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Highly efficient and clean synthesis of verbenone over well ordered two-dimensional mesoporous chromium silicate 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 609-735, Republic of Korea*
[b] *Department of Inorganic Chemistry, University of Madras, Chennai 600025, India*
[c] *Department of Polymer Science & Engineering, Pusan National University, Busan 609-735, Republic of Korea*

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ABSTRACT

Two-dimensional mesoporous SBA-15 catalysts synthesized by different hydrothermal methods have been used, for the first time, in the liquid-phase oxidation of α-pinene with *t*-butyl hydrogen peroxide (TBHP) for the synthesis of verbenone (V═O). The recyclable CrSBA-15 catalysts have also been reused in this reaction to find their catalytic activities. To investigate the leaching of chromium species on the silica surface, CrSBA-15(8) has been treated with ammonium acetate solution, and it has been also treated with boiling water for the investigation of hydrothermal stability. The treated CrSBA-15(8) catalyst has been used in the catalytic reaction for finding the effects of catalytic stability. The influences of various reaction parameters such as temperature, time, ratios of reactant (α-pinene-to-TBHP) have been extensively investigated for the synthesis of V═O. In addition, the liquid-phase oxidation of α-pinene has been conducted with different solvents to find the best solvent with a good catalytic activity. On the basis of all investigations with a hypothetical reaction pathway of α-pinene oxidation, the CrSBA-15(8) catalyst is found to be a highly active, recyclable and promising heterogeneous catalyst in the liquid-phase oxidation of α-pinene for highly selective synthesis of V═O. Furthermore, CrSBA-15(8) catalyst has higher selectivity of V═O (88.2%) than other CrSBA-15 and CrMCM-41.

1. Introduction

α-Pinene is a cheap and renewable raw material with a great potential application in the production of various flavors, fragrances, agrochemicals, and therapeutically active substances [1]. Particularly, the oxygenated derivatives (verbenol (V–OH), verbenone (V═O) and α-pinene oxide (PO)) obtained from the oxidation of α-pinene are of high practical importance as flavor chemicals and precursors of a range of fine chemicals, including citral, menthol, sandalwood fragrance santalol, and taxol, as well as vitamins A and E [1–3].

V═O is a bicyclic ketone terpene and valuable fine chemical, and it is used in perfumery, aromatherapy, herbal teas, spices and herbal remedies. V═O is synthesized with a low total selectivity of V–OH/V═O by the autoxidation of α-pinene, which is conducted with free-catalysts [4]. The selectivity of V═O is found to improve when the catalytic reaction is carried out with the transition metals and their complexes [5–7]. For example, the homogeneous catalysts such as $Co(NO_3)_2$ and $Co(4\text{-}MeC_5H_3N)_2Br_2$ [8,9], are used in the oxidation of α-pinene for the synthesis of V═O with the maximal selectivity of V–OH/V═O (76%). Several attempts to heterogenize cobalt-containing catalysts effective in the oxidation of α-pinene are made, including encapsulation of Co(II)Saloph complexes in zeolite-Y [6] and immobilization of $Co(NO_3)_2$ in silica matrix by the sol–gel method [10]. However, the selectivity of V═O is low in the catalytic systems under unkind reaction conditions, and the leaching of the active metal species and recyclability of the catalysts are not clearly reported to demonstrate the catalyst stability.

Generally, fine chemicals or high value chemicals are frequently produced by “green oxidants and catalysts”, which reduce the chemically contaminated effluents that cause a great environmental impact [11,12]. Since 1996, the green heterogeneous catalysts are used in the production of V═O with a good selectivity. Microstructured CrAPO-5 catalyst is used in the oxidation of α-pinene with *t*-butyl hydrogen peroxide (TBHP), and it produces a conversion of α-pinene (85%) and selectivity of V═O (77%) [13]. The conversion of α-pinene (32%) and selectivity of V═O (63%) are obtained when the liquid phase of the oxidation of α-pinene with TBHP over silica–titania co-gel catalyst [14]. Several single site catalysts (solid catalysts containing Ti(IV), Zr(IV) and Fe(III) isolated in inorganic matrixes) are used in the oxidation of α-pinene with hydrogen peroxide (H_2O_2) for obtaining a good conversion of α-pinene with the total selectivity of V–OH/V═O (82%) [15]. The

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

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liquid-phase oxidation of α-pinene is also carried out using H_2O_2 over TiMCM-41 catalyst, which gives a good selectivity of V=O [16].

A new mesoporous SBA-15 material is prepared using Pluronic P123 triblock copolymer as the structuring agent under strong acidic hydrothermal condition [17], but 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. For solving this problem, the high amount of metal species such as Al, Fe, Ga, Ti, Mn, Sn and Nb, are successfully substituted/incorporated into SBA-15 under different direct hydrothermal conditions [18–28]. Generally, a better hydrothermal stability of mesoporous materials 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 due to pore walls that are thicker than those of MMCM-41 [29]. Particularly, Selvaraj and Kawi extensively reported the well uniformly ordered CrSBA-15 catalysts along with enhanced hydrothermal stability [25], and the CrSBA-15 catalysts are used in the oxidation of anthracene for the selective synthesis of anthraquinone with 100% selectivity [30]. Recently, Co-POM/NH_2-SBA-15 catalyst is used in the aerobic oxidation of α-pinene with molecular oxygen for the synthesis of V=O with a good selectivity [31]. However, a few mesoporous MMCM-41 and MSBA-15 catalysts are used in the oxidation of α-pinene for the production of V=O with a good selectivity, and to the best of our knowledge, the liquid-phase oxidation of α-pinene over CrSBA-15 has not been clearly reported with a high selectivity of V=O, in the open literature so far.

Herein we report the selective synthesis of V=O by the oxidation of α-pinene over CrSBA-15 catalysts. The CrSBA-15 catalysts synthesized with different hydrothermal conditions have been used in the liquid-phase oxidation of α-pinene for the synthesis of V=O. The oxidation of α-pinene has been carried out with different optimal conditions such as temperature, time and reactant ratios. The catalytic activity of CrSBA-15 with different solvents has been also investigated. For the investigation of catalytic stability, the recyclable CrSBA-15 catalysts have also been reused in this catalytic reaction. CrSBA-15(8) has been washed with ammonium acetate solution to investigate the leaching of chromium species on the silica surface of SBA-15, and the washed CrSBA-15(8) catalyst has been also used in the catalytic reaction to find the effects of catalytic activity. Furthermore, the CrSBA-15(8) treated with boiling water for the investigation of hydrothermal stability has also been used to find the effects of catalytic activity. The catalytic results of all mesoporous catalysts have been correlated and compared for the selective synthesis of V=O.

2. Experimental

2.1. Materials

For the syntheses of CrSBA-15 and CrMCM-41 mesoporous catalysts, all chemicals viz. triblock copolymer poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) (Pluronic P123, molecular weight = 5800, $EO_{20}PO_{70}EO_{20}$), cetyltrimethylammonium bromide, tetraethylorthosilicate (TEOS), hydrochloric acid (HCl), ammonium fluoride (NH_4F) and Cr(III) nitrate nonahydrate (CN) were purchased from Aldrich Chemical Inc. All the chemicals were used as received without further purification. Millipore water was used in all experiments.

For the synthesis of V=O, all chemicals viz. α-pinene (98%), *t*-butyl hydrogen peroxide (70% TBHP), hydrogen peroxide (30% H_2O_2), acetone (AC), acetonitrile (MeCN), chlorobenzene (CB), toluene (TE), were also purchased from Aldrich Chemical Inc. and used as received without further purification.

2.2. pH-adjusting direct hydrothermal (pH-aDH) method

Mesoporous CrSBA-15 catalysts with n_{Si}/n_{Cr} = 8, 16, 20, 25 and 50 in gel, were synthesized using pH-adjusting method according to our previous published procedure [25]. In a typical synthesis of CrSBA-15, 4 g of Pluronic P123 was stirred with 25 ml water to get a clear solution with pH < 1.6. 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 CN solution (n_{Si}/n_{Cr} = 8, 16, 20, 25, and 50) were 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 gel was 1 TEOS/0.02–0.125 Cr_2O_3/0.016 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 CrSBA-15(8), CrSBA-15(16), CrSBA-15(20), CrSBA-15(25) and CrSBA-15(50).

2.3. Ammonium fluoride (NH_4F) acidic method

Mesoporous CrSBA-15 catalysts were synthesized under NH_4F acidic method according to the published procedure [30]. In a typical synthesis of CrSBA-15(0.04F), 2 g of Pluronic 123 triblock copolymer and 0.04 mol% of NH_4F were dissolved in 75 ml of HCl solution (pH 1.5) to get solution A. Then, 4.6 ml of TEOS and a certain amount of CN solution (molar ratio of n_{Si}/n_{Cr} = 10) were added to 5 ml of HCl aqueous solution (pH 1.5) to get solution B. Solution B was stirred at room temperature for about 0.5–3 h before it was added dropwise to solution A. The solution mixture was then stirred vigorously for 24 h at 313 K before it was transferred into an autoclave to age for 24 h at 373 K. The resultant solid was filtered, washed, and dried at 333 K for 15 h. After the solid was calcined at 813 K for 10 h, mesoporous CrSBA-15 samples were finally obtained. Additionally, the CrSBA-15(0.07F) catalyst was also synthesized with 0.07 mol% of NH_4F under the similar procedure. To find the effects of mesostructural order, the CrSBA-15(WF) was synthesized without NH_4F under similar procedure as mentioned above [30].

2.4. Synthesis of CrMCM-41(40)

Mesoporous CrMCM-41 catalyst with a ratio of n_{Si}/n_{Cr} = 40 in gel, was synthesized using cetyltrimethylammonium bromide as the structuring agent with a molar ratio, 1 SiO_2/0.025 Cr_2O_3/0.25 CTMABr/100 H_2O under hydrothermal condition according to the previous published procedure [32]. The calcined catalyst is denoted as CrMCM-41(40). All the catalysts synthesized for this work are listed in Table 1.

2.5. Characterization

The calcined CrSBA-15 mesoporous catalysts synthesized by different hydrothermal conditions were characterized by inductively coupled plasma atomic emission spectroscopy (ICP-AES), X-ray diffraction (XRD), nitrogen adsorption/desorption, electron spin resonance spectroscopy (ESR), ^{29}Si magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy, field-emission scanning electron microscopy (FE-SEM) and transmission

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

Catalysts	n_{H_2O}/n_{HCl} (molar ratio)	n_{Si}/n_{Cr}		a_0 (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
CrSBA-15(8)	295	8	9.9	127.4	999	1.10	89.4	38.0
CrSBA-15(16)	295	16	17.3	122.7	1015	1.09	88.5	34.2
CrSBA-15(20)	295	20	45.0	121.3	1024	1.08	87.3	34.0
CrSBA-15(25)	295	25	52.1	118.5	1037	1.08	87.2	31.3
CrSBA-15(50)	295	50	99.8	114.5	1063	1.09	86.5	28.0
CrSBA-15(8)[b]	–	–	12.3	127.3	985	1.10	89.4	37.9
CrSBA-15(8)[c]	–	–	9.9	127.4	986	1.10	89.4	38.0
CrMCM-41(40)[d]		40	45	44.4	883	0.70	26.9	17.5

[a] n_{Si}/n_{Cr} ratios of products are determined by ICP-AES.
[b] Washed catalyst.
[c] Hydrothermal stability was investigated in boiling water at 373 K for 168 h.
[d] CrMCM-41 was synthesized under basic direct hydrothermal method [32].

electron microscopy (TEM) according to the published procedure [25,30]. Additionally, ultraviolet (UV)–vis diffuse-reflectance spectroscopy (DRS) spectra of CrSBA-15 catalysts synthesized by different hydrothermal conditions were also recorded at room temperature with a PerkinElmer Lambda 950 equipped with diffuse-reflectance attachment, with $BaSO_4$ as the reference. For the investigation of textural and structural integrity with the nature of chromium species, the CrSBA-15(8) catalyst washed with ammonium acetate solution was also characterized by ICP-AES, XRD, nitrogen adsorption/desorption and UV–vis DRS. Mesoporous CrMCM-41(40) catalyst was also characterized by ICP-AES, XRD, nitrogen adsorption/desorption and UV–vis DRS according to the published procedure [32].

2.6. Oxidation of α-pinene

Oxidation of α-pinene for the synthesis of V=O was carried out under vigorous stirring in a thermostatted glass vessel reactor. In a typical experimental procedure, 2 mmol of α-pinene, 15 ml of CB (solvent), 0.1 g of nonane (internal standard) and 0.2 g of CrSBA-15(8) were taken in the glass vessel reactor. The reaction mixture was stirred under constant stirring, and subsequently the reaction temperature was slowly raised to 358 K. After that, 10 mmol of TBHP was carefully added through the septum to the reactant mixture and refluxed for 24 h. After completion of the reaction, the CrSBA-15(8) catalyst was filtered, and the products were collected. The oxidation of α-pinene was conducted with different catalysts. To find an optimal condition in the presence of CrSBA-15(8), the catalytic reaction was further carried out with different reaction conditions such as time, temperature, stoichiometric molar ratios of reactants (α-pinene-to-TBHP). For the identification of a better solvent, the oxidation of α-pinene was carried out with different solvents like acetone (AC), acetonitrile (MeCN), chlorobenzene (CB) and toluene (TE). The oxidation of α-pinene was also carried out with H_2O_2 (30%) and excess of gaseous oxygen.

The collected liquid products were analyzed with authentic samples using a gas chromatograph equipped with a flame ionization detector (FID) using a silica capillary column CPSil-5 CB (50 m × 0.32 mm) and a semi-capillary column CP Wax 52 CB (25 m × 0.53 mm). Additionally, the products were further confirmed using gas chromatography combined mass spectroscopy (Shimadzu GCMS-QP 5050).

2.7. Experimental procedures for stability of catalyst

The Cr-containing mesoporous catalysts viz. CrSBA-15(8), CrSBA-15(50), CrSBA-15(0.04F), CrSBA-15(0.07F), CrSBA-15(WF) and CrMCM-41(40) were reused in the oxidation of α-pinene for finding their stabilities. In a typical experimental procedure, the CrSBA-15(8) catalyst used in a catalytic run was separated from the reaction mixture, washed with acetone several times and dried at 393 K. Finally, the CrSBA-15(8) catalyst was calcined at 773 K for 6 h in air to remove the adsorbed species and again reused for further catalytic runs. The similar procedure was used for recycling studies of other catalysts like CrSBA-15(50), CrSBA-15(0.04F), CrSBA-15(0.07F), CrSBA-15(WF) and CrMCM-41(40). After completion of the reaction, the catalyst was filtered and analyzed by ICP-AES for finding the percentage of Cr, and the conversion of α-pinene and selectivity of V=O were calculated with the standard formulas followed by analyzing results of GC and GC–MS.

In another experiment for finding the catalytic stability of CrSBA-15(8), the original catalyst was treated with ammonium acetate in order to remove the extra-framework chromium species. In a typical procedure, about 0.5 g of the calcined CrSBA-15(8) catalyst was washed with 1 M ammonium acetate (150 ml) solution under constant stirring for 12 h at an ambient temperature. Finally, the CrSBA-15(8) catalyst was filtered, calcined at 773 K for 6 h in air to remove the adsorbed species. This treatment of catalyst is denoted as washed CrSBA-15(8) catalyst. The catalyst was used in the catalytic studies of α-pinene oxidation, and subsequently the filtrate solution by separating the catalyst was carried out for the α-pinene oxidation under the similar reaction condition.

CrSBA-15(8) was treated with boiling water at 373 K for 168 h for the investigation of hydrothermal stability, and it was characterized according to the previous published procedure [25]. The treated catalyst was also used in the catalytic oxidation of α-pinene.

3. Results and discussion

The CrSBA-15 catalysts synthesized by the methods of NH_4F and pH-aDH have been thoroughly characterized by the above sophisticated instrumental techniques, and they have been used in the liquid-phase oxidation of α-pinene for selective synthesis of V=O.

3.1. Effect of pH-aDH method

Two-dimensional hexagonally mesostructured CrSBA-15 catalysts with higher Cr species loadings have been prepared using pH-aDH method according to the published procedure [25]. Mesoporous CrSBA-15 synthesized under highly acidic condition (pH < 1) has a low amount of Cr incorporated into SBA-15, possibly due to the high solubility of chromium 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 CN used as the chromium precursor, may not be equally matched with each other. Therefore, an attempt to increase the amount of Cr-ions (n_{Si}/n_{Cr} ratio = 8 in gel) incorporated in the framework has been done in this

Table 2
Structural and textural parameters of calcined CrSBA-15 catalysts prepared with different amount of NH_4F.

Sample	NH_4F (mol%)	n_{Si}/n_{Cr} ratio		a_0 (Å)	A_{BET} (m^2/g)	d_p (Å)	V_p (cm^3/g)	$t_w = a_0 - d_p$ (Å)
		Gel	Product[a]					
CrSBA-15(WF)[b]	–	10	26.5	124.2	948	88.3	1.08	35.9
CrSBA-15(0.04F)	0.04	10	37.6	127.1	983	92.9	1.09	34.2
CrSBA-15(0.07F)	0.07	10	48.7	113.1	848	80.5	1.08	32.6

[a] n_{Si}/n_{Cr} ratios of products are determined by ICP-AES.
[b] Sample was prepared at pH = 1.5 without NH_4F.

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. This synthetic mechanism is thoroughly explained in the published article [25]. The CrSBA-15 catalysts synthesized by pH-aDH method have been characterized by ICP–AES, XRD, N_2 adsorption, ESR, FE-SEM, and TEM according to the published procedure [25]. ICP–AES studies show that higher amounts of Cr-ions are incorporated on the silica pore walls [25]. The elemental composition of CrSBA-15 materials synthesized with different n_{Si}/n_{Cr} ratios is listed in Table 2. The XRD patterns of CrSBA-15 synthesized by pH-aDH method exhibit 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 of the 2D-hexagonal space group *p*6*mm*, as shown in Fig. 1 for calcined CrSBA-15(8), and the unit cell parameter (a_0) in the calcined CrSBA-15 catalysts increases with increasing Cr-ion content, as shown in Table 1. After washing treatment, the structural integrity of the washed CrSBA-15(8) remains constant (Fig. 1). By increasing the Cr-ion content, N_2 adsorption results reveal that the pore diameter (d_p) of CrSBA-15 can be tuned from 86.5 to 89.4 Å, with an increase of pore volume (V_p) from 1.08 to 1.10 cm^3/g accompanied by the concomitant decrease of surface area (A_{BET}) from 1063 to 999 m^2/g (Table 1). After washing treatment the textural parameters of the washed CrSBA-15(8) also remain constant [25] with a good IV type isotherm according to the IUPAC classification (Fig. 2). The ESR results (Fig. 3(b)) confirm that the Cr^{5+} and Cr^{6+} ions in the calcined CrSBA-15 catalysts are tetrahedrally coordinated to Si^{4+} on the silica walls [25]. Furthermore, the results of ^{29}SiMAS NMR spectra show that the intensity of Q_3 peak in CrSBA-15 is much lesser than that of siliceous SBA-15, as shown in Fig. 4; this observation clearly supports the stabilization of chromium ions via silanol groups (defect sites). However, Cr(VI) polychromate species dispersed on the surface of SBA-15 cannot be found by the ESR analysis. Thus the calcined CrSBA-15 catalysts and washed CrSBA-15(8) have been further characterized

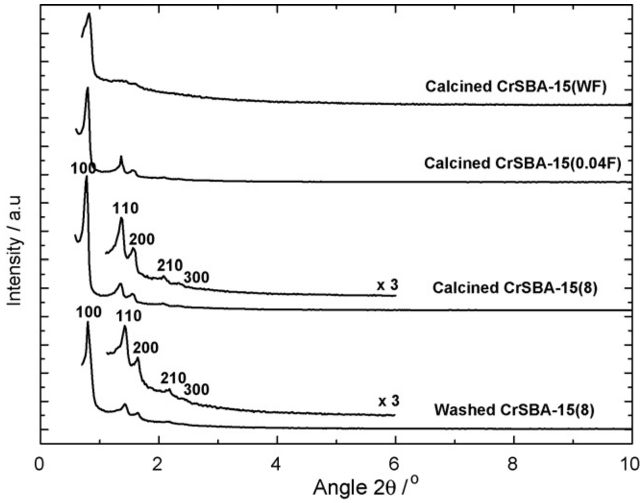


Fig. 1. XRD powder patterns of different CrSBA-15 catalysts.

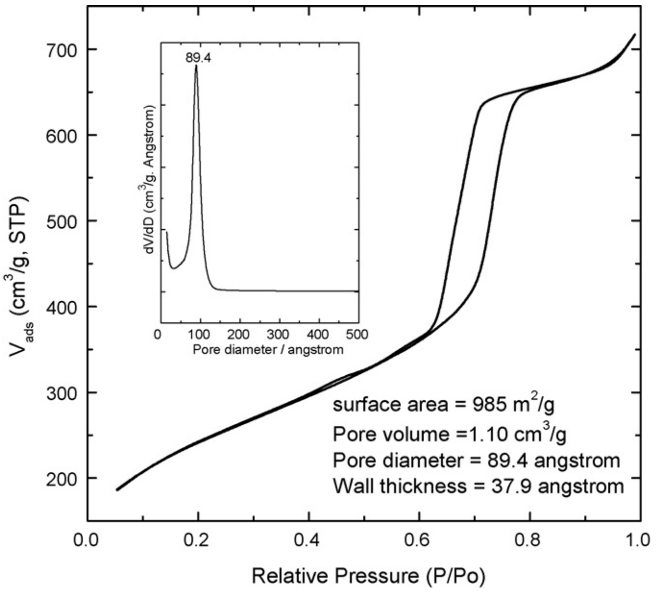


Fig. 2. Nitrogen adsorption isotherms of washed CrSBA-15(8).

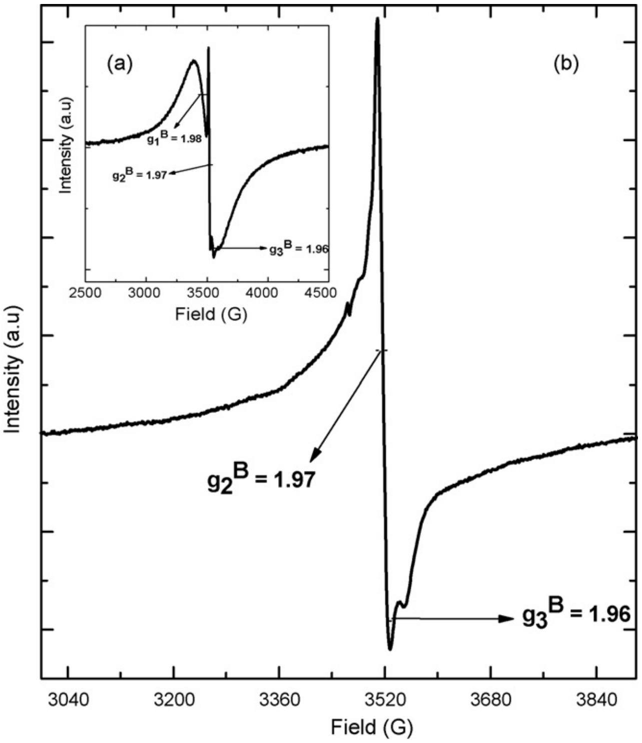


Fig. 3. ESR spectra of calcined (a) CrSBA-15(0.04F) and (b) CrSBA-15(8).

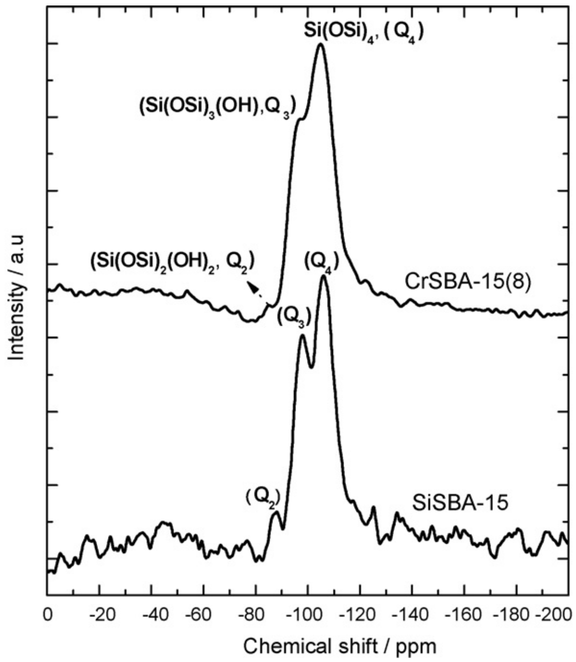


Fig. 4. ^{29}Si MAS NMR spectra of calcined CrSBA-15(8) and SiSBA-15.

by UV–vis DRS. The UV–vis DRS bands around 275 and 365 nm in the calcined CrSBA-15 and washed CrSBA-15(8) can be assigned to the O–Cr(VI) charge transfer of the chromate species, as shown in Fig. 5. A week shoulder around 455 nm in calcined CrSBA-15(8) is clearer than that of washed CrSBA-15(8), as shown in Fig. 5, and it can be attributed to Cr(VI) polychromate species. Based on the UV–vis DRS results, it is remarkably found that the Cr^{6+} species can be tetrahedrally coordinated into SBA-15, and small amounts of Cr(VI) polychromate species are dispersed on the SBA-15 (Fig. 5(a)). Most of the polychromate ions dispersed on the surface of CrSBA-15(8) are completely removed by the washing process (Fig. 5(b)). The results of TEM and FE-SEM correspondingly show the uniform pore diameter and rope-like hexagonal mesoporous structure of CrSBA-15 [25]. The studies of FTIR and UV–vis DRS confirm that the Cr species are tetrahedrally coordinated in the framework of MCM-41 [32].

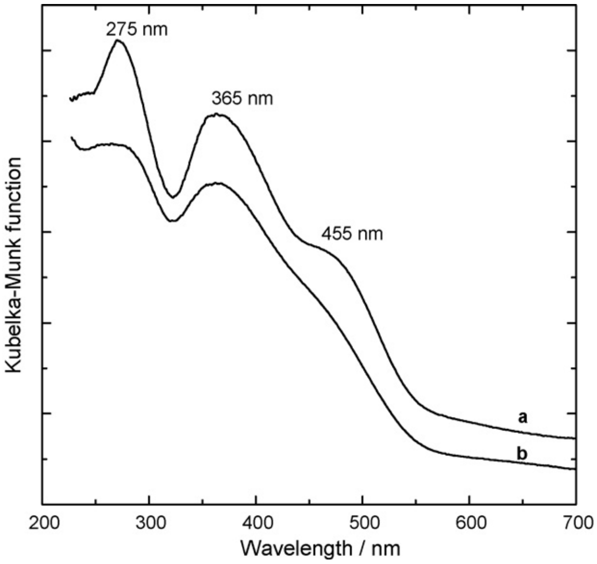


Fig. 5. UV–vis DR spectra of (a) calcined CrSBA-15(8) and (b) Washed CrSBA-15(8).

3.2. Effect of NH_4F acidic method

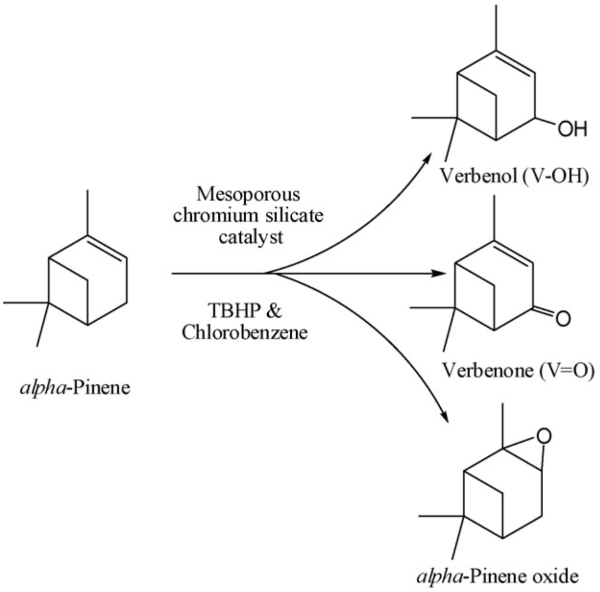
The CrSBA-15 catalysts synthesized using NH_4F acidic method have been clearly discussed along with their synthesis mechanism and showed in the published article [30]. For easy understanding of CrSBA-15 catalysts synthesized by NH_4F method, some important points have been indicated from their characterization, as follows. The XRD results confirm that CrSBA-15 catalysts have 2D-hexagonal mesostructures with space group *p*6*mm*, as shown in Fig. 1 for CrSBA-15(0.04F) [30], and the mesostructural order of the materials is obviously improved with the addition of fluoride [30]. However, the incorporation of Cr decreases with increasing concentration of fluoride precursor [30], since the hydrolysis of CN is much faster than that of TEOS under acidic condition. Generally, based on the ICP-AES analysis, the Cr content in the product is found to decrease as compared to that of gel because the production of chromium-oxo complex is much less in acidic synthesis medium. The N_2 adsorption results reveal that the textural properties of CrSBA-15 such as specific surface area, pore diameter, pore volume and pore wall thickness increase with decreasing concentration of fluoride precursor (Table 2). Since the hydrolysis rate of both TEOS and CN may well match with each other in the synthesis gel by adding a small amount of fluoride precursor, the amount of Cr incorporated in the inner pore silica surface increases with the decrease of the amount of fluoride precursor in the synthesis gel (Table 2). When NH_4F has not been added for the synthesis of CrSBA-15 catalyst, the mesostructural order of CrSBA-15 is affected with higher Cr content (Table 2) that is confirmed by the results of XRD (Fig. 1 for CrSBA-15(WF)) and N_2 adsorption [30]. The ESR results confirm that both the octahedral Cr^{3+} and tetrahedral Cr^{5+} species in calcined CrSBA-15(*x*F) catalysts are coordinated on the silica surface, as shown in Fig. 3(a) for CrSBA-15(0.04F) [33]. This may be due to either the reversible formation of few tetrahedral Cr^{5+} after the calcination process or irreversible formation of few octahedral Cr^{3+}, which is not completely oxidized during the calcination process. However, Cr(VI) polychromate species dispersed on the surface of SBA-15 cannot be found by the ESR analysis. But, in the UV–vis DRS peaks, a week UV–vis DR shoulder around 455 nm in calcined CrSBA-15 synthesized by NH_4F method clearly shows that a small amount of Cr(VI) polychromate species are dispersed on the SBA-15, and another two UV–vis DRS bands around 275 and 365 nm show the Cr^{6+} tetrahedrally coordinated into SBA-15.

3.3. Oxidation of α-pinene

The oxidation of α-pinene has been carried out over CrSBA-15 catalysts. The effects of reaction parameters such as temperature, time, α-pinene-to-TBHP ratios and solvents have been studied to find an optimal of conversion of α-pinene and selectivity of V=O. The performance of catalytic stability has been also found through the studies of recycles. The chromium concentrations and catalytic activity in the CrSBA-15(8) catalysts have been investigated by the chemical and hydrothermal treatments.

The liquid-phase oxidation of α-pinene conducted with CrSBA-15 catalyst proceeds *via* a radical-chain mechanism [33]. In this reaction α-pinenehydroperoxide (PHP) intermediate primarily forms on the catalytic surface. The PHP decomposes in the presence of suitable Lewis active sites of CrSBA-15 into V=O, as a major product with V–OH, as minor byproduct. Due to unexpected less active conditions, only very trace amount of α-pinene oxide (PO) as a byproduct is obtained, as shown in Scheme 1.

The oxidation of α-pinene has been carried out with 1:5 ratio of $n_{\alpha\text{-pinene}}/n_{\mathrm{TBHP}}$ (2 mmol of α-pinene and 10 mmol of TBHP) and 15 ml of CB at 358 K for 10 h over mesoporous Cr-containing catalysts viz. CrSBA-15(8), CrSBA-15(16), CrSBA-15(20), CrSBA-15(25), CrSBA-15(50), CrSBA-15(0.04F), CrSBA-15(0.07F),



Scheme 1. Reaction pathway of α-pinene oxidation.

CrSBA-15(WF) and CrMCM-41(40), as shown in Table 3. This reaction also produces V–OH as a minor byproduct and a very trace amount of PO as byproduct. The order of catalytic activity found in the selectivity of V=O is as follows: CrSBA-15(8) > CrSBA-15(16) > CrSBA-15(20) > CrSBA-15(WF) > CrMCM-41(40) > CrSBA-15(0.04F) > CrSBA-15(25) > CrSBA-15(0.07F) > CrSBA-15(50). CrSBA-15(8) exhibits the best performance with a conversion of α-pinene (91.5%) and selectivity of V=O (88.2%). Very trace amounts of V–OH and PO are also formed with selectivity of 3.5% and 8.3, respectively. Furthermore, the other CrSBA-15 catalysts synthesized by different hydrothermal conditions produce PO with a small selectivity. CrSBA-15(8) synthesized by pH-aDH method has higher selectivity of V=O than other CrSBA-15 catalysts, as shown in Table 3. The higher activity observed in CrSBA-1(8) is presumably ascribed to its two-dimensional space and high loading of tetrahedral Cr^{5+}/Cr^{6+} species on the surface of SBA-15, resulting in a high numbers of accessible active sites because the tetrahedral Cr^{5+}/Cr^{6+} ions incorporated in the framework of SBA-15 produce high numbers of Lewis acid sites for enhanced catalytic activity in the oxidation of α-pinene. CrSBA-15(0.04F) synthesized by NH$_4$F method has higher conversion of α-pinene and selectivity of V=O than CrSBA-15(0.07F) due to the higher number of Cr species dispersed in the framework of pore walls. However, CrSBA-15(WF) has much higher catalytic activity than CrSBA-15(0.04F) and CrSBA-15(0.07F) because of the large numbers of tetrahedral Cr^{5+}/Cr^{6+} incorporated in the framework of inner pore walls. Moreover, the CrSBA-15(WF) has also higher conversion of α-pinene and selectivity of V=O than CrSBA-15 catalysts (CrSBA-15(25) and CrSBA-15(50)) synthesized by pH-aDH method. It may be assumed that the catalysts have smaller amounts of tetrahedral chromium species than CrSBA-15(WF). Additionally, CrSBA-15(0.04F) catalyst synthesized by NH$_4$F method gives more selectivity of V–OH than other CrSBA-15 catalysts because of the high numbers of octahedral Cr^{3+} dispersed on the silica pore walls. Based on the catalytic activity obtained by all the mesoporous CrSBA-15 catalysts, the pH-aDH method is found to be a good method for the synthesis of CrSBA-15 catalysts. Also, the simple method renders to make possibly a high numbers of tetrahedral chromium species loadings on the silica surface with the formation of more chromium-oxo complex. Although the NH$_4$F method is a good method for the synthesis of CrSBA-15, the formation chromium-oxo complex is much less because it is highly acidic condition. CrSBA-15(xF) catalysts synthesized by NH$_4$F method cannot produce a high number of Lewis active sites on the silica surface in the oxidation of α-pinene for the selective synthesis of V=O. Moreover, with the similar chromium content of the CrSBA-15(20) and CrMCM-41(40) as shown in Table 1, the selectivity of V=O in CrSBA-15(20) is significantly higher as compared to CrMCM-41(40), as shown in Table 3. It may be concluded from this evidence that the well ordered mesoporosity material with a high chromium loadings plays an important catalytic role in the production of V=O with a high selectivity. On the basis of catalytic activity of different Cr-containing mesoporous catalysts, a uniformly hexagonal ordered two-dimensional CrSBA-15(8) is found to be a promising heterogeneous catalyst in the liquid-phase oxidation of α-pinene for the highly selective synthesis of V=O.

Table 3
Oxidation of α-pinene: different CrSBA-15 catalysts[a].

Catalysts	α-Pinene conversion (%)	Product selectivity (%)			
		V=O	V–OH	Others	
				PO	PHP
CrSBA-15(8)	91.5	88.2	3.5	8.3	–
CrSBA-15(16)	73.4	68.7	15.6	7.5	8.2
CrSBA-15(20)	63.2	57.4	13.2	7.0	22.4
CrSBA-15(25)	38.7	30.6	10.5	6.6	52.3
CrSBA-15(50)	25.4	18.6	7.6	5.8	68.0
CrSBA-15(0.04F)	55.4	35.7	20.4	15.7	28.2
CrSBA-15(0.07F)	40.5	26.3	15.4	12.6	45.7
CrSBA-15(WF)	60.0	54.3	12.4	6.3	27.0
CrMCM-41(40)	53.2	47.3	17.3	14.5	20.9
3rd run[b]	85.2	80.1	3.0	5.2	11.7
3rd run[c]	23.4	16.4	7.4	5.7	70.5
3rd run[d]	49.3	31.4	18.7	1.3	48.6
3rd run[e]	37.6	21.9	14.3	2.0	61.8
3rd run[f]	57.6	49.6	10.9	6.2	33.3
3rd run[g]	47.6	45.3	16.2	14.1	24.4
CrSBA-15(8)[h]	84.3	78.9	3.0	5.2	12.9
CrSBA-15(8)[i]	84.4	79.4	3.2	5.1	12.3
SiSBA-15	15.3	7.5	1.5	1.0	90.0
Blank	10.6	5.4	1.0	1.0	92.6

[a] *Reaction conditions*: 0.2 g of catalyst, 1:5 ratio of α-pinene-to-TBHP (2 mmol of α-pinene and 10 mmol of TBHP), reaction time = 24 h, 15 ml of CB, temperature = 358 K; V=O: verbenone, V–OH: verbenol, PO: α-pinene oxide, PHP: α-pinenehydroperoxide.
[b] Recyclable CrSBA-15(8) catalyst was used for recycling reaction.
[c] Recyclable CrSBA-15(50) catalyst was used for recycling reaction.
[d] Recyclable CrSBA-15(0.04F) catalyst was used for recycling reaction.
[e] Recyclable CrSBA-15(0.07F) catalyst was used for recycling reaction.
[f] Recyclable CrSBA-15(WF) catalyst was used for recycling reaction.
[g] Recyclable CrMCM-41(40) catalyst was used for recycling reaction.
[h] Washed catalyst.
[i] The catalyst was treated with boiling water (at 373 K for 168 h) for the investigation of hydrothermal stability.

Several catalysts viz. CrSBA-15(8) and CrSBA-15(50), CrSBA-15(0.04F), CrSBA-15(0.07F), CrSBA-15(WF) and CrMCM-41(40), have been examined for finding their catalytic stabilities as follows. Initially, the CrSBA-15 catalysts used in the catalytic reaction usually suffer from the loss of 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 α-pinene molecules. The treated catalysts have been reused for this reaction (Table 3). The conversion of α-pinene and selectivity of V=O decrease in the first two runs (not shown in Table 3). On the basis of first and second runs, it is observed that the polychromate and pentavalent chromium species (the range of $n_{\mathrm{Si}}/n_{\mathrm{Cr}}$ ratio obtained by ICP-AES is from 12.2 to 99.9) slightly leach on the catalytic surface. After third run, the conversion of α-

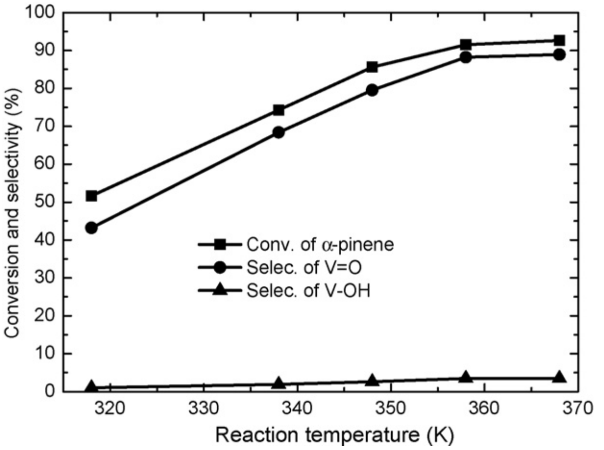


Fig. 6. Variation of reaction temperature on the synthesis of V=O by oxidation of α-pinene with TBHP. *Reaction conditions*: 0.2 g of CrSBA-15(8) catalyst, 1:5 ratio of α-pinene-to-TBHP (2 mmol of α-pinene and 10 mmol of TBHP), reaction time = 24 h, 15 ml of CB.

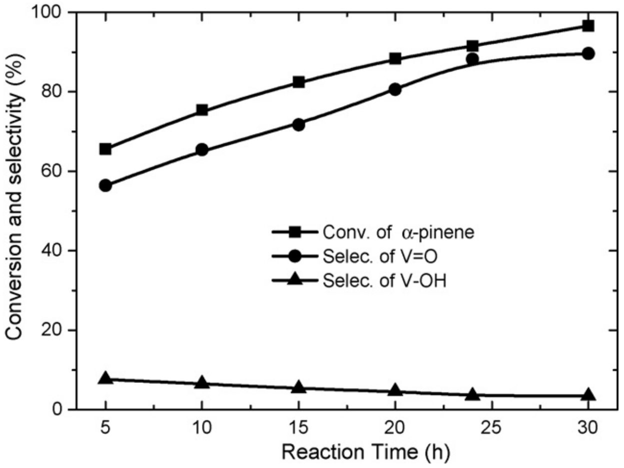


Fig. 7. Variation of reaction time on the synthesis of V=O by oxidation of α-pinene with TBHP. *Reaction conditions*: 0.2 g of CrSBA-15(8) catalyst, 1:5 ratio of α-pinene-to-TBHP (2 mmol of α-pinene and 10 mmol of TBHP), reaction temperature = 358 K, 15 ml of CB.

pinene and selectivity of V=O remain constant, indicating that the chromium species cannot be further leached on the mesoporous matrix, which is in good agreement with ICP-AES results of filtrate solutions where no chromium ion is detected. We suspect that the aqueous *t*-butanol generated as a byproduct in this reaction is responsible for the extraction of a small amount of loosely bound pentavalent chromium (extra-framework) in CrSBA-15 catalysts. Furthermore, the washed CrSBA-15(8) has also been used in this reaction for the investigation of catalytic stability. Effect of this study is nearly similar to that of third run of CrSBA-15(8), as shown in Table 3. The result of ICP-AES confirms that after third run the chromium species is not further leached on the surface of washed CrSBA-15(8). This reaction was also carried out using SiSBA-15 synthesized by pH-aDH method [24] as well as without catalyst. In both cases, about ∼10–15% conversion of α-pinene and ∼90–92% selectivity of PHP have been obtained (Table 3), thus indicating that major activity is only due to chromium species incorporated in the framework of SBA-15.

CrSBA-15(8) catalyst treated with boiling water for the investigation of hydrothermal stability has been used in the liquid-phase oxidation of α-pinene, and its catalytic activity is similar to that of washed CrSBA-15(8), as shown in Table 3. Since the CrSBA-15(8) is a promising catalyst in this catalytic oxidation reaction, it has been further used to find the best optimal conditions.

To find the best optimal conditions for highly selective synthesis of V=O over CrSBA-15(8), the liquid-phase oxidation of α-pinene has been carried out using the different optimal conditions such as reaction temperature, reaction time, ratios of reactant (α-pinene: TBHP) and solvents.

The oxidation of α-pinene has been conducted with different reaction temperatures using the reaction conditions showed in Fig. 6, for obtaining a high selective synthesis of V=O. When the reaction temperature is decreased from 358 to 318 K, the rate of both α-pinene consumption and V=O formation decrease. The feasible α-pinene conversion decreases with decreasing temperature. This may be due to the less activity of Lewis active sites on the surface of the catalyst at low reaction temperature, which could not support for the decomposition of PHP into V–OH whereas the conversion of V–OH to V=O is less at low reaction temperature due to the less efficiency of TBHP. Moreover, the conversion of α-pinene and selectivity of V=O have not been significantly increased when the reaction temperature is increased to 368 K. However, at above 368 K the conversion of α-pinene and selectivity of V=O decrease due to leading the oligomerization/polymerization products. This evidence strongly supports that a low (<313 K) or high (>403 K) reaction temperature is unsuitable to be highly produced V=O with an excellent selectivity. One can solidly conclude from the catalytic results obtained with different reaction temperatures that the reaction temperature of 358 K promotes the selective decomposition of PHP into V=O and gives a high conversion of α-pinene and selectivity of V=O.

To find an optimum reaction time for the highly selective synthesis of V=O, the liquid-phase oxidation of α-pinene has been carried out with different times using the reaction conditions showed in Fig. 7. When this catalytic reaction is carried out with 24 h, the conversion of α-pinene and selectivity of V=O are 91.5% and 88.2%, respectively. Even this reaction is carried out at 30 h under the similar reaction condition, the conversion of α-pinene and selectivity of V=O cannot be largely increased. At above 30 h, the conversion of α-pinene increases, however, selectivity of V=O decreases due to the formation of overoxidation products (not shown in Fig. 6). Moreover, the conversion of α-pinene and selectivity of V=O decrease when the reaction time is decreased from 20 to 5 h. This may be due to the formation byproduct, PO with a small selectivity whereas PHP may not be decomposed into V–OH/V=O at low reaction time. Based on the catalytic activity of CrSBA-15(8) with different times, it is clearly found that the reaction time of 24 h is favorable in the production of an excellent selectivity of V=O.

To find the best ratio of α-pinene-to-TBHP for the highly selective synthesis of V=O, the oxidation of α-pinene has been carried out with different ratios of $n_{\alpha\text{-pinene}}/n_{\text{TBHP}}$ using the reaction conditions showed in Fig. 8. When this reaction is carried out with 1:5 ratio, the increase of conversion of α-pinene and selectivity of V=O are observed. One reason may be that the reactants in 1:5 ratio mutually react with each other on the catalytic surface. The decrease of V=O selectivity is observed in other ratios of 1:1, 1:3, 2:5 and 3:5. It is considered that the quantity of reactants is insufficient to react with each other on the catalyst surface while the diffusion rate of the catalyst decreases because of blocking of the pore size by the unreacted organics, and an importantly note that overoxidation byproducts may be formed by using unevenly ratios of reactants. On the basis of the effect of the ratios, it is clear to note that 1:5 mmol ratio of α-pinene-to-TBHP is an optimum ratio for the highly selective synthesis of V=O.

Table 4
Oxidation of α-pinene: different solvents[a].

Temperature (K)	Solvent (15 ml)	α-Pinene conversion (%)	Product selectivity (%)			
			V=O	V–OH	Others	
					PO	PHP
310	AC[b]	57.3	29.2	5.2	15.6	50.0
343	MeCN[b]	69.6	57.2	8.4	20.5	13.9
358	CB	91.5	88.2	3.5	8.3	–
343	CB	79.6	73.5	3.4	7.0	16.1
310	CB	29.6	23.6	1.0	5.0	70.4
358	CB[c]	40.4	35.0	2.0	7.3	55.7
358	TE[b]	45.0	25.0	4.3	40.7	30.0
358	–	15.6	13.4	1.0	2.3	83.3

[a] *Reaction conditions*: 0.2 g of CrSBA-15(8) catalyst, 1:5 ratio of α-pinene-to-TBHP (2 mmol of α-pinene, 10 mmol of TBHP), reaction time, 24 h.

[b] 20 mmol of 30% H_2O_2 was used instead of TBHP.

[c] Gaseous oxygen (excess) was used instead of TBHP.

The oxidation of α-pinene has been carried out with different solvents like AC, MeCN, CB and TE using the reaction conditions noted in Table 4, for obtaining a high selective synthesis of V=O. AC is a good solvent that gives a very low selectivity of V=O (Table 4). TE is an apolar aprotic solvent that gives a low selectivity of V=O (Table 4) because the byproduct, PO forms with 40.7% selectivity while the both solvents, AC and TE may not be supported in the oxidation of α-pinene with H_2O_2 under the similar reaction condition as shown in Table 4. When the liquid-phase oxidation of α-pinene is carried out with H_2O_2 instead of TBHP in the presence of MeCN under the similar reaction condition, the conversion of α-pinene as well as selectivity of V=O is low because the formation of byproduct, PO with 20.5% selectivity. CB is a common and high-boiling solvent that has a high ability to form the complexes on the catalytic surface for long time in the liquid-phase catalytic oxidations. It gives more conversion of α-pinene and selectivity of V=O than the other solvents like AC, MeCN and TE. Moreover, CB preferentially attacks the active sites on the surface of catalyst to complete the conversion of α-pinene. Additionally, when the oxidation of α-pinene is investigated with gaseous oxygen instead of TBHP in the presence of CB under the similar reaction condition, the selectivity of V=O (35.0%) is low because the gaseous oxygen may not be completely reacted with PHP on the catalytic surface (Table 4). When this reaction is carried out with 8 ml of CB under the similar reaction condition, the conversion of α-pinene and selectivity of V=O are low because the high quantity of α-pinene may not be completely dissolved as homogeneously and reacted completely with TBHP (not shown in Table 4). Moreover, when the CB has been contacted with a low temperature (343 K), the conversion of α-pinene also decreases. However, under the similar condition the conversion of α-pinene in CB at 358 K is higher than that of other solvents. Based on the catalytic results of different solvents, it is noteworthy observed that the catalytic activity of CrSBA-15(8) on this catalytic reaction depends upon the polarity nature of the solvents. The conversion and selectivity are less when the reaction is carried out without solvents. Overall, comparing the catalytic activity with different solvents, it is obviously found that CB is the best solvent for highly selective synthesis of V=O.

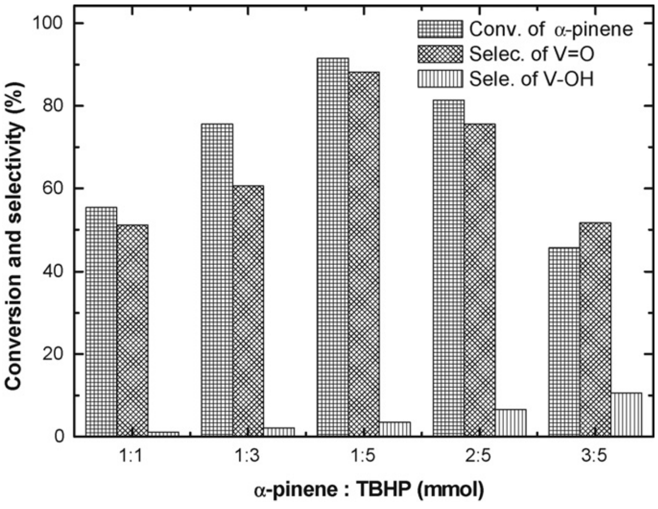
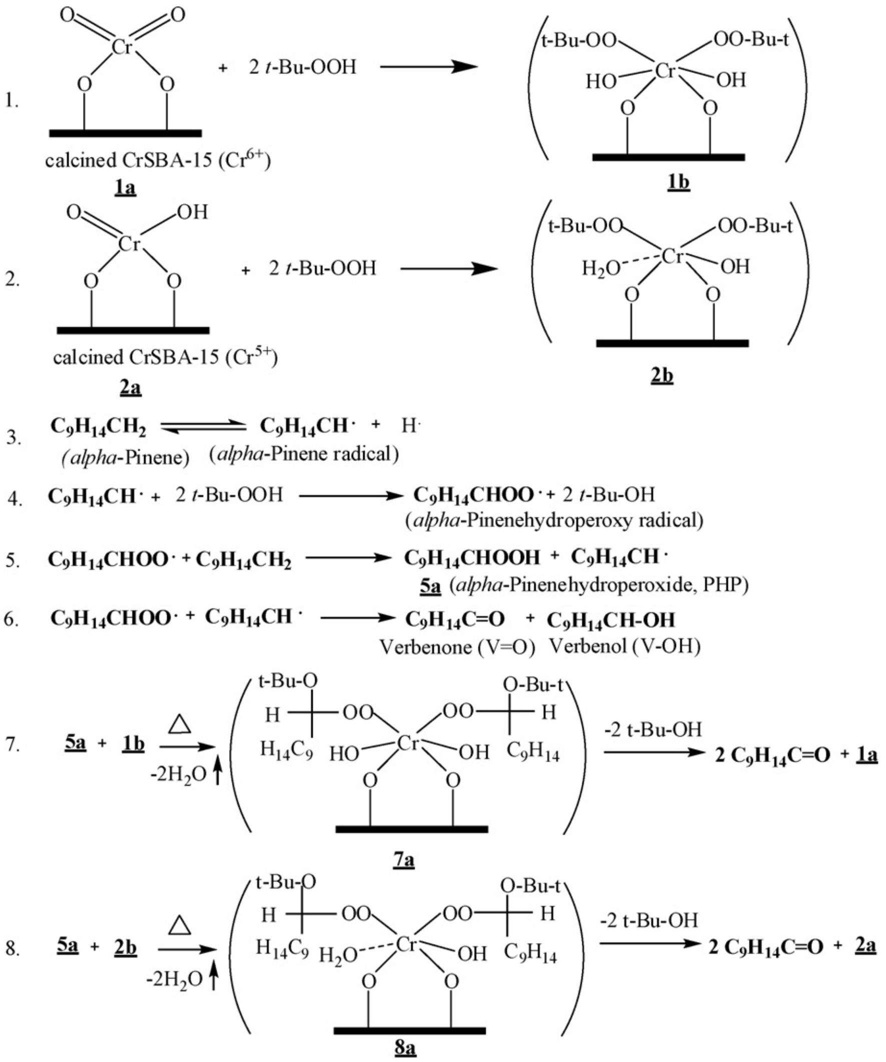


Fig. 8. Variation of α-pinene-to-TBHP ratios over CrSBA-15(8). *Reaction conditions*: 0.2 g of CrSBA-15(8) catalyst, reaction temperature = 358 K, reaction time = 24 h, 15 ml of CB.

In our study, V=O is the major product for the all reactions over CrSBA-15. Hence, the observed reaction results with CrSBA-15 are indicative of the reaction occurring predominantly via a heterolytic pathway, because a homolytic pathway (Haber–Weiss mechanism) would afford V–OH as the major product. This type of mechanism is operative at propagation step. A similar mechanism is reported for the oxidation of alkylaromatics over Cr-containing silica catalysts [34]. Accordingly, we have proposed a hypothetical reaction pathway of liquid-phase oxidation of α-pinene by TBHP catalyzed with CrSBA-15 catalysts, as shown in Scheme 2. It is generally recognized that this type of oxidation proceeds via radical-chain mechanism [33]. Concurrently, tetrahedral Cr^{5+}/Cr^{6+} species in the CrSBA-15 may react initially with TBHP to produce catalytically active, *t*-butylated Cr^{5+}/Cr^{6+} peroxo complex species with six-coordination (1, 2). The tetrahedral Cr^{5+}/Cr^{6+} species is confirmed by the results of UV–vis DRS and ESR [29,33]. α-Pinene subsequently forms α-pinene radical ($C_9H_{14}CH^{\bullet}$) after initiation reaction (3). Then $C_9H_{14}CH^{\bullet}$ may react with TBHP to produce α-pinenehydroperoxy radical ($C_9H_{14}CHOO^{\bullet}$) with the elimination of *t*-butanol (4). After that, the $C_9H_{14}CHOO^{\bullet}$ may react with another α-pinene molecule to produce an intermediate, α-pinenehydroperoxide (PHP, $C_9H_{14}CHOOH$, 5a, (5)). These occur in the sequence of propagation reactions (3–5). The PHP short-timely, thermally, reacts with *t*-butylated Cr^{5+}/Cr^{6+} peroxo complex species to form α-pinene *t*-butylated Cr^{5+}/Cr^{6+} peroxo complex species with six-coordination after complete removal of water molecule (7a, 8a). The resulting species is then oxidized to V=O ($C_9H_{14}C{=}O$) and V–OH ($C_9H_{14}CH{-}OH$) with the elimination of *t*-butanol and the regeneration of tetrahedral Cr^{5+}/Cr^{6+} (7, 8). In the major chain-termination step, the $C_9H_{14}CHOO^{\bullet}$ mutually constitutes with $C_9H_{14}CH^{\bullet}$ for the formation of V=O ($C_9H_{14}C{=}O$) and V–OH ($C_9H_{14}CH{-}OH$). It has been assumed that V=O is produced on the suitable active sites at the termination step (6). This reaction may occur with the non-framework of polychromate/pentachromate species.



Scheme 2. Mechanism of α-pinene oxidation with TBHP over CrSBA-15.

4. Conclusions

The CrSBA-15 catalysts have been successfully used for the synthesis of V═O. The active sites of these catalysts are highly efficient for the generation and decomposition of PHP intermediate to V═O. CrSBA-15 catalyst are found to be an efficient catalyst for the highly selective synthesis of V═O. When CrSBA-15(8) is washed with ammonium acetate, it is observed the leaching of small quantity of chromium species on the surface of the catalyst. From the studies of washing and recyclables, it is found that the CrSBA-15(8) has higher catalytic stability in the liquid-phase oxidation of α-pinene as compared to other Cr-containing mesoporous catalysts. From the optimized conditions, it is found that the higher selectivity of V═O and conversion of α-pinene are obtained at 358 K for 24 h using 1:5 ratio of α-pinene-to-TBHP with 15 ml of CB. From the different solvent studies, it is found that CB is a better solvent than other solvents. On the basis of all catalytic studies with a hypothetical reaction pathway of α-pinene oxidation, it is clearly found that the CrSBA-15(8) catalyst is a highly active, recyclable and promising heterogeneous catalyst for the selective synthesis of V═O. On the base of V═O selectivity obtained using CrSBA-15 catalysts synthesized by different methods, it is found that pH-aDH method is a better method for the synthesis of highly ordered CrSBA-15 catalysts with high loadings of tetrahedral chromium species.

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