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PAPER

Selective synthesis of vitamin K_3 over mesoporous NbSBA-15 catalysts synthesized by an efficient hydrothermal method†

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Well hexagonally ordered NbSBA-15 catalysts synthesized by an efficient hydrothermal method were used, for the first time, for the selective synthesis of vitamin K_3 by liquid-phase oxidation of 2-methyl-1-naphthol (2MN1-OH) under various reaction conditions. The recyclable NbSBA-15 catalysts were also reused to find their catalytic activities. To investigate the leaching of non-framework niobium species on the surface of silica networks, the results of original and recyclable NbSBA-15 catalysts were correlated and compared. To find an optimum condition for the selective synthesis of vitamin K_3, the washed NbSBA-15(2.2pH) was extensively used in this reaction with various reaction parameters such as temperature, time and ratios of reactant (2M1N-OH to H_2O_2), and the obtained results were also demonstrated. Additionally, the liquid-phase oxidation of 2M1N-OH was carried out with different solvents to find the best solvent with a good catalytic activity. Based on the all catalytic studies, the vitamin K_3 selectivity (97.3%) is higher in NbSBA-15(2.2pH) than that of other NbSBA-15 catalysts, and the NbSBA-15(2.2pH) is found to be a highly active and eco-friendly heterogeneous catalyst for the selective synthesis of vitamin K_3.

1. Introduction

Vitamin K_3 (2-methyl-1,4-naphthoquinone or menadione) is widely used as a blood coagulating agent and is an important intermediate in the synthesis of other vitamins,[1] such as vitamin K_1 (phylloquinone), vitamin K_2 (menaquinone) and vitamin K_4 (acetomenaphthone). The catalytic oxidation of 2-methylnaphthalene (MN) to vitamin K_3 over CrO_3 in sulfuric acid is firstly reported.[2,3] In this catalytic system the vitamin K_3 yield is reported at around 30–60%, ~18 kg of inorganic waste is produced in the production of 1 kg of the target product, and there is an essential treatment for the removal of inorganic waste from the target product.[2,3] The diverse catalysts are also applied in the production of vitamin K_3 by the oxidation of MN with hydrogen peroxide (H_2O_2) or *tert*-butyl hydroperoxide (TBHP).[4–10] Even though the above catalytic systems produce a reasonably yield of vitamin K_3 by the catalytic oxidation of MN, some catalysts become homogeneous with the leaching of the active species from the solid catalysts during the oxidation process. These catalytic systems cause the well-known problems with catalyst separation and inevitably lead to contamination of the product with traces of hazardous transition metals, and are thus considered as a "dirty" fine chemical industry process.[2,3,11] Since vitamin K_3 is found to be more active than vitamin K_1 and vitamin K_2 as an antihemorrhagic agent, the catalytic oxidation of MN using different oxidizing agents over different catalysts is extensively reported.[2,12–15] Recently, the new inorganic and organic modified mesoporous SBA-15 materials are used as eco-friendly catalysts[16,17] and as light-emitting support materials.[18,19]

Since the development of clean catalytic methods for the production of fine chemicals has received increasing attention over the last two decades, the development of cleaner, catalytic methods for the synthesis of vitamin K_3 is therefore a challenging goal. Using different catalytic methods, the catalytic oxidation of MN is carried out over diverse microporous and mesoporous solid catalysts.[6–10,20–22] The vitamin K_3 selectivity is moderate due to the formation of numerous side-products; the main one is an isomeric 6-methyl-1,4-naphthoquinone (6-MNQ). To avoid byproducts such as 6-MNQ and methyl group oxidized products from MN, 2-methyl-1-naphthol (2M1N-OH) instead of MN is used as a substrate for the synthesis of vitamin K_3 with high selectivity.[23,24] Mo–V-phosphoric Keggin heteropoly acids can be used as the reversibly acting oxidants to convert 2M1N-OH into vitamin K_3 with a yield around 80–85%.[25] In addition to synthesis of vitamin K_3 with a higher selectivity, the non-catalytic oxidation of 2M1N-OH with molecular oxygen is also carried out at elevated pressure (3 atm) at room temperature.[26]

An atom-efficient, clean oxidizing agent as well as a very active heterogeneous catalyst remains a great challenge in the

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development of a clean catalytic process for the oxidation of 2M1N-OH. Recently, vitamin K_3 has been synthesized by the liquid-phase oxidation of 2M1N-OH over the mesoporous titanosilicate catalysts, TiMMM-2 and TiSBA-15.[23,27] However, to the best of our knowledge, the oxidation of 2M1N-OH using NbSBA-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 literature so far.

In this report, using the pH-aDH method, the two-dimensional mesostructured NbSBA-15 catalysts synthesized with different concentrations of niobium species have been used for the selective synthesis of vitamin K_3 by the oxidation of 2M1N-OH with H_2O_2. To prepare the highly selective synthesis of vitamin K_3 over washed NbSBA-15(2.2pH), the oxidation of 2M1N-OH has been carried out with different reaction parameters and solvents. For the investigation of catalytic stabilities, the recyclable NbSBA-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 synthesis of mesoporous NbSBA-15 catalysts, all chemicals *viz.*, triblock copolymer poly(ethylene glycol)-*block*-poly (propylene glycol)-*block*-poly(ethylene glycol) (Pluronic P123, molecular weight = 5800, $EO_{20}PO_{70}EO_{20}$), tetraethylorthosilicate (98%, TEOS), hydrochloric acid (37%, HCl) and niobium chloride (>99.9%) were purchased from Sigma-Aldrich Chemical Inc. All the chemicals were used as received without further purification.

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), acetone (Ac), 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 and characterization of mesoporous NbSBA-15 catalysts

In our synthesis conditions, no mineral acid was added to the synthesis mixture. The mesostructured NbSBA-15 catalysts (n_{Si}/n_{Nb} = 10) have been synthesized by the pH-aDH method using the molar gel composition, 1 TEOS/0.1 Nb_2O_5/0.016 P123/127–210 H_2O according to our previously published procedure.[28] The synthesized NbSBA-15 catalysts are named as NbSBA-15(1.6pH), NbSBA-15(1.8pH), NbSBA-15(2.0pH) and NbSBA-15(2.2pH), and the pH-adjusting values in the preparation of samples were 1.6, 1.8, 2.0 and 2.2, accordingly. All the synthesized catalytic samples were characterized using the relevant instrumental techniques such as ICP-AES, XRD, N_2 adsorption–desorption, UV-vis DRS, TEM, TEM-EDS, SEM and XPS, according to the published procedure.[28]

2.3. Oxidation of 2-methyl-1-naphthol

Oxidation of 2M1N-OH to vitamin K_3 was carried out under vigorous stirring in a thermostated glass vessel reactor at different temperatures. In a typical experimental procedure, 4 mg of NbSBA-15(2.2pH) catalyst and 0.05 mmol of 2M1N-OH dissolved in 7 ml of acetonitrile (MeCN) were added to the reactor. Thereafter, the reaction mixture was stirred under constant stirring, and subsequently the reaction temperature was slowly raised to 348 K, and 0.25 mmol of H_2O_2 was carefully added through the septum to the reactant mixture and refluxed for 45 min. After completion of the reaction, the NbSBA-15(2.2pH) catalyst was filtered, and the products were collected. The oxidation of 2M1N-OH was also conducted with other NbSBA-15 mesoporous catalysts.

The preliminary oxidation product was analyzed with an 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.

Mesoporous NbSBA-15 catalysts *viz.*, NbSBA-15(2.2pH) and NbSBA-15(1.6pH) were reused in the oxidation of 2M1N-OH to find their stabilities. In a typical experimental procedure, the NbSBA-15(2.2pH) catalyst used in a catalytic run was separated from the reaction mixture, washed with acetone several times and dried at 393 K. Finally, the catalyst was calcined at 773 K for 6 h in air to remove the adsorbed species. The treated catalyst is defined as 'recyclable NbSBA-15(2.2pH)', which was again used in further catalytic runs. A similar procedure was used for recycling studies of NbSBA-15(1.6pH). The hot-catalysts filtration experiments were examined twice after four runs, to find the catalytic activity of NbSBA-15(2.2pH). After completion of the reaction, the catalyst was filtered and analyzed by ICP-AES, EDS and XPS to find the percentage of niobium content, and the 2M1N-OH conversion and vitamin K_3 selectivity were calculated with standard formulae followed by analyzing results of GC and GC-MS.

To remove the non-framework niobium ions, a high amount of NbSBA-15(2.2pH) was washed with acetone several times and dried at 393 K. The treated catalyst is named as 'washed NbSBA-15(2.2pH)', which is used to find an optimal condition with different reaction parameters such as time, temperature and stoichiometric molar ratios of reactants (2M1N-OH to H_2O_2). For the identification of a better solvent over washed NbSBA-15(2.2pH) catalyst, the oxidation of 2M1N-OH was carried out with different solvents including MeCN, Ac, AcOH, MeOH and EtOH.

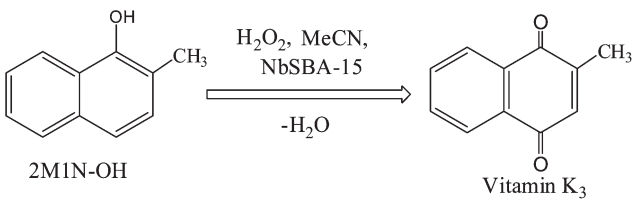
3. Results and discussion

The mesoporous SBA-15 material is usually prepared using Pluronic P123 triblock copolymer as the structuring agent under strong acidic hydrothermal conditions. Under these conditions, 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 reduced. To overcome this problem, the pH-aDH method has been introduced and used for the synthesis of MSBA-15 catalysts (M = Al, Cr, Mn, Sn, Ga, Ce, Ti and V) with high metal content, and the synthesized MSBA-15 catalysts have been used for certain catalytic reactions.[29–39] A high amount of niobium species are successfully substituted/incorporated into SBA-15 under the pH-aDH method without mineral acid.[24] The mesoporous NbSBA-15 catalyst has more hydrothermal stability than NbMCM-41 due to having thicker silica pore walls.[28,40,41]

The NbSBA-15 catalysts synthesized by the pH-aDH method have been characterized by ICP-AES, XRD, N_2 adsorption–desorption, UV-vis DRS, TEM, TEM-EDS, SEM and XPS according to the published procedure.[28] ICP-AES and TEM-EDS studies show that the rich Nb ions are highly incorporated on the silica pore walls. The elemental composition of NbSBA-15 catalysts is listed in Table 1. XRD results confirm that the calcined NbSBA-15 catalysts have well ordered 2D hexagonal mesostructures with space group *P6mm*, and the unit cell parameter in the calcined NbSBA-15 catalysts increases with increasing Nb ion content, and with increasing pH from 1.6 to 2.2, as shown in Table 1 and Fig. 1S.† After washing treatments, the washed NbSBA-15(2.2pH) has almost the same structural integrity. By increasing the Nb ion content, N_2 adsorption results reveal that the textural parameters of NbSBA-15(2.2pH) increase as compared to other NbSBA-15 catalysts (Table 1). The niobium content on the surface of the silica network also increases when the pH is increased from 1.6 to 2.2 (Fig. 2S†). The textural parameters of the washed NbSBA-15(2.2pH) also remain constant with a good isotherm related to IUPAC classification. The UV-vis DRS results prove that the Nb^{5+} ions in the calcined NbSBA-15 catalysts are tetrahedrally coordinated to Si^{4+} on the silica walls, and it can be also observed that their intensities increase with increasing pH from 1.6 to 2.2 (Fig. 3S†). However, the non-framework Nb_2O_5 species dispersed on the surface of SBA-15 cannot be easily found by UV-vis DRS analysis. The calcined NbSBA-15 catalysts and washed NbSBA-15(2.2pH) have been further characterized by XPS (Fig. 4S†). The XPS results clearly confirm that the Nb^{5+} species can be tetrahedrally coordinated into SBA-15, whereas a small amount of Nb_2O_5 species is dispersed on the SBA-15.[28] Most of the Nb_2O_5 species dispersed on the surface of NbSBA-15(2.2pH) are completely removed by the washing treatments.[28] The results of TEM and FE-SEM correspondingly show the uniform pore diameter and rope-like hexagonal mesoporous structure of NbSBA-15 catalysts (Fig. 5S and 6S†). On the basis of characteristic results, it is interestingly to note that the well-ordered NbSBA-15 catalysts with a huge number of tetrahedral Nb^{5+} species have been successfully synthesized using the pH-aDH method.

The mesoporous NbSBA-15 catalysts have been used in the liquid-phase oxidation of 2M1N-OH (Scheme 1) with the reaction conditions noted in Table 2, and their catalytic activities based on vitamin K_3 selectivity are in the following order: NbSBA-15(2.2pH) > NbSBA-15(2.0pH) > NbSBA-15(1.8pH) > NbSBA-15(1.6pH). Among the all NbSBA-15 catalysts, the mesoporous NbSBA-15(2.2pH) exhibits the best catalytic activity and gives a higher 2M1N-OH conversion and vitamin K_3 selectivity than other NbSBA-15 catalysts (Table 2) due to the higher loading of tetrahedral Nb^{5+} species on the surface of inner silica pore walls. The higher catalytic activity of NbSBA-15(2.2pH) is also tentatively ascribed to its two-dimensional mesostructure that leads the higher number of accessible active sites, and the large number of tetrahedral Nb^{5+} species incorporated in the framework of SBA-15 produces high numbers of Lewis acid sites[28,42] to enhance catalytic activity in the oxidation of 2M1N-OH. Strukul *et al.* reported that the vitamin K_3 selectivity is 93% in the oxidation of 2M1N-OH over Nb_2O_5–SiO_2 catalyst.[43] On the basis of catalytic activity, the NbSBA-15(2.2pH) has superior catalytic activity in the synthesis of vitamin K_3 than other NbSBA-15 and Nb_2O_5–SiO_2



Scheme 1 2M1N-OH oxidation over NbSBA-15.

Table 1 Structural and textural parameters of mesoporous NbSBA-15 catalysts[a]

		n_{Si}/n_{Nb} ratio								
			Product							
Sample	pH in gel	Gel	ICP-AES	EDS	XPS	a_o (Å)	A_{BET} ($m^2\ g^{-1}$)	d_p (Å)	V_p ($cm^3\ g^{-1}$)	$t_w = a_o - d_p$ (Å)
NbSBA-15(1.6pH)	1.6	10	20.6	20.5	20.6	104.0	788	71.7	1.22	32.3
NbSBA-15(1.8pH)	1.8	10	18.7	18.4	18.5	105.8	810	72.8	1.22	33.0
NbSBA-15(2.0pH)	2.0	10	16.2	16.0	16.1	107.0	850	73.8	1.23	33.2
NbSBA-15(2.2pH)	2.1	10	12.6	12.2	12.3	108.4	903	74.6	1.24	33.8
NbSBA-15(2.2pH)[b]	—	—	12.9	12.9	12.8	108.3	901	74.6	1.24	33.7
NbSBA-15(2.2pH)[c]	—	—	12.9	12.8	12.9	108.3	904	74.6	1.24	33.7
NbSBA-15(1.6pH)[c]	—	—	22.0	22.1	22.0	102.9	780	71.2	1.21	31.7

[a] a_o, unit cell parameter; A_{BET}, specific surface area; V_p, pore volume; d_p, pore diameter, T_w, wall thickness. [b] The catalyst was washed four times using acetone and dried at 393 K, prior to use in this reaction. [c] The results were obtained for the reusable catalysts used for the 4th run in the oxidation of 2M1N-OH.

Table 2 Oxidation of 2M1N-OH over mesoporous NbSBA-15 catalysts[a]

Catalysts	2M1N-OH conversion (%)	Vitamin K_3 yield (%)	Vitamin K_3 selectivity (%)
NbSBA-15(1.6pH)	91.4	81.2	88.9
NbSBA-15(1.8pH)	93.2	84.0	90.2
NbSBA-15(2.0pH)	95.5	91.7	96.0
NbSBA-15(2.2pH)	100	97.3	97.3
NbSBA-15(2.2pH)[b]	96.5	91.2	94.5
NbSBA-15(2.2pH)[c]	96.6	91.5	94.7
NbSBA-15(1.6pH)[c]	90.4	70.1	77.6
Filtrate solution[d]	3.5	<1	2.5
SBA-15	30.5	1.0	3.5

[a] *Reaction conditions*: 4 mg of catalyst, 1 : 5 ratio of 2M1N-OH to H_2O_2 (0.05 mmol of 2M1N-OH and 0.25 mmol of H_2O_2), reaction time = 45 min, 7 ml of MeCN, temperature = 348 K. [b] Washed catalyst. [c] The recyclable catalysts were used for the 4th run. [d] The results obtained from the hot-filtrate solution after the NbSBA-15(2.2pH) catalyst removal.

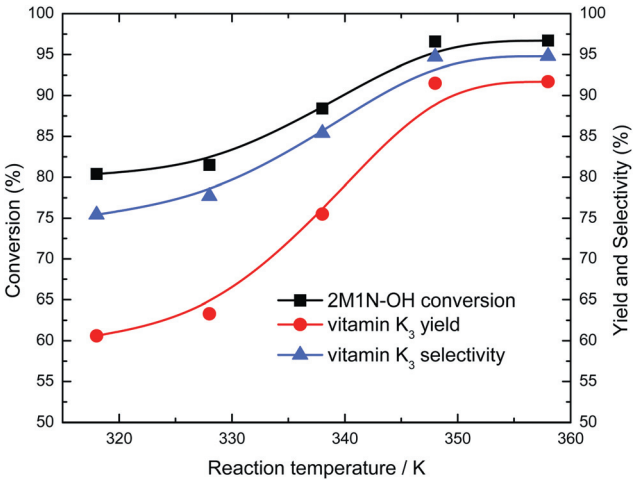


Fig. 1 Synthesis of vitamin K_3 with different reaction temperatures. *Reaction conditions*: 4 mg of washed NbSBA-15(2.2pH), 1 : 5 ratio of 2M1N-OH to H_2O_2 (0.05 mmol of 2M1N-OH and 0.25 mmol of H_2O_2), reaction time = 45 min, 7 ml of MeCN.

catalysts and 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.

For recycling studies, the two mesoporous catalysts *viz.*, NbSBA-15(2.2pH) and NbSBA-15(1.6pH) synthesized using different pH values in the gel under the pH-aDH method 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. In the first two runs 2M1N-OH conversion decreases, and vitamin K_3 yield as well as its selectivity also decreases (values not shown in Table 2). On the basis of first two runs, it is observed that the extra framework Nb_2O_5 and their nanoparticles can be leached on the inner silica surface of pore walls, as shown in Table 1. But, after four runs the 2M1N-OH conversion and vitamin K_3 selectivity remain constant, indicating that the niobium ions have not been further leached on the mesoporous matrix, which is in good agreement with the results of ICP-AES and EDS of filtrate solutions where no niobium ions are detected, and the absence of non-framework Nb_2O_5 and their nanoparticles have been further confirmed by the XPS results of 4th run of the catalysts (Table 1). Additionally, the washed NbSBA-15(2.2pH) was also used in this reaction to find its catalytic activity. The effect of this result is nearly the same as that of NbSBA-15(2.2pH) used for the 4th run, as shown in Table 2. In a similar trend, the vitamin K_3 yield also increases with increasing tetrahedral Nb^{5+} species on the surface of inner silica pore walls of SBA-15. After finding the results of four runs, hot-catalyst filtration experiments were also carried out twice at 348 K during oxidation of 2M1N-OH over NbSBA-15(2.2pH). In this case, the filtrate solution gives a very low 2M1N-OH conversion (3.5%) with a trace amount of vitamin K_3 yield due to leaching of non-framework Nb_2O_5 on the surface of catalyst, indicating that the oxidation of 2M1N-OH takes place on the surface of NbSBA-15 (2.2pH) and that this is a true heterogeneous process.[44] This reaction was also carried out using pure SBA-15 synthesized by the pH-aDH method.[29,31] In this case, conversion of 2M1N-OH (~30%) forms with a trace amount of vitamin K_3 selectivity (Table 2), thus indicating that major activity is only due to niobium ions incorporated in the framework of SBA-15.

Since the washed NbSBA-15(2.2pH) catalyst is a promising catalyst in this catalytic oxidation reaction, it has been further used in this reaction with different reaction parameters such as reaction temperature, time, ratios of reactant (2M1N-OH to H_2O_2) and solvents, to find the best reaction conditions for the highly selective synthesis of vitamin K_3.[23]

The oxidation of 2M1N-OH over washed NbSBA-15(2.2pH) catalyst has been carried out with different reaction temperatures and times using the reaction conditions shown in Fig. 1 and 2, for obtaining a high selective synthesis of vitamin K_3. When the reaction temperature and time are decreased from 348 to 318 K and 45 to 15 min, respectively, the rate of vitamin K_3 formation with 2M1N-OH conversion decreases due to the formation of C–C coupling products such as dinaphthol and dinaphthaquinone due to lower catalytic activity on the surface of the catalyst at a low reaction temperature or time.[45] The 2M1N-OH conversion and vitamin K_3 yield as well as its selectivity are similar at 348 and 358 K. These results show that a higher temperature (358 K) does not affect the catalytic activity of washed NbSBA-15(2.2pH). After 45 min, the 2M1N-OH conversion slightly increases whereas the vitamin K_3 yield as well as its selectivity decreases due to the formation of C–C coupling products with some amount of tars.[23,45] This result shows that the vitamin K_3 can be affected at a longer reaction time. One can conclude from the corresponding catalytic results that the suitable parameters like 348 K and 45 min promote the decomposition of an intermediate, 2-methyl-1-naphthol peroxo-niobium complex, which further reacts with H_2O_2 for the selective formation of vitamin K_3 with an excellent selectivity.

To find the best ratio of 2M1N-OH to H_2O_2 over washed NbSBA-15(2.2pH) catalyst for the selective synthesis of vitamin

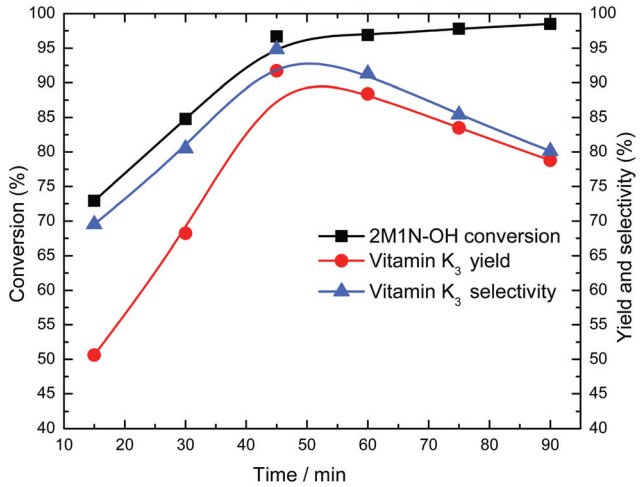


Fig. 2 Synthesis of vitamin K_3 with different reaction times. *Reaction conditions*: 4 mg of washed NbSBA-15(2.2pH), 1 : 5 ratio of 2M1N-OH to H_2O_2 (0.05 mmol of 2M1N-OH and 0.25 mmol of H_2O_2), reaction temperature = 348 K, 7 ml of MeCN.

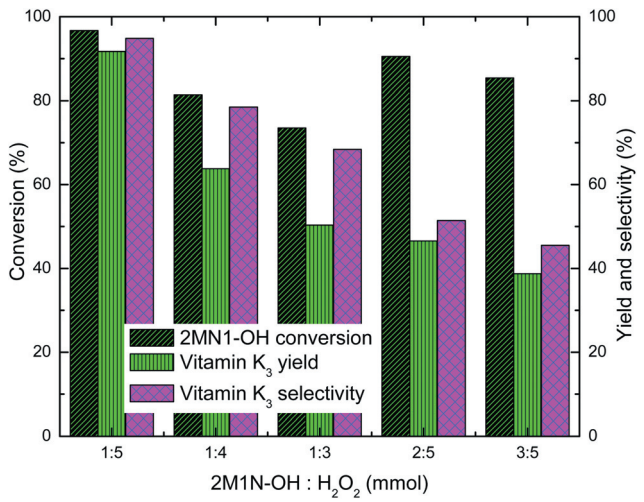


Fig. 3 Synthesis of vitamin K_3 with different ratios of 2M1N-OH to H_2O_2. *Reaction conditions*: 4 mg of washed NbSBA-15(2.2pH), reaction temperature = 348 K, reaction time = 45 min, 7 ml of MeCN.

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 noted in Fig. 3. The 2M1N-OH conversion (96.5%) and vitamin K_3 yield (91.2%) as well as its selectivity (94.5%) can be observed in the ratio of 1 : 5. The vitamin K_3 selectivity decreases in other ratios in the following order 1 : 4 < 1 : 3 < 2 : 5 < 3 : 5. In addition, the 2M1N-OH conversion and vitamin K_3 selectivity gradually decrease in the order of ratios, 1 : 5 < 1 : 4 < 1 : 3. But, in the ratios of 2 : 5 and 3 : 5 the 2M1N-OH conversion only increases whereas the vitamin K_3 selectivity decreases. A possible reason is that the formation of C–C coupling products such as dinaphthol and dinaphthoquinone as the byproducts can be observed when the concentration of 2M1N-OH is increased. But, the formation of menadione epoxide can be only observed when the concentration of H_2O_2 is increased. However, a trace amount of menadione epoxide is observed with a very low selectivity due to the formation of its cleavage products.[45] The C–C dimer products can be formed when the reaction is conducted with uneven ratios of 2M1N-OH to H_2O_2.[23,24,27] In addition, the somewhat active surfaces on the catalyst may be deactivated by the C–C dimer products and unreacted substrates. On the basis of the ratio results, 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.

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

Solvent (7 ml)	2M1N-OH conversion (%)	Vitamin K_3 yield (%)	Vitamin K_3 selectivity (%)
MeCN	96.5	91.2	94.5
Ac[b]	96.4	87.1	90.4
AcOH	95.4	39.6	41.5
MeOH	97.4	18.0	25.6
EtOH	81.0	14.9	18.5
MeCN[c]	85.0	53.8	63.3
MeCN[d]	97.2	52.5	54.0
Ac[e]	95.5	73.8	77.3
Solvent free	67.0	7.1	10.6

[a] *Reaction conditions*: 4 mg of washed NbSBA-15(2.2pH), 1 : 5 ratio of 2M1N-OH to H_2O_2 (0.05 mmol of 2M1N-OH and 0.25 mmol of H_2O_2), reaction time = 45 min, temperature = 348 K; [b] 328 K. [c] 2 ml of solvent. [d] 5 mmol of water. [e] 318 K.

The oxidation of 2M1N-OH over washed NbSBA-15(2.2pH) catalyst has been carried out with different solvents like MeCN, Ac, AcOH, MeOH and EtOH, using the reaction conditions noted in Table 3. MeCN is a dipolar solvent that produces a higher 2M1N-OH conversion as well as vitamin K_3 selectivity because of the formation of reactant complexes on the catalytic surface for a long time in the liquid-phase catalytic oxidation. A similar effect was obtained for Ac. However, the Ac solvent involves in the formation acetone peroxide and produces a large amount of undesired side products at a low temperature (Table 3) with a decrease in vitamin K_3 selectivity.[43] Although MeOH, EtOH and AcOH are green solvents, they give the low vitamin K_3 selectivity because of leading low catalytic activity on the surface of catalysts. When this reaction is carried out with 2 ml of MeCN under similar reaction conditions, the 2M1N-OH conversion and vitamin K_3 selectivity decrease because the high quantity of 2M1N-OH may not be homogeneously dissolved and react completely with H_2O_2 (Table 3). It is clearly found that vitamin K_3 selectivity dropped only with maximum 2M1N-OH conversion when the catalytic reaction is conducted with addition of more quantity of water under similar condition (Table 3). This may be due to the formation of C–C coupling products. The vitamin K_3 forms with ~10.6% of selectivity when the catalytic reaction was carried out without solvent under similar reaction conditions. Overall, from the catalytic activity compared with different solvents, it is obviously found that MeCN is the best solvent for the selective synthesis of vitamin K_3.

4. Conclusions

The mesostructured NbSBA-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. From the recycling studies, it is

found that NbSBA-15(2.2pH) has a higher catalytic activity in the liquid-phase oxidation of 2M1N-OH as compared to other NbSBA-15 catalysts. From the optimized reaction conditions over washed NbSBA-15(2.2pH), it is obviously found that a higher vitamin K_3 selectivity can be obtained at 348 K for 45 min using 1 : 5 ratio of 2M1N-OH to H_2O_2 with 7 ml of MeCN. From the studies of different solvents, it is found that MeCN is the optimal solvent. On the basis of all catalytic studies, it can be clearly observed that the NbSBA-15(2.2pH) catalyst is a highly active, recyclable and promising heterogeneous catalyst for the selective synthesis of vitamin K_3.

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