

# Oxidative Cleavage of C=C Bond of Styrene and Its Derivatives with H<sub>2</sub>O<sub>2</sub> using Vanadyl (IV) Acetylacetonate Anchored SBA-15 Catalyst

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**Abstract** Cleavage of C=C bond of styrene and its derivatives into two carbonyl compounds with H<sub>2</sub>O<sub>2</sub> is accomplished at mild conditions using Vanadyl(IV) acetylacetonate anchored SBA-15 catalyst, which is prepared and characterized by BET surface area, low angle XRD and FT-IR. It is a highly efficient, recyclable and reusable catalyst.

**Keywords** Vanadyl (IV) acetylacetonate · SBA-15 · Cleavage of C=C bond · Styrene · Benzaldehyde

## 1 Introduction

The cleavage of C=C bonds of alkenes to afford two carbonyl products is a vital transformation in synthetic organic chemistry [1]. Ozonolysis is one of the frequently used methods for the cleavage of alkenes into two carbonyl compounds [2]. But, ozonolysis requires special equipment to avoid explosion [3]. Oxidative cleavage of C=C bonds of alkenes using heavy metals such as RuO<sub>4</sub> and OsO<sub>4</sub> is also a standard method, but these heavy metals are expensive and/or toxic. Additionally, usage of stoichiometric quantity of oxygen donors is other limitation of this method [4].

There are several reports associated with the oxidative cleavage of alkenes with different homogeneous catalysts such as Au(I) [5], potassium permanganate [6], ruthenium [7], cobalt [8], vanadium peroxo complexes [9], Mn(II) [10] etc. Albeit these catalysts are well suited for the cleavage of C=C bonds into carbonyl compounds,

involvement of high cost, difficulty in recovery and reuse and also the requirement of toxic oxidants are the major drawbacks of these homogeneous catalysts.

Recently, to combine the advantages of both homogeneous and heterogeneous catalytic systems, heterogenization of homogeneous catalysts on solid supports has been initiated [11–14]. At this juncture, the studies on preparation, characterization and catalytic application of metal acetylacetonate anchored onto porous supports have been under intensive investigation [15–20]. In one of our recent reports, Fe(III) acetylacetonate containing salen anchored SBA-15 catalyst has been prepared [21] and found that it is an efficient solid catalyst for the oxidative cleavage of C=C bond of styrene and its derivatives into corresponding carbonyl compounds. Aiming at exploring the similar eco-friendly catalytic systems, SBA-15 supported VO(acac) catalyst has been prepared and found that the performance of this catalyst is far better than that of SBA-Fe(acac:salen) catalyst, which is published recently [21]. Furthermore, SBA-VO(acac) catalyst has not yet been studied for the oxidative cleavage of C=C bonds of alkenes.

Hence, herein, for the first time, the high activity of vanadyl (IV) acetylacetonate anchored SBA-15 heterogeneous catalyst towards the oxidative cleavage of C=C bond of styrene and its derivatives at mild conditions (room temperature) with green H<sub>2</sub>O<sub>2</sub> oxidant has been delineated.

## 2 Experimental

### 2.1 Catalyst Preparation

As shown in Scheme 1, SBA-VO(acac) catalyst was synthesized using the post synthetic approach. The parent SBA-15 was synthesized in accordance with the literature

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reports [22–25]. Aminopropylation of SBA-15 (SBA-NH<sub>2</sub>) followed by anchoring of vanadyl (IV) acetylacetonate through Schiff base condensation between –NH<sub>2</sub> group of SBA-NH<sub>2</sub> and the –C=O group of acetylacetonate ligand coordinated to vanadyl(IV)acetylacetonate have been performed following the methods reported for the anchoring of metal acetylacetonates onto solid supports [18, 21, 26–29]. The detailed synthetic procedure is as follows.

In a typical synthesis, 20 g of P123 triblock copolymer surfactant (EO<sub>20</sub>–PO<sub>70</sub>–EO<sub>20</sub>, Aldrich, USA) was dispersed in 465 g of deionized water and added 137.5 g of HCl (35%v/v). To this homogeneous solution 44 g of tetraethyl orthosilicate (TEOS, Aldrich, USA) was added. The mixture was stirred at 40 °C for 8 h followed by aging at 100 °C for 24 h. The resultant mixture was filtered, washed with deionized water, dried at room temperature, and then calcined at 550 °C for 6 h to remove the template. This calcined SBA-15 is taken as parent SBA-15 for amine functionalization and subsequent anchoring of VO(acac)<sub>2</sub>.

In a typical aminopropylation, 3 g of calcined SBA-15 was pretreated for 3 h at 150 °C in vacuum and then refluxed with a solution containing 2.1 ml (9 mmol) of 3-(Aminopropyl)triethoxysilane (APTES) in 50 ml of dry toluene for 24 h. The mixture was filtered, washed with 150 ml of toluene and dried in oven at 100 °C for 12 h, designated as SBA-15 NH<sub>2</sub>.

In a typical vanadyl(IV) anchoring, approximately 2.5 g of SBA-NH<sub>2</sub> was added to a solution containing 0.5 g of VO(acac)<sub>2</sub> in toluene (250 ml), refluxed for 24 h. The resulting solid product was filtered, extensively washed with toluene and then soxhlet extracted with dichloromethane for 6 h, and dried in an oven at 100 °C for overnight, and designated as SBA-VO(acac).

## 2.2 Characterization of the Catalysts

### 2.2.1 BET Surface Area

The BET surface areas of parent SBA-15, SBA-NH<sub>2</sub> and SBA-VO(acac) catalyst were determined using SMART SORB 92/93 (M/s. SMART Instruments, India) under dynamic conditions in the flow of a gas mixture containing

30% nitrogen and 70% helium at liquid nitrogen temperature (–196 °C).

### 2.2.2 Low Angle X-ray Diffraction (XRD)

The XRD patterns were obtained on Rigaku (Altima IV, Japan) diffractometer using Cu K $\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ) at 40 kV and 40 mA in the  $2\theta$  range of 0.7–5° at room temperature.

### 2.2.3 FT-IR Spectral Analysis

The FT-IR spectra for (a) parent SBA-15, (b) SBA-NH<sub>2</sub>, and (c) SBA-VO(acac) and (d) VO(acac)<sub>2</sub> were obtained on a PerkinElmer (Spectrum GX) FT-IR spectrometer over the wavenumber range of 4000–500 cm<sup>–1</sup> with a spectral resolution of 2 cm<sup>–1</sup>.

### 2.2.4 C, H, N and S Analysis

To estimate the amount of propylamine and acetylacetonate moieties on the surface of SBA-15, carbon, hydrogen, nitrogen and sulfur (CHNS) elemental analysis was made using an elemental analysis equipment (Elementar, Vario microcube, Germany).

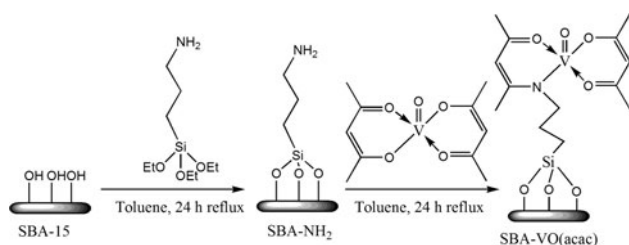
## 2.3 Cleavage of C=C Bond of Styrene and Its Derivatives

All the reactions were carried out at room temperature in a 25 ml round bottom flask. In a typical experiment, to a mixture of 50 mg catalyst, 3 ml acetonitrile and 1 mmol substrate, 3.5 mmol of hydrogen peroxide (30%) was added at room temperature and stirred for 5 h. Unless otherwise specified, the applied reaction conditions are same as above. The products were identified and analyzed by GC–MS (QP-5050 model, M/s. Shimadzu Instruments, Japan) equipped with DB-5 capillary column (0.32 mm diameter and 25 m long, supplied by M/s. J & W Scientific, USA).

## 3 Results and Discussion

### 3.1 Catalyst Characterization

In the vanadyl(IV)acetylacetonate anchored SBA-15 heterogeneous catalyst, the loading of propylamine, acetylacetonate ligands were determined from C, H, N and S elemental analysis and the loading of vanadium was determined by ICPMS. The details of the analysis data are presented in Table 1, which reveals that the loading of propylamine in SBA-NH<sub>2</sub> is around 1.73 mmol/g. The loading of acac moiety and vanadium are approximately



**Scheme 1** Pictorial representation of SBA-VO(acac) catalyst synthesis

**Table 1** Elemental analysis of SBA-15, SBA-NH<sub>2</sub> and SBA-VO(acac) samples

Sample	Analysed by	C (%)	H (%)	N (%)	S (%)	V (%)
SBA-15	CHNS	NF	NF	NF	NF	–
SBA-NH <sub>2</sub>	CHNS	6.5	1.55	2.01	NF	–
SBA-VO(acac)	CHNS	10.5	2.15	1.89	NF	–
SBA-VO(acac)	ICPMS	–	–	–	–	1.80 <sup>a</sup>
SBA-VO(acac)	ICPMS	–	–	–	–	1.74 <sup>b</sup>
SBA-VO(acac)	ICPMS	–	–	–	–	1.78 <sup>c</sup>
SBA-VO(acac)	ICPMS	–	–	–	–	1.76 <sup>d</sup>

NF stands for not found

a, b, c, d Vanadium loading in fresh, after first, second and third recycled SBA-VO(acac) catalyst

0.34 mmol/g. The characteristic of SBA-15, SBA-NH<sub>2</sub> and SBA-VO(acac) samples obtained from N<sub>2</sub> adsorption, low-angle XRD and FT-IR techniques are discussed in the following sections.

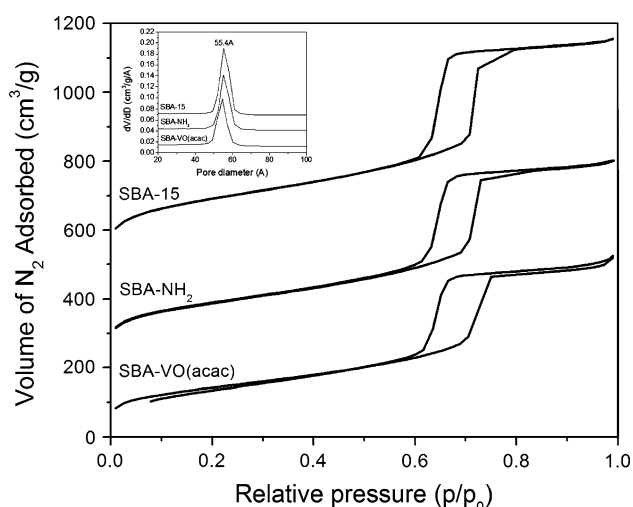
### 3.1.1 N<sub>2</sub> Adsorption

N<sub>2</sub> adsorption–desorption isotherms were recorded for SBA-15, SBA-NH<sub>2</sub> and SBA-VO(acac) samples to determine the textural parameters. Figure 1 shows the irreversible type IV adsorption isotherms [30] and the sharp increase in the adsorbed amount of N<sub>2</sub> at a relative pressure (P/P<sub>0</sub>) of 0.6–0.9, features typical curves of mesoporous structures which remain intact in both SBA-NH<sub>2</sub> and SBA-VO(acac) samples. The pore size distribution (Fig. 1, inset) was calculated using the BJH equation, which shows a narrow pore size distribution with an average pore size of 55 Å. The structural and textural characteristics of SBA-15, SBA-NH<sub>2</sub> and SBA-VO(acac) samples are presented in Table 2. The BET surface area of parent SBA-15 is 880 m<sup>2</sup>/g, which has been decreased to 654 m<sup>2</sup>/g after

functionalization with propylamine spacer group. Further decrease in the surface area has been observed after covalent attachment of vanadyl (IV) acetylacetonate onto SBA-NH<sub>2</sub> (Table 2). Similar, decreasing trend in the pore volume has been observed upon propylamine functionalization and subsequent tethering of VO(acac)<sub>2</sub>. The gradual decrease in both surface area and pore volume from parent SBA-15 to SBA-NH<sub>2</sub> and to SBA-VO(acac) shows the sequential anchoring of propylamine and vanadyl(IV)acetylacetonate, respectively.

### 3.1.2 Low-Angle XRD

The low-angle XRD patterns of (a) parent SBA-15, (b) SBA-NH<sub>2</sub>, (c) SBA-VO(acac) are depicted in Fig. 2. The structural characteristics of all the three materials are summarized in Table 2. For parent SBA-15, three reflections were observed in XRD (Fig. 2), and these could be indexed to *p6mm* symmetry with a lattice spacing of 111.1 Å [22]. After functionalization of propylamine and subsequent vanadyl(IV)acetylacetonate anchoring, the position of the (100) reflection remained the same, suggesting that the basic hexagonal pore arrangement was intact [28] and also appearance of high ordered reflection peaks reveals the retention of overall pore structure of parent SBA-15 [22]. However, there is a small reduction in the diffraction peak intensities of SBA-NH<sub>2</sub> and SBA-VO(acac). The loss in the intensity of (100) reflection is substantial and also the intensity of (110) and (200) reflections became weak. The decrease in signal intensity may be due to loss of some regularity in the 2D hexagonal structural ordering or due to reduction of the scattering contrast between the SBA-15 silica walls and filled pores with propylamine and VO(acac) moieties. These XRD results are in good agreement with the reported literature [28]. After functionalization of propylamine and subsequent vanadyl(IV)acetylacetonate anchoring, the width of the d<sub>100</sub> reflections became narrow, which is an evidence for the homogeneous distribution of the pore structure brought



**Fig. 1** N<sub>2</sub> adsorption–desorption isotherms and pore size distribution curves as inset



the stretching ( $3750\text{--}3000\text{ cm}^{-1}$ ) and bending ( $957\text{ cm}^{-1}$ ) regions, implies the consumption of  $\text{--OH}$  groups due to anchoring of propylamine onto SBA-15 support through chemical bonding.

There are significant changes in the spectrum (Fig. 3c) of SBA-VO(acac) catalyst particularly in the vibrational range of  $1750\text{--}1200\text{ cm}^{-1}$ . Substantial increment in the intensity and shifting of the vibrational bands [33] through combined C=C and C=O stretching vibrations of the conjugated chelate ring system and stretching vibration modes of the new C=N introduced in the chelate ring of the acac ligand by the Schiff condensation reaction between the amine groups of the propylamine functionalized SBA-15 and the C=O group from the coordinated acetylacetonate ligand. The peak due to V=O is supposed to be observed around at  $997\text{ cm}^{-1}$  in VO(acac)<sub>2</sub> spectrum [34] but it could not be resolved in the spectrum of SBA-VO(acac) due to strong Si–O–Si stretching vibration [33]. However, there is a close proximity in the infrared bands of free VO(acac)<sub>2</sub> (Fig. 3d) and the SBA-VO(acac) catalyst particularly in the regions of  $1750\text{--}1200\text{ cm}^{-1}$  and at  $997\text{ cm}^{-1}$ .

### 3.2 Oxidative Cleavage of C=C Bond of Styrene

The catalytic activity of SBA-VO(acac) towards the cleavage of C=C bonds of styrene and its derivatives in the

presence of H<sub>2</sub>O<sub>2</sub> was determined and the results are depicted in Table 3. Initially, styrene was used as a substrate and observed the formation of benzaldehyde as a major product. Additionally, three oxygenates, such as (i) styrene epoxide (Epoxide), (ii) 1-phenylethane-1, 2-diol (Diol) and (iii) benzoic acid (Acid) were detected in the product mixture. The formation of the above cited four products is quite common in the oxidation of styrene both on homogeneous and heterogeneous catalytic systems [39, 40].

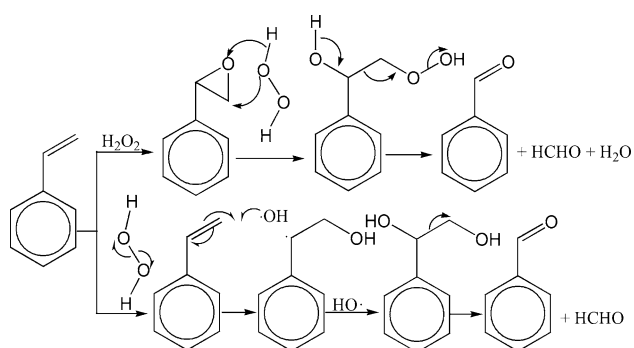
As reported by Hulea et al. [40], the formation of benzaldehyde (major product) takes place via two different mechanisms. (i) In the presence H<sub>2</sub>O<sub>2</sub> styrene gets oxidized to styrene epoxide, which transforms into a hydroxyl-hydroperoxystyrene intermediate when H<sub>2</sub>O<sub>2</sub> attacks on it as a nucleophile. As shown in Scheme 2, cleavage of hydroxyl-hydroperoxystyrene produces both benzaldehyde and formaldehyde. (ii) Direct oxidative cleavage of C=C bond of styrene via radical mechanism yields both benzaldehyde and formaldehyde as shown in Scheme 2. Benzoic acid is one of the three minor products, which is expected to form from benzaldehyde through oxidation, [40–42]. Another minor product is 1-phenyl ethane-1, 2-diol, which is believed to be produced through hydrolysis of styrene epoxide making use of the H<sub>2</sub>O present in aqueous 30% H<sub>2</sub>O<sub>2</sub> [40, 43].

**Table 3** The catalytic activity of SBA-VO(acac) catalyst on different substrates with 30% H<sub>2</sub>O<sub>2</sub>

Entry	Ar	R	Conversion (%)	Yield (%)	Selectivity (%)	TOF <sup>a</sup> (h <sup>-1</sup> )
1	Ph	H	84	81	96	9.5
2	<i>p</i> -F(C <sub>6</sub> H <sub>4</sub> )	H	80	79	99	9.1
3	<i>p</i> -Cl(C <sub>6</sub> H <sub>4</sub> )	H	90	82	91	10.2
4	<i>p</i> -Br(C <sub>6</sub> H <sub>4</sub> )	H	88	78	89	10.0
5	<i>p</i> -CH <sub>3</sub> (C <sub>6</sub> H <sub>4</sub> )	H	93	80	86	10.5
6	Ph	CH <sub>3</sub>	90	81	90	10.2
7	<i>O</i> , <i>p</i> -(CH <sub>3</sub> ) <sub>2</sub> (C <sub>6</sub> H <sub>3</sub> )	H	95	80	84	10.8
8	<i>m</i> -NO <sub>2</sub> (C <sub>6</sub> H <sub>4</sub> )	H	89	79	89	10.1
9	<i>O</i> , <i>p</i> -(OCH <sub>3</sub> ) <sub>2</sub> (C <sub>6</sub> H <sub>3</sub> )	H	95	80	84	10.8
10	<i>p</i> -OCH <sub>3</sub> (C <sub>6</sub> H <sub>4</sub> )	H	85	77	91	9.6
11	Ph	C <sub>6</sub> H <sub>5</sub>	42	40	95	4.8
12	Ph	CHO	60	58	97	6.8
13	Ph	COCH <sub>3</sub>	38	24	63	4.3
14	Ph	COC <sub>6</sub> H <sub>5</sub>	40	25	63	4.5
15	Ph	CH=CHCH <sub>2</sub> OH	75	67	89	8.5

Reaction conditions: Substrate 1 mmol, H<sub>2</sub>O<sub>2</sub>(30%) 3.5 mmol, solvent 3 ml, catalyst 50 mg, temperature RT, pressure 1 atm., time 5 h

<sup>a</sup> Turn over frequency Moles of substrate converted per hour per mole of vanadium



**Scheme 2** Oxidative cleavage of styrene into benzaldehyde by two different mechanisms

In the catalytic point of view, SBA-VO(acac) is superior to the reported heterogeneous catalysts. Despite the room temperature reactions are economic and eco-friendly, most of the C=C bond cleavage reactions were reported at and above 70 °C [41, 42, 44], however the activity is comparable to that of present SBA-VO(acac) catalyst. Dhakshinamoorthy et al. [45] reported a clay anchored iron-salen complex for the oxidation of C=C bond cleavage in the presence of oxygen using 30% H<sub>2</sub>O<sub>2</sub> as a terminal oxidant at room temperature for 24 h. Under the optimized conditions, the yield of benzaldehyde is only 30%, whereas in the present study it is 78% (Table 3, entry 1).

Indeed, SBA-Fe(acac:salen) heterogeneous catalyst is superior among the heterogeneous catalysts for the oxidative cleavage of C=C bond of styrene and its derivatives [21]. SBA-VO(acac) heterogeneous catalyst has been proved as a better catalyst compared to SBA-Fe(acac:salen) solid catalyst. The catalytic activity of SBA-Fe(acac:salen) in terms of turn over number (TON) is 6, whereas the TON of SBA-VO(acac) solid catalyst is 86, which implies that the SBA-VO(acac) catalyst is about 14 times better than that of SBA-Fe(acac:salen) catalyst. In both of these catalysts, the support is same. The catalytic activity mainly depends on the active species, which has already been reported by Choudary and Reddy [9], using vanadium complexes as homogeneous catalysts. These vanadium complexes exhibited awesome catalytic activity towards the conversion of C=C bond cleavage.

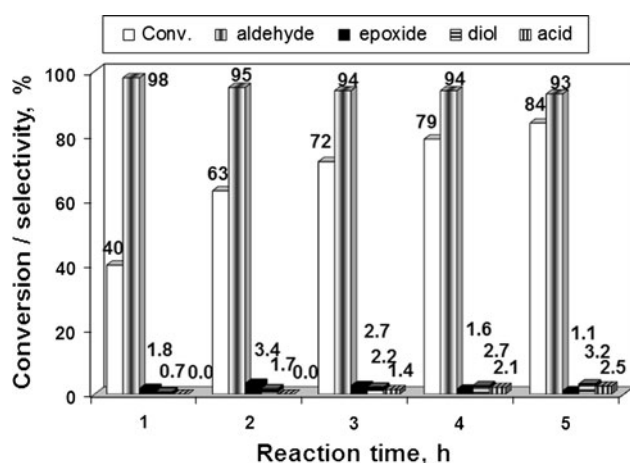
Aiming at understanding the nature of the reaction and the catalytic activity, different experiments were carried out. At this juncture, a blank experiment was conducted without adding any catalyst and found that the reaction has not been proceeded, which implies that the oxidative cleavage of C=C bond of styrene process is certainly catalytic. Later on, to understand the role of SBA-15 support different experiments were conducted using SBA-15 and SBA-NH<sub>2</sub> as catalysts and found that there is no appreciable conversion of styrene. In the subsequent experiment, free VO(acac)<sub>2</sub> has been used as a catalysts and found that

the conversion of styrene is 80% and the selectivity of benzaldehyde is only 63%. But with SBA-VO(acac) heterogeneous catalyst the conversion of styrene is 84% and the selectivity of benzaldehyde is 93% (Table 3). Marginal hike in styrene conversion and a significant improvement in benzaldehyde selectivity imply the influence of support. The high performance of this supported catalyst is mainly due to isolated distribution of VO(acac) species on the pore surfaces of hexagonally ordered mesopores of SBA-15. Isolated distribution of active VO(acac) species during the course of anchoring onto SBA-15 support can be rationalized through the availability of ample space in pore surfaces of SBA-15 support. The higher ability of supported catalyst is mainly due to the existence of large and uniform mesopores, which are capable of minimizing the diffusion limitations. The steady activity of SBA-VO(acac) catalysts is due to prevention of active VO(acac) species leaching (Table 1), which is due to firm anchoring of active species through Schiff base condensation.

To verify the catalytic activity of SBA-VO(acac) catalyst towards the transformation of styrene, different reaction parameters were applied such as reaction time, reaction temperature, amount of oxidant, amount of catalyst, and nature of solvent. Based on these results, optimized reaction conditions were established to get better activity, which are as follows.

### 3.2.1 Influence of Reaction Time

The catalytic activity (conversion of styrene and selectivity of products) of SBA-VO(acac) catalyst with respect to reaction time has been determined and the results are depicted in Fig. 4. The conversion of styrene in 1 h is about 40% with 98% selectivity of benzaldehyde. In 2 h, the conversion has been significantly increased to 63%



**Fig. 4** Reaction time versus conversion/selectivity over SBA-VO(acac) catalyst

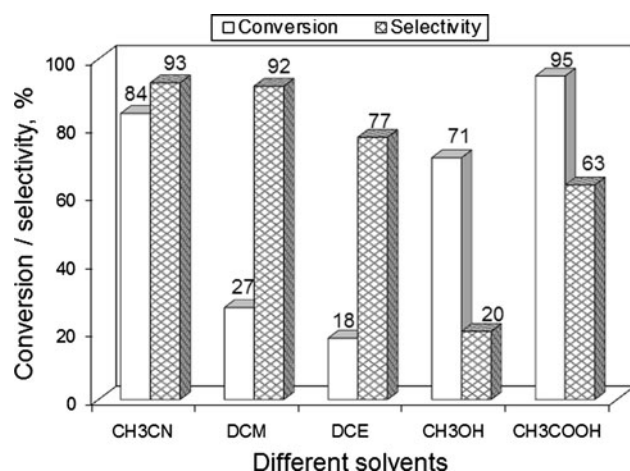
maintaining the selectivity at about 95%. Similar increasing trend in the conversion is observed in 3, 4 and 5 h of reaction time with marginal decrease in the selectivity of benzaldehyde. Selectivity of benzoic acid increased with increase in reaction time. This is due to oxidation of benzaldehyde [46]. When compared to the catalytic activity of SBA-VO(acac) catalyst in 4 and 5 h of reaction time, increment in the conversion of styrene is not so significant and furthermore, the formation of by-products is about to initiate. Hence, 5 h of reaction time has been fixed for establishing the other reaction parameters.

### 3.2.2 Effect of Solvents

The influence of catalytic activity with different solvents is shown in Fig. 5. With the polar solvents like CH<sub>3</sub>CN, DCM and DCE the SBA-VO(acac) catalyst is active, whereas with nonpolar solvents (benzene and toluene) it is quite inactive. With methanol as solvent the conversion is reasonably good, but the abrupt drop in selectivity of benzaldehyde is observed. There observed an apparent control over the conversion of styrene and the selectivity of benzaldehyde with different solvents.

### 3.2.3 The Effect of H<sub>2</sub>O<sub>2</sub> Concentration

As shown in Table 4, with increase in H<sub>2</sub>O<sub>2</sub> concentration, there is a substantial increase in the conversion of styrene, whereas there is a gradual decrease in the selectivity of benzaldehyde. At about 1:3.5 mol ratio of styrene to H<sub>2</sub>O<sub>2</sub>, the conversion of styrene and selectivity of benzaldehyde seems to be better. Hence, this molar ratio of styrene to H<sub>2</sub>O<sub>2</sub> has been fixed to optimize other reaction conditions. When the same amount of H<sub>2</sub>O<sub>2</sub> (1:3.5 mol ratio) is added to the reaction mixture in four different



**Fig. 5** Effect of solvents against conversion/selectivity over SBA-VO(acac) catalyst

spells in a time interval of 1 h, there is a marginal increase in the conversion of styrene, but the decrease in the selectivity of benzaldehyde is significant within 5 h. These results reveal that certain amount of H<sub>2</sub>O<sub>2</sub> may be decomposing when it is added at a time.

### 3.2.4 Effect of Catalyst Amount

The activity of SBA-VO(acac) catalyst towards the oxidative cleavage of C=C bond of styrene has been investigated using different amounts of catalysts and the results are depicted in Table 4. It is clear that there is a considerable improvement both in conversion of styrene and the selectivity of benzaldehyde when the catalyst amount is increased from 25 to 50 mg, whereas, further increase of catalyst amount (75 mg) demonstrate no change in either conversion or selectivity. Due to large amount of catalyst in the reaction mixture, it may be facilitating adsorption/chemisorption of reactant/oxidant/intermediate chemicals on different catalytic sites. From this study, it is found that the optimum amount of the catalyst is 50 mg. Similar observation put forward by Maurya et al. [39] over zeolite encapsulated Cu(II) complex catalyst.

### 3.2.5 Effect of Reaction Temperature and Reusability

Effect of reaction temperature on the activity of SBA-VO(acac) catalyst has been displayed in Fig. 6. With rise in reaction temperature from RT to 60 °C change in the conversion is marginal (85%), but the selectivity of benzaldehyde is abruptly decreased to 71%. Further increase in the reaction temperature from 60 to 80 °C, again increase in the conversion is marginal and drastic decrease in the selectivity of benzaldehyde is noticed. Based on these results, to maintain the high selectivity, RT operation seems to be optimal.

The catalyst is recycled three times and the obtained results are displayed in Fig. 6, from which it is clear that the catalytic activity is more or less constant in three repeated cycles. It can be understood that the active VO(acac) species is stable under the operated reaction conditions, which may be due to firm anchoring of VO(acac) to the pore surfaces of SBA-15 through chemical bonding. Deactivation of the catalyst due to leaching of active VO(acac) species (Table 1) is suspended up to three cycles through rigid anchoring.

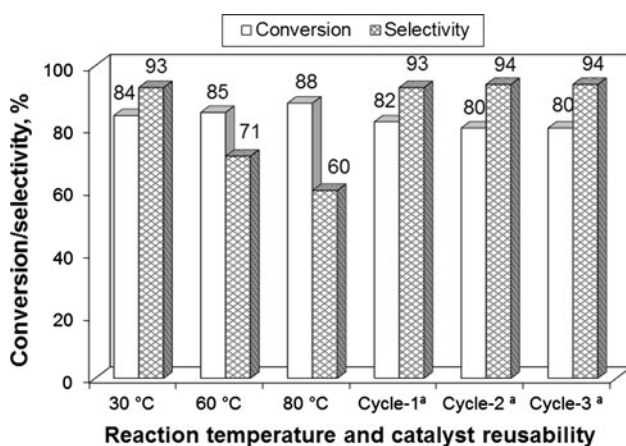
### 3.2.6 C=C Bond Cleavage of Styrene Derivatives

Oxidative cleavage of C=C bonds of styrene and its derivatives to corresponding carbonyl compounds over a solid SBA-VO(acac) catalyst and the results are depicted in Table 3. The results indicate that SBA-VO(acac) catalyst is

**Table 4** Effect of styrene to H<sub>2</sub>O<sub>2</sub> mol ratio and catalyst amount against catalytic activity

Styrene to H <sub>2</sub> O <sub>2</sub> mol ratio	Conversion (%)	Selectivity (%)
1:3	62	95
1:3.5	84	93
1:4	88	83
1:4.5	95	76
1:3.5 <sup>a</sup>	89	78
Weight of the catalyst (mg)	Conversion (%)	Selectivity (%)
0	3	0
25	65	88
50	84	93
75	85	94

<sup>a</sup> 3.5 mmol of H<sub>2</sub>O<sub>2</sub> is divided into four parts and added each portion after every 1 h

**Fig. 6** Influence of reaction temperature and recyclability against catalytic activity. <sup>a</sup>Reaction was carried out at RT

highly active towards the cleavage of C=C bond of styrene derivatives. The catalytic activity of SBA-VO(acac) in the case of halogenated (entries 2–4), methylated (entry 5), methoxylated (entry 10) styrenes is similar to that of styrene. Even in the case of dimethylated (entry 7) and dimethoxylated (entry 9) styrenes smooth functioning of SBA-VO(acac) catalyst is observed. However in the case of conjugated double bond containing styrenes the reactivity of the catalyst is sluggish. For example in the case of trans stilbene (entry 11), its conversion is only 42% with 95% selectivity of benzaldehyde. Indeed the yield of benzaldehyde is 80%, but it is considered as 40%, because, in this particular reaction, 1 mol of stilbene produces 2 mol of benzaldehyde. Hence, in this example the yield of benzaldehyde is taken as half of the original one.

The low activity of SBA-VO(acac) catalyst is observed in the case of (i) 3-phenyl-propenal (entry 12), (ii) 4-phenyl-but-3-en-2-one (entry 13), and (iii) 1, 3-diphenyl-

propenone (entry 14) substrates. The oxidative cleavage products formed from (i) 3-phenyl-propenal (entry 12), (ii) 4-phenyl-but-3-en-2-one (entry 13), and (iii) 1, 3-diphenyl-propenone (entry 14) are glyoxal, methylglyoxal and phenylglyoxal respectively, which are important chemical intermediates. Separation of these products from the product mixture is difficult due to low boiling and readily polymerizing nature. However, these are analysed by mass spectrum. The molar mass of phenylglyoxal is 134 and its structure was confirmed from the M/Z values of three different fragments 51, 77 and 105 (100% intense peak). Methylglyoxal molar mass is 72, M/Z: 15, 29, and 43 (100% intense peak), 45 and 72. The molar mass of glyoxal is 58, M/Z: 29 (100% intense peak).

To understand the low activity of conjugated double bonded substituted styrenes and conjugated double bond lacking substituted styrenes, a reaction is conducted using cinnamyl alcohol and found that its conversion is 67% with the selectivity of benzaldehyde is 89%. From this data, it seems that the performance of SBA-VO(acac) catalyst is superior in the case of styrenes that are not having conjugated double bond substituents compared to conjugated double bond substituted styrenes. However, at present it cannot be drawn any constructive conclusion towards the cleavage activity of these two kinds of styrene derivatives. On the whole, the performance of SBA-VO(acac) catalyst is worth noting.

## 4 Conclusions

SBA-VO(acac) is a versatile, recyclable, and reusable solid catalyst for the oxidative cleavage of C=C bonds of styrene and its derivatives to corresponding carbonyl compounds up to 38–95% conversion levels with 63–99% selectivity of cleavage products under mild reaction conditions particularly at one atmospheric pressure, room temperature, with eco-friendly aqueous H<sub>2</sub>O<sub>2</sub> oxidant.

High surface area and highly ordered mesopores of SBA-15 may be provided a platform for isolated distribution of vanadyl catalytic sites that are responsible for higher conversion and selectivity.

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