaction mixture, washed with acetone several times and dried at 393 K. Finally, the TiSBA-15(6) catalyst was calcined at 773 K for 6 h in air to remove the adsorbed species. The treated catalyst is defined as 'recyclable TiSBA-15' catalyst, which is again reused to further catalytic runs. The similar procedure was used for recycling studies of other catalysts like TiSBA-15(60) and TiMCM-41(40). After completion of the reaction, the catalyst was filtered and analyzed by ICP-AES for finding the percentage of titanium, and the conversion of 2M1N-OH and selectivity of vitamin K_3 were calculated with the standard formulas followed by analyzing results of GC and GC–MS.

3. Results and discussion

3.1. *Inductively coupled plasma atomic emission spectroscopy*

For the analysis of elemental compositions, calcined TiSBA-15 catalysts synthesized using TIP as the titanium source and with different n_{Si}/n_{Ti} ratios are characterized by ICP-AES, and the results are listed in Table 1. Generally, in all cases, the n_{Si}/n_{Ti} ratios of the calcined catalysts are higher than n_{Si}/n_{Ti} ratios in the synthesis gel because the materials have been synthesized under acidic conditions; however, in this condition, titanium precursors are highly dissociated. In this synthesis method, the n_{Si}/n_{Ti} ratio decreases from 88.6 to 18.9 due to the higher titanium incorporated on the pore walls of SBA-15 by the formation of more titanium hydroxyl groups due to increasing the pH value from 1.6 to >2.

3.2. *X-ray diffraction*

Fig. 1 shows the powder XRD patterns of TiSBA-15 catalysts synthesized with different n_{Si}/n_{Ti} ratios. All samples show five well-resolved peaks, which are indexed to the (1 0 0), (1 1 0), (2 0 0), (2 1 0) and (3 0 0) reflections, as shown in Fig. 1. Due to increasing the titanium content, the XRD peaks shift to lower angle, and an increase in the *d*-spacing values and unit cell parameters is observed as compared to the purely siliceous SBA-15, as shown in Table 1. The expansion in the unit cell dimension with decreasing n_{Si}/n_{Ti} ratio could be attributed to the larger radius of Ti^{4+} than that of Si^{4+}, and/or the longer Ti–O bond distance as compared to the Si–O bond distance. Therefore, these results show that the mesostructural order has not been affected by tetravalent titanium ions incorporated in the framework of SBA-15.

3.3. *N_2 adsorption*

Fig. 2 shows the nitrogen adsorption isotherms of calcined TiSBA-15 catalysts prepared with different n_{Si}/n_{Ti} ratios. All isotherms show a sharp condensation step at relative pressures in the range of 0.63–0.91. It can also be seen that the capillary condensation step shifts to the higher relative pressures with increasing titanium content in the calcined TiSBA-15 catalysts, resulting in the

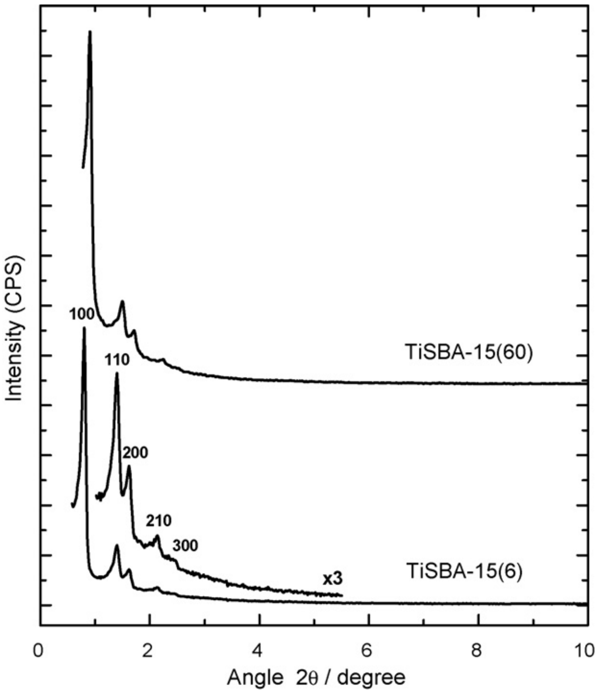


Fig. 1. XRD powder patterns of calcined TiSBA-15 catalysts.

increase of pore diameter with the increase of titanium content in the catalysts. Moreover, the physicochemical properties such as pore diameter, pore volume and pore wall thickness increase but the specific surface area decreases with the decrease of n_{Si}/n_{Ti} up to 33.4 in the calcined TiSBA-15 catalysts (Table 1). This evidence supports that the higher titanium ions are incorporated on the surface pore walls of SBA-15. In addition, the TiSBA-15 catalysts almost keep the well textural properties even the ratio of n_{Si}/n_{Ti} is decreased up to 18.9 (Table 1). It is interesting to note that the structural and textural properties of TiSBA-15 catalysts synthesized with very high loadings of titanium are still maintained with structural regularity. From the observation of the textural properties of TiSBA-15(6) and TiSBA-15(15) catalysts, it is observed that a trace amount of TiO_2 nanoparticles can be dispersed on the silica pore walls. A more information is given in the part of UV–vis DRS of TiSBA-15 catalysts.

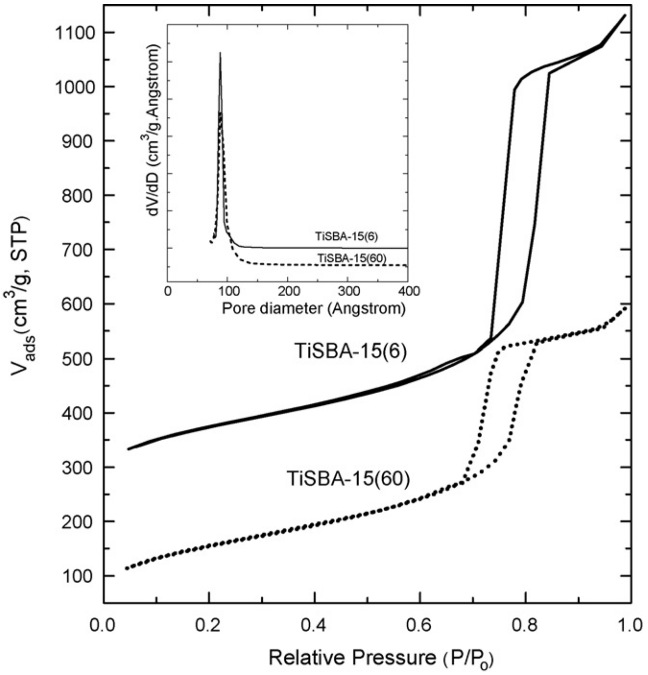


Fig. 2. Nitrogen adsorption isotherms of calcined TiSBA-15 catalysts.

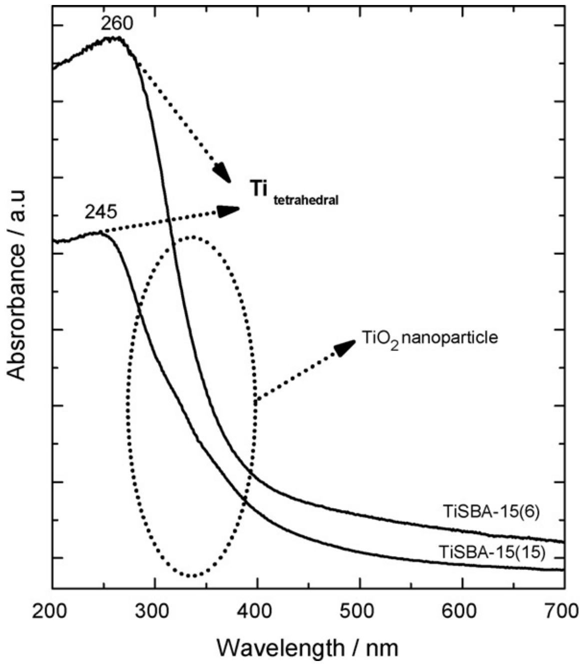


Fig. 3. UV–vis DR spectra of calcined TiSBA-15 catalysts.

3.4. Ultraviolet–vis diffuse reflectance spectroscopy

UV–vis DRS has been used to verify whether titanium species is substituted in the framework of SBA-15 or its corresponding oxide is formed on the surface of SBA-15. The UV–vis DRS spectra for calcined TiSBA-15 catalysts show about the nature and the coordination of titanium species incorporated into the mesoporous silica (Fig. 3). The all TiSBA-15 catalysts possess the absorption bands around 230–260 nm, but the TiSBA-15(6) and TiSBA-15(15) catalysts show the week absorption bands around 310–340 nm only. The absorption peaks showed around 230–260 nm are typically associated with Ti–O bonds which are unambiguously assigned to a low-energy charge-transfer transition of tetrahedral oxygen ligands and central Ti^{4+} species. These results suggest that the most of the titanium species in the calcined TiSBA-15 catalysts have been tetrahedrally incorporated into the framework of SBA-15; in addition, a trace amount of extra framework TiO_2 nanoparticles can be formed together with the titanium species tetrahedrally substituted on the silica surface of TiSBA-15(6) and TiSBA-15(15). This evidence directly confirms that the tetrahedral Ti^{4+} species are coordinated in the calcined TiSBA-15 catalysts. In literature, the similar results have also been reportedly confirmed in direct-synthesis of TiMCM-41 [35,36]. The results of UV–vis DRS noticeably confirm that the pH-aDH method favors for the synthesis of TiSBA-15 with very high amounts of tetrahedral titanium species loadings.

3.5. ^{29}Si magic angle spinning nuclear magnetic resonance spectroscopy

^{29}Si MAS NMR spectra of calcined TiSBA-15(6) catalyst and SiSBA-15 are shown in Fig. 4. On the basis of the results of NMR,

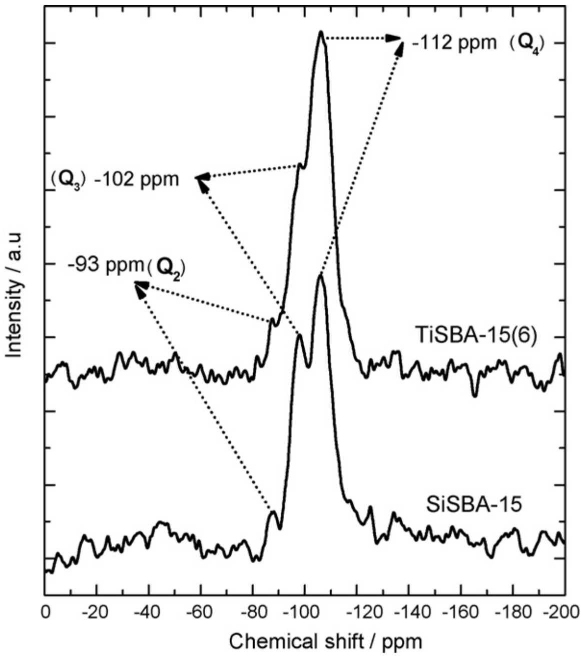


Fig. 4. ^{29}Si MAS NMR spectra of calcined SiSBA-15 and TiSBA-15(6).

it is observed that the chemical shift peak at −112 ppm assigns to the $Si(OSi)_4$ (Q_4) sites, and other chemical shift peaks at −102 and −93 ppm are attributed to the $Si–(OSi)_3OH$ (Q_3) and $Si–(OSi)_2(OH)_2$ (Q_2) sites, respectively. The spectra observed for the calcined TiSBA-15 catalysts are relatively poor in comparison to that of SiSBA-15. There is a progressive reduction in the intensity of Q_3 (due to the large number of silanol groups in SBA-15 Q_3 intensity is always higher) sites with increasing titanium species content [29]. The same effect is found by Selvaraj and Lee when both V and Mo species are incorporated into MCM-41 using direct hydrothermal method [37]. From the results, it is found that the Ti^{4+} species is strongly bonded to the mesoporous silica walls.

3.6. Field-emission scanning electron microscopy and transmission electron microscopy

Fig. 5 shows the images of FE-SEM and TEM for calcined TiSBA-15(6) catalyst. The FE-SEM images show that the TiSBA-15(6) catalyst synthesized with n_{Si}/n_{Ti} ratio of 18.9 has the rope-like hexagonal morphology, and it can have a long rope-like aspect of as much as several hundred micrometers that is made up of a bundle of ropes of diameter ~12 μm (Fig. 5 (top)). The TEM images show the uniform size and ordered hexagonal arrays for the calcined TiSBA-15 catalysts, as shown in Fig. 5 (bottom) for calcined TiSBA-15(6). A nice uniform pore size and the best channels form with increasing titanium species. It is remarkably confirmed that the TEM images show well-ordered hexagonal arrays of 1D mesoporous channels which are further confirming that TiSBA-15 catalysts have a 2D *p*6*mm* hexagonal structure [22]. From the TEM image, the average thickness of the wall is ~3.7 nm, which is much larger than that for MCM-41. The pore diameter is around ~8.7 nm, which is in agreement with the N_2 adsorption measurements.

Two-dimensional hexagonally mesostructured TiSBA-15 catalysts with very high titanium species loadings have thus been prepared using pH-aDH method. Mesoporous TiSBA-15 catalysts synthesized under highly acidic condition ($pH < 1$) has a low amount of titanium incorporated into SBA-15, possibly due to the high solubility of titanium precursors, which hinder their incorporation into the silica walls of SBA-15. However, the hydrolysis rate of both TEOS used as the silica precursor and TIP used as the titanium precursor, may not be equally matched with each other. Therefore, an attempt to increase the amount of titanium species

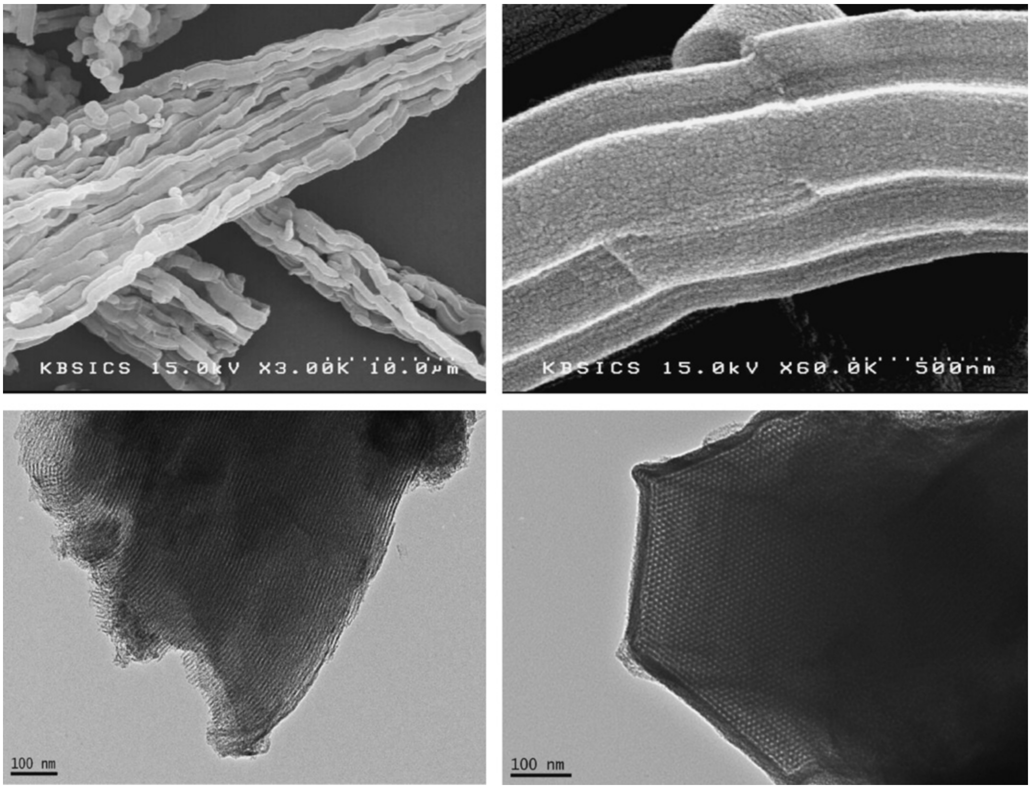
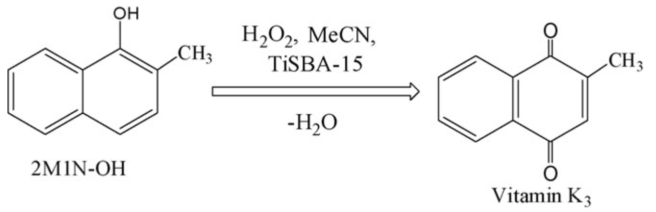


Fig. 5. FE-SEM (top) and TEM (bottom) images for TiSBA-15(6).



Scheme 1. Reaction pathway of 2M1N-OH oxidation.

(n_{Si}/n_{Ti} ratio = 6 in gel) incorporated in the framework has been done in this study by simply adjusting the gel pH using the aqueous HCl solution prepared with n_{H_2O}/n_{HCl} molar ratio of 295 without changing the structural integrity of the parent SBA-15 materials. Several oxidation catalysts (CrSBA-15, MnSBA-15, SnSBA-15 and NbSBA-15) prepared using the similar synthesis mechanism by Selvaraj and his research group are thoroughly explained in the published articles [30–33]. The mesoporous nature of TiSBA-15 catalysts synthesized with very high tetrahedral titanium loadings by pH-aDH method has been confirmed by the characteristic result of ICP-AES, XRD, N_2 adsorption, UV–vis DRS, ^{29}Si MAS NMR, FE-SEM, and TEM.

3.7. Catalytic activity of TiSBA-15 catalysts in the oxidation of 2-methyl-1-naphthol

The oxidation of 2M1N-OH with H_2O_2 has been carried out over TiSBA-15 catalysts, as shown in Scheme 1. Effects of various reaction parameters such as reaction temperature, time, ratios of 2M1N-OH-to-H_2O_2, solvents and recycles have been studied to obtain higher 2M1N-OH conversion as well as vitamin K_3 selectivity.

The oxidation of 2M1N-OH has been carried out over mesoporous Ti-containing silica catalysts using the reaction conditions noted in Table 2. The order of catalytic activity found in the selectivity of vitamin K_3 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 conversion of 2M1N-OH (100%) and selectivity of vitamin K_3 (93.2%), and it has higher selectivity of vitamin K_3 than other TiSBA-15 catalysts, as shown in Table 2. The observed higher activity of TiSBA-15(6) is tentatively ascribed to its two-dimensional space and high loading of tetrahedral Ti^{4+} species on the surface of SBA-15, resulting in a higher number of accessible active sites because the tetrahedral Ti^{4+} species incorporated in the framework of SBA-15 produces the high numbers of Lewis acid sites to enhance catalytic activity in the oxidation of 2M1N-OH. Moreover, when the catalytic oxidation of 2M1N-OH is carried out under the similar reaction condition using the similar titanium content of the catalysts, viz., TiSBA-15(20) and TiMCM-41(40), as shown in Table 1, the selectivity of vitamin K_3 in TiSBA-15(20) is significantly higher as compared to that of TiMCM-41(40), as shown in Table 2. A state point can conclude from this evidence that the well uniformly ordered mesoporosity material with high titanium loadings plays an important catalytic role in the production of vitamin K_3 with a good selectivity. On the basis of catalytic activity of different Ti-containing mesoporous catalysts, a well uniformly hexagonal ordered TiSBA-15(6) is found to be a promising heterogeneous catalyst in the liquid-phase oxidation of 2M1N-OH for the highly selective synthesis of vitamin K_3.

Table 2
Oxidation of 2M1N-OH over mesoporous Ti-containing silica catalysts[a].

Catalysts	Conversion of 2M1N-OH (%)	Selectivity of vitamin K_3 (%)
TiSBA-15(6)	100	93.2
TiSBA-15(15)	90.7	75.2
TiSBA-15(20)	80.6	53.4
TiSBA-15(30)	75.6	41.5
TiSBA-15(60)	65.3	27.4
TiMCM-41(40)	70.3	48.7
3rd run[b]	94.3	84.7
3rd run[c]	65.0	27.1
3rd run[d]	65.3	45.3
SiSBA-15	30.4	3.0
Blank	20.2	2.0

[a] Reaction conditions: 3 mg of catalyst, 1:5 ratio of 2M1N-OH-to-H_2O_2 (0.03 mmol of 2M1N-OH and 0.15 mmol of H_2O_2), reaction time = 40 min, 5 ml of MeCN, temperature = 358 K.

[b] Recyclable TiSBA-15(6) catalyst was used for recycling reactions.

[c] Recyclable TiSBA-15(60) catalyst was used for recycling reactions.

[d] Recyclable TiMCM-41(40) catalyst was used for recycling reactions.

For recycling studies, several titanium containing mesoporous catalysts viz., TiSBA-15(6), TiSBA-15(60) and TiMCM-41(40), have been examined to find their catalytic stabilities as follows. Initially, the mesoporous catalysts used in the catalytic reaction usually suffer from the loss of their catalytic activities, and hence the catalysts need to be regenerated by calcination. The recycled catalysts were washed four times with acetone and dried at 393 K overnight. Finally the catalysts were calcined at 773 K for 6 h in air for complete removal of the organics and unreacted 2M1N-OH molecules. The treated catalysts have been reused for this reaction as shown in Table 2. The conversion of 2M1N-OH and selectivity of vitamin K_3 can be decreased in the first two runs (values not shown in Table 2). On the basis of first two runs, it is observed that the extra framework TiO_2 nanoparticles leach on the catalytic surface (the range of n_{Si}/n_{Ti} ratios obtained by ICP-AES is from 21.4 to 88.6 as shown in Table 1). But, runs of conversion and selectivity remain constant after three runs, indicating that the titanium species cannot be further leached on the mesoporous matrix, which is in good agreement with ICP-AES results of filtrate solutions where no titanium ion is detected and the absence of non-framework titanium is further confirmed by the UV–vis DRS result of third run of the catalysts. This reaction was also carried out using SiSBA-15 synthesized by pH-aDH method [30] as well as without catalyst. In both cases, conversion of 2M1N-OH (~20–30%) forms with a trace amount of selectivity of vitamin K_3 (Table 2), thus indicating that major activity is only due to titanium species incorporated in the framework of SBA-15.

Since the TiSBA-15(6) is a promising catalyst in this catalytic oxidation reaction, it has been further used in this reaction with different reaction parameter such as reaction temperature, time, ratios of reactant (2M1N-OH and HP) and solvents, to find the best reaction conditions for the highly selective synthesis of vitamin K_3.

The oxidation of 2M1N-OH has been conducted with different reaction temperatures and times using the reaction conditions shown in Figs. 6 and 7, for obtaining a high selective synthesis of vitamin K_3. When the reaction temperature and time are decreased from 358 K to 338 K and 40–20 min respectively, the rate of vitamin K_3 formation, decreases. This may be due to the less activity of Lewis active sites on the surface of the catalyst at low reaction temperature and time. One can solidly conclude from the catalytic results obtained with different reaction temperatures and times that, the suitable parameters like 358 K and 40 min promote the decomposition of an intermediate, 2-methyl-1-naphthol peroxo-titanium complex, which further reacts with H_2O_2 for the selective formation of vitamin K_3 with an excellent selectivity [19,20].

To find the best ratio of 2M1N-OH-to-HP for the highly selective synthesis of vitamin K_3, the oxidation of 2M1N-OH has been carried out with different ratios of $n_{2M1N\text{-}OH}/n_{H_2O_2}$ using the reaction conditions shown in Fig. 8. When this reaction is carried out with 1:5 ratio, a conversion of 2M1N-OH (100%) as well as selectivity of vitamin K_3 (93.2%) is observed. The selectivity of vitamin K_3 decreases in other ratios 1:4, 1:3, 2:5

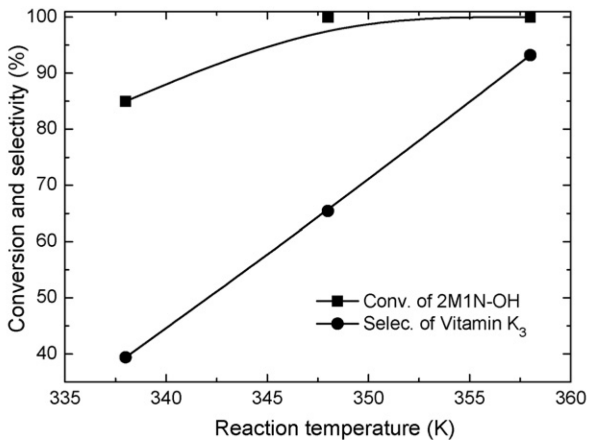


Fig. 6. Variation of reaction temperature on the synthesis of vitamin K_3 by oxidation of 2MN1-OH with H_2O_2. Reaction conditions: 3 mg of TiSBA-15(6) catalyst, 1:5 ratio of 2M1N-OH-to-H_2O_2 (0.03 mmol of 2M1N-OH and 0.15 mmol of H_2O_2), reaction time = 40 min, 5 ml of MeCN.

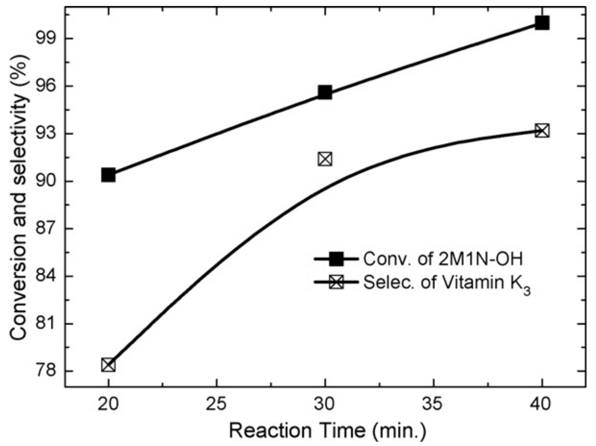


Fig. 7. Variation of reaction time on the synthesis of vitamin K_3 by oxidation of 2MN1-OH with H_2O_2. Reaction conditions: 3 mg of TiSBA-15(6) catalyst, 1:5 ratio of 2M1N-OH-to-H_2O_2 (0.03 mmol of 2M1N-OH and 0.15 mmol of H_2O_2), reaction time = 40 min, 5 ml of MeCN, reaction temperature = 358 K.

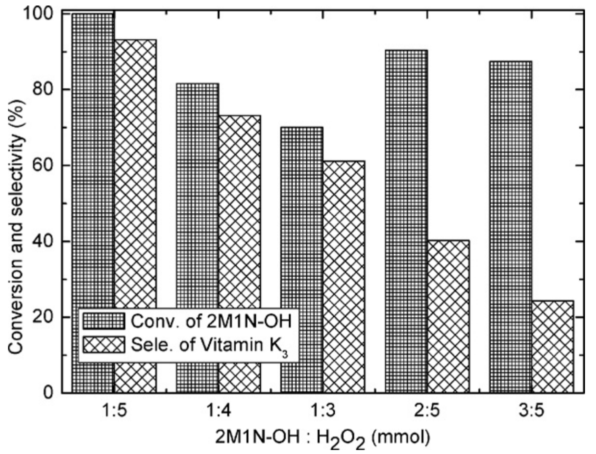


Fig. 8. Variation of 2M1N-OH-to-H_2O_2 over TiSBA-15(6) catalyst. Reaction conditions: 3 mg of TiSBA-15(6) catalyst, reaction temperature = 358 K, reaction time = 40 min, 5 ml of MeCN.

Table 3
Oxidation of 2M1N-OH with different solvents[a].

Solvent (5 ml)	Conversion of 2M1N-OH (%)	Selectivity of vitamin K_3 (%)
MeCN	100	93.2
AC	65.0	43.4
EtAc	93.6	52.6
AcOH	100	43.5
MeOH	100	29.6
EtOH	85.0	21.5
MeCN[b]	90.0	65.3
MeCN[c]	100	57.0
Solvent free	67.0	15.6

[a] Reaction conditions: 3 mg of TiSBA-15(6) catalyst, 1:5 ratio of 2M1N-OH-to-H_2O_2 (0.03 mmol of 2M1N-OH and 0.15 mmol of H_2O_2), reaction time = 40 min; reaction temperature = 358 K.

[b] 1 ml of solvent.

[c] 4 mmol of water.

and 3:5. A possible reason in conclusion is that the formation of coupling/overoxidation products, such as 4,4-di(2-methyl-1-naphthol) and 4,4-di(2-methylnaphthoquinone) as the byproducts, is found when the concentration of 2M1N-OH or H_2O_2 is increased. Note that the vitamin K_3 is formed by one electron oxidation mechanism, and it involves the formation of aryl radicals which easily promotes the coupling or overoxidation byproducts when the reaction is conducted with unevenly ratios of 2M1N-OH-to-H_2O_2 [19,20]. In addition, the pore size/active surface of the catalyst may be blocked by the coupling/overoxidation products. On the basis of the effects of the ratios, it is manifestly found that 1:5 mmol ratio of 2M1N-OH-to-H_2O_2 is an optimum ratio for the highly selective synthesis of vitamin K_3.

The oxidation of 2M1N-OH has been carried out with different solvents like, MeCN, EtAc, AcOH, MeOH and EtOH using the reaction conditions noted in Table 3, for obtaining a high selective synthesis of vitamin K_3. MeCN is a dipolar solvent that gives a high conversion and selectivity because it has a high ability to form the complexes on the catalytic surface for a long time in the liquid-phase catalytic oxidations. Other solvents like EtAc, AcOH, MeOH and EtOH give the low selectivity of vitamin K_3 because they lead low catalytic activity on the surface of TiSBA-15(6). When this reaction is carried out with 1 ml of MeCN under the similar reaction condition, the conversion of 2M1N-OH and selectivity of vitamin K_3 decrease because the high quantity of 2M1N-OH may not be homogeneously dissolved and reacted completely with H_2O_2 (Table 3). It is clearly found that selectivity of vitamin K_3 dropped only (Table 3) with maximum conversion of 2M1N-OH when the catalytic reaction is conducted with addition of more quantity of water under similar condition, because, under this condition, the coupling/overoxidation products may be formed. The vitamin K_3 forms with ~15.6% of selectivity when the catalytic reaction is conducted without solvent under the similar reaction condition. Overall, comparing the catalytic activity with different solvents, it is obviously found that MeCN is the best solvent for highly selective synthesis of vitamin K_3.

4. Conclusions

The pH-aDH method is an environmentally friendly and efficient hydrothermal method, and it has been developed for the synthesis of TiSBA-15 catalysts with very high mesostructural order and high titanium content. ICP-AES results of TiSBA-15 catalysts show that the amounts of titanium species are highly incorporated into SBA-15. The studies of XRD and N_2 adsorption show that the structural and textural properties of TiSBA-15 catalysts have not been affected by the higher amounts of titanium species incorporated in the pore walls of SBA-15. The results of UV–vis DRS and ^{29}Si

MAS NMR confirms that most of the Ti^{4+} ions in calcined TiSBA-15 catalysts exist as tetrahedral in the framework of SBA-15. The studies of SEM and TEM confirm that TiSBA-15 catalysts have a long rope-like morphology and uniform pore diameter, respectively. The TiSBA-15 catalysts have been successfully used in the liquid-phase oxidation of 2M1N-OH with H_2O_2 for the synthesis of vitamin K_3. When the TiSBA-15 catalysts are reused in the catalytic reaction, the leaching of non-framework titanium nanoparticles on the surface of the catalyst can be found in first two runs, but the catalytic activity of TiSBA-15 catalysts remains constant after three runs because no leaching of titanium on the silica surface is observed. From the studies of recyclables, it is found that the TiSBA-15(6) has higher catalytic stability in the liquid-phase oxidation of 2M1N-OH as compared to other titanium containing mesoporous catalysts. From the optimized reaction conditions, it is obviously found that a higher selectivity of vitamin K_3 is obtained at 358 K for 40 min using 1:5 ratio of 2M1N-OH-to-H_2O_2 with 5 ml of MeCN. From the studies of different solvents, it is clearly found that MeCN is a better solvent than other solvents. On the basis of all catalytic studies, it is clearly found that the TiSBA-15(6) catalyst is a highly active, recyclable and promising heterogeneous catalyst for the selective synthesis of vitamin K_3.

References

[1] J. Rodriguez, E. Quinoa, R. Riguera, B.M. Peters, L.M. Abrell, P. Crews, Tetrahedron 48 (1992) 6667–6680.
[2] H. Hiranuma, S.I. Miller, J. Org. Chem. 47 (1982) 5083–5088.
[3] R.A. Sheldon, Top. Curr. Chem. 164 (1993) 21–43.
[4] A.B. Sorokin, A. Tuel, New J. Chem. 23 (1999) 473–476.
[5] M. Periasamy, M.V. Bhatt, Tetrahedron Lett. 4 (1978) 4561–4562.
[6] R.P. Kreh, R.M. Spotnitz, J.T. Lundquist, J. Org. Chem. 54 (1989) 1526–1531.
[7] J. Kowalski, J. Ploszynska, A. Sobkowiak, J. Appl. Electrochem. 28 (1998) 1261–1264.
[8] W. Bonrath, T. Netscher, Appl. Catal. A: Gen. 280 (2005) 55–73.
[9] W. Adam, W.A. Herrmann, W. Lin, Ch.R. Saha-Moller, R.W. Fischer, J.D.G. Correia, Angew. Chem. Int. Ed. 33 (1994) 2475–2477.
[10] W.A. Herrmann, J.J. Haider, R.W. Fischer, J. Mol. Catal. A: Chem. 138 (1999) 115–121.
[11] J. Kowalski, J. Ploszynska, A. Sobkowiak, Catal. Commun. 4 (2003) 603–608.
[12] O.S. Anunziata, L.B. Pierella, A.R. Beltramone, J. Mol. Catal. A: Chem. 149 (1999) 255–261.
[13] A. Sorokin, A. Tuel, Catal. Today 57 (2000) 45–59.
[14] S. Yamaguchi, M. Inone, S. Enomoto, Chem. Lett. (1985) 827–828.
[15] S. Narayanan, K.V.V.S.B.S.R. Murthy, K.M. Reddy, N. Premchander, Appl. Catal. A: Gen. 228 (2002) 161–165.
[16] O.S. Anunziata, A.R. Beltramone, J. Cussa, Appl. Catal. A: Gen. 270 (2004) 77–85.
[17] R. Song, A. Sorokin, J. Bernadou, B. Meunier, J. Org. Chem. 62 (1997) 673–678.
[18] M. Selvaraj, J. Kim, T.G. Lee, Stud. Surf. Sci. Catal. 156 (2005) 867–872.
[19] O.A. Kholdeeva, O.V. Zalomaeva, A.N. Shmakov, M.S. Melgunov, A.B. Sorokin, J. Catal. 236 (2005) 63–68.
[20] M. Frostin-Rio, D. Pujol, C. Bied-Charreton, M. Perree-Fauvet, A. Gaudemer, J. Chem. Soc., Perkin Trans. 1 (1984) 1971–1979.
[21] K.I. Matveev, V.F. Odjakov, E.G. Zhizhina, J. Mol. Catal. A: Chem. 114 (1996) 151.
[22] D. Zhao, J. Feng, Q. Huo, N. Melosh, G.H. Fredrickson, B.F. Chmelka, G.D. Stucky, Science 279 (1998) 548–552.
[23] S. Wu, Y. Han, Y.-C. Zou, J.-W. Song, L. Zhao, Y. Di, S.-Z. Liu, F.-S. Xiao, Chem. Mater. 16 (2004) 486–492.
[24] Y. Li, L. Zhang, Q. Yang, Z. Wei, Z. Feng, C. Li, J. Phys. Chem. B 108 (2004) 9739–9744.
[25] M. Selvaraj, S. Kawi, Stud. Surf. Sci. Catal. 165 (2007) 219–222.
[26] Y. Li, Z. Feng, Y. Lian, K. Sun, L. Zhang, G. Jia, Q. Yang, C. Li, Microporous Mesoporous Mater. 84 (2005) 41–46.
[27] M. Selvaraj, S. Kawi, Catal. Today 131 (2008) 82–89.
[28] M. Selvaraj, S. Kawi, D.-W. Park, C.S. Ha, Microporous Mesoporous Mater. 117 (2009) 586–595.
[29] W. Zhang, J. Lu, B. Han, M. Li, J. Xiu, P. Ying, C. Li, Chem. Mater. 14 (2002) 3413–3421.
[30] M. Selvaraj, S. Kawi, Chem. Mater. 19 (2007) 509–519.
[31] M. Selvaraj, T.G. Lee, J. Phys. Chem. B 110 (2006) 21793–21802.
[32] M. Selvaraj, S. Kawi, J. Mater. Chem. 17 (2007) 3610–3621.
[33] M. Selvaraj, S. Kawi, D.-W. Park, C.S. Ha, J. Phys. Chem. C 113 (2009) 7743–7749.
[34] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, Nature 359 (1992) 710–712.
[35] M. Selvaraj, B.H. Kim, T.G. Lee, Chem. Lett. 34 (2005) 1290–1291.
[36] A. Corma, J.L. Jorda, M.T. Navarro, F. Ray, Chem. Commun. (1998) 1899–1900.
[37] M. Selvaraj, T.G. Lee, Micropor. Mesopor. Mater. 85 (2005) 39–51.