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# Heterogeneous Baeyer–Villiger oxidation of cyclic ketones using *tert*-BuOOH as oxidant

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#### ABSTRACT

The  $[Sn(salen)]^{2+}$  complex moiety has been immobilized into NaY zeolite by *in situ* synthesis of the salen complex in NaY matrix to prepare a new catalyst, Sn(salen)-NaY. The catalyst has been characterized by UV–vis, infrared (IR) spectroscopy, X-ray powder diffraction, Mössbauer and <sup>119</sup>Sn NMR spectroscopy. The catalyst shows impressive catalytic performance (with high selectivity) in Baeyer–Villiger oxidation of various cyclic ketones including 2-adamantanone, cyclohexanone, cyclopentanone, 4-methylcyclohexanone, 2-methylcyclohexanone using *tert*-butyl hydroperoxide (*tert*-BuOOH) as an oxidant. The yield of  $\varepsilon$ -caprolactone from catalytic oxidation of cyclohexanone over Sn(salen)-NaY catalyst was *ca*. 75%. The catalyst can be recycled for several times without any major decline in catalytic activity.

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#### 1. Introduction

The Baeyer–Villiger reaction owes its name to the pioneering work of Adolf Baeyer and Victor Villiger who first reported the conversion of menthone and tetrahydrocarvone to the corresponding lactones using Caro's acid as an oxidant [1]. Since then the Baeyer–Villiger reaction has become an immensely important reaction in organic chemistry because the lactones or esters are important industrial intermediates in the production of polymers, agrochemicals, pharmaceuticals and herbicides [2–4]. Currently, the main industrial process for the production of  $\varepsilon$ -caprolactone is the oxidation of cyclohexanone with *m*-chloroperbenzoic acid [5]. The most common reagents used for this reaction are peroxycarboxylic acids. These are expensive, shock-sensitive, and potentially explosive, which limits their application, thereby necessitating the development of alternative oxidation methods which are commercially viable [6].

Supported catalysis processes, in particular, show growing potential because of easy separation of the products; such processes permitting the recycling and reuse of the catalyst with operational and economical advantages. The development of heterogeneous systems for Baeyer–Villiger reactions along with some mechanistic points was recently reviewed by Jiménez-Sanchidrián and Ruiz [7]. Polymer–anchored metal complexes [8–10], zeolites [11], solid acids [11,12], sulphonated resins [13], titanium silicalites [14], transition metal-functionalized hydrotalcites [15], Sn-synthesized hydrotalcites [16], cellulose supported dendritic Sn(II) complexes [17], aminomethyl polystyrene resin supported tin complex [18], chloromethyl polystyrene incorporated dendritic Sn complexes [19] are examples of some of the heterogeneous catalysts used to perform the Baeyer–Villiger reaction. Lei et al. have used palygorskite and montmorillonite as supports for Sn(II) complexes [20,21] and SnCl<sub>2</sub> [22], respectively.

Corma et al. have undertaken extensive research on Baeyer–Villiger oxidation reactions [23–29]. Tin-containing beta zeolite, developed by Corma et al. has become one of the most effective catalysts for the Baeyer–Villiger reaction [23]; the material can catalyze the oxidation of adamantanone and cyclohexanone to their corresponding lactones with excellent selectivity. Additionally, the catalyst was amenable to reuse with a virtually constant activity in up to four catalytic cycles. The catalyst tin-beta zeolite was also proved to be highly chemoselective in the Baeyer-Villiger oxidation of unsaturated ketones. In a recent publication, Corma et al. summarized the peculiarities of the Sn-Beta active sites, in respect of titanium containing molecular sieves [30]. Sn(IV) centers have been grafted onto mesoporous MCM-41 using different  $R_n Sn X_{4-n}$  precursors which are active for the Baeyer-Villiger oxidation of various substrates with hydrogen peroxide [25]. The oxidation system Sn-MCM-41/hydrogen peroxide provides the Baeyer–Villiger oxidation product of  $\alpha$ , $\beta$ -

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unsaturated- or aromatic aldehydes with excellent selectivities and conversions [25,31]. Corma et al. also proposed a mechanism for this oxidation process by combining the theoretical and experimental data [32].

Alkyl hydroperoxides are extensively used in industrial epoxidation reactions, for example in Halcon-Arco and Sumitomo processes [33]. The recycling of the co-product, that is, *tert*-BuOH, has been realized in the Sumitomo process. However, the use of tert-BuOOH in the Baeyer-Villiger reactions is not well documented. The salen complexes have been widely used as catalysts both in homogeneous and heterogeneous catalytic oxidation reactions [34-43]. Salen can efficiently bind both tin(II) and tin(IV) centers. Lewis acidic tin(II) and tin(IV) complexes are found to be quite useful in organic synthesis [44] and catalysis [45-47]. However, Schiff-base complexes of Sn(IV) have received only limited attention as catalysts [48-50]. Under homogeneous conditions, Sn(IV) chloride shows very low catalytic activity in Baeyer-Villiger oxidation by hydrogen peroxide [51]. To our knowledge the [Sn(salen)]<sup>2+</sup> moiety has never been employed as a catalyst in a Baeyer-Villiger reaction.

Herein, we report the preparation of a new heterogeneous catalyst by immobilizing the [Sn(salen)]<sup>2+</sup> complex moiety into NaY zeolite. The Sn(salen)-NaY catalyst has been characterized with the help of X-ray powder diffraction (XRD), UV–vis, infrared, Mössbauer and <sup>119</sup>Sn MAS NMR spectroscopy and its catalytic efficacy in Baeyer–Villiger oxidation reaction of cyclic ketones has been examined using *tert*-BuOOH as oxidant.

#### 2. Experimental

#### 2.1. Materials

The zeolite NaY (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 5.7) was purchased from Tosoh Company Ltd., Japan and used for immobilization. The ligand, N,N'-Bis(salicylaldehyde)-ethylenediimine (salenH<sub>2</sub>) was prepared by condensation of salicylaldehyde with 1,2-ethanediamine [52]. The solvents were purchased from Merck (India) and were distilled and dried before use. Tin(IV) chloride, 2-adamantanone, cyclohexanone, cyclopentanone, 4-methylcyclohexanone, 2-methylcyclohexanone and *tert*-BuOOH (70% aq.) were purchased from Aldrich and were used as received.

#### 2.2. Preparations

#### 2.2.1. Preparation of Sn(salen)Cl<sub>2</sub> complex

Sn(salen)Cl<sub>2</sub> complex was prepared by refluxing the mixture of SnCl<sub>4</sub>·5H<sub>2</sub>O (3.50 g, 0.01 mol) and salenH<sub>2</sub> ligand (2.68 g, 0.01 mol) in 10 mL of ethanol at 85 °C for 24 h under N<sub>2</sub> atmosphere, followed by dropwise addition of triethylamine (2.02 g, 0.02 mol) [53]. Triethyleamine solution was added to facilitate the de-protonation of salenH<sub>2</sub>. The complex obtained was light yellow in color. Anal. Calc. for C<sub>16</sub>H<sub>14</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>2</sub>Sn: C, 42.1; H, 3.1; N, 6.1. Found: C, 42.0; H, 3.2; N, 6.0%.

#### 2.2.2. Incorporation of Sn(IV) in NaY

To incorporate Sn(IV) into zeolite matrix we stirred an aqueous solution of  $SnCl_4$ ·5H<sub>2</sub>O (0.5 g in 25 mL H<sub>2</sub>O) with NaY (1 g) in suspension overnight. The white powder thus obtained was filtered and washed thoroughly with copious amounts of water and was dried under vacuum. This product is hereinafter designated as Sn-NaY.

#### 2.2.3. Preparation of Sn(salen)-NaY

Sn(salen)Cl<sub>2</sub> complex was incorporated in zeolite micropore by the "ship in a bottle" synthesis procedure [54]. At first 1 g of Sn-NaY was mixed very well with an excess amount of salenH<sub>2</sub>. The whole mass was then transferred to a round bottom flask and triehtyl-amine was added. The flask was evacuated and filled with N<sub>2</sub>. Then it was heated at 140 °C and stirred overnight. The whole mass was allowed to cool and was then taken out. It was soxhlet washed with ethanol, acetonitrile, and dichloromethane to wash out excess salenH<sub>2</sub>; complex thus formed onto the surface of catalyst. This pale yellow powder was employed as catalyst for Baeyer–Villiger reactions.

#### 2.3. Catalyst characterization

Electronic spectra were measured in the solid state on Hitachi U-3400 spectrophotometer. XRD studies were undertaken on a Rigaku Miniflex diffractometer using a CuKα radiation source. Mössbauer absorption spectra were obtained in standard transmission geometry, using a source Ca<sup>119m</sup>SnO<sub>3</sub> (10 mCi; Radiochemical Centre, Amersham, UK) that moved with constant acceleration and triangular waveform. The velocity calibration was made using a <sup>57</sup>Co Mössbauer source (10 mCi). A piece of iron foil enriched to 95% in 57Fe was used as the absorber. The tin content of the sample was estimated on a Varian Techtron AA-ABQ atomic absorption spectrometer. <sup>119</sup>Sn MAS NMR were recorded in solid state at 223.66 MHz by applying a high power decoupling technique on a Bruker Avance 600 (600 MHz, 14.09 T) instrument at Yokohama City University, Japan. Chemical shifts and shielding tensors are quoted with reference to tetramethyltin and SnO<sub>2</sub> was used as the secondary reference ( $\delta = -604$  ppm). Cross polarization was used: with contact time of 1 ms: recycle delay was generally 50 s. Magic-angle spinning rate was from 5 kHz, using 7 mm o.d. rotors. The reaction products were analyzed in a Varian CP-3800 gas chromatograph equipped with an FID detector and CP-Sil 8 CB capillary column and yields were determined by integration relative to an alkane internal standard. Other instruments used in this study were the same as those reported earlier [55].

#### 2.4. Catalytic reactions

The Baeyer–Villiger reactions were carried out in a glass batch reactor. In a typical reaction, 1 g of the substrate was taken in 5 mL of 1,4-dioxane. The solution was taken in a two neck round bottom flask. In the reaction mixture, 50 mg of catalyst was added and the temperature of the solution was equilibrated at 80 °C. Then 2 mL of *tert*-BuOOH was added to this with continuous stirring. The products of the oxidation reactions were collected at different time intervals and were identified by gas chromatography.

#### 3. Results and discussion

#### 3.1. Synthesis of catalyst

The catalyst Sn(salen)-NaY was prepared by a simple method called a "ship in a bottle" synthesis procedure. In this synthesis process, salenH<sub>2</sub> ligand is allowed to diffuse freely through the zeolite pores, and after formation of the complex with previously exchanged tin metal ion, the complex moiety becomes too large and rigid to escape from the NaY cages. The approach is well adapted for encapsulation of metal-salen complexes [salenH<sub>2</sub> = *N*,*N*'-bis-(salicylaldehyde)-ethylenediimine], as this ligand offers the desired flexibility. Thus a large variety of cobalt, manganese, iron, rhodium and palladium–salen complexes were prepared according to this method within the Y-zeolite supercages [42,55,56]. The tin content in Sn(salen)-NaY is given in Table 1. The elemental analysis show the molar ratio for N:Sn ≈ 1.82 and C:Sn ≈ 15.5 for Sn(salen)-NaY.

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Table 1
Elemental analyses for Sn(salen)Cl <sub>2</sub> and Sn(salen)-NaY

Species	Sn(IV) content (wt.%)	Sn(salen) complex concentration (mol/g)
Sn(salen)Cl <sub>2</sub> Sn(salen)-NaY	26.05 <sup>a</sup> (26.1) <sup>b</sup> 1.5 <sup>a</sup>	$-1.26 \times 10^{-4}$

<sup>a</sup> From atomic absorption study.

<sup>b</sup> Calculated value.

#### 3.2. Catalyst characterization

#### 3.2.1. Infrared spectroscopy

To verify the presence of complex [Sn(salen)]<sup>2+</sup> moiety in prepared catalyst, we have measured the IR spectra of the free Sn(salen)Cl<sub>2</sub> and the catalyst. The IR spectrum of the complex shows a sharp band at *ca*.  $1630 \text{ cm}^{-1}$ ; which can be attributed to the vibration band of azomethine group (Fig. 1) [57]. The lowering of this band by *ca*.  $20 \text{ cm}^{-1}$  in comparison to that of the free ligand is consistent with the donation of the nitrogen lone pair of the azomethine group to the metal ion. But the hybrid materials usually tend to absorb moisture. So, this band in the case of Sn(salen)-NaY may overlap with the H–O–H bending band appearing in this region. The bending band of H<sub>2</sub>O can be eliminated upon careful drving of the zeolite material. The Sn(salen)-NaY was heated in an air-oven at 120°C for two hours and was immediately dried in a vacuum desiccator, so that water can not be absorbed. No band for NaY appears in this region. So, the appearance of a band at 1630 cm<sup>-1</sup> can be attributed to the azomethine vibration bands and it can be predicted that Sn(salen) moiety is really present in the NaY zeolite matrix. The symmetric stretching and bending bands of the Al-O-Si framework of the zeolite appear at *ca*. 732 and  $454 \,\mathrm{cm}^{-1}$  respectively, indicating that the zeolite network remains intact [58,59]. But the vibration bands of the host zeolite obscure the IR bands of the complex in other regions.

Upon complex formation with salenH<sub>2</sub>, the charge of Sn(IV) is not fully balanced by the ligand. After de-protonation SalenH<sub>2</sub> can only balance two charges. Two more positive charges may be balanced by the anionic centers present in the framework. This requires that Sn–O vibration bands should appear in the IR spectra of Sn(salen)-NaY. The band appearing at  $565 \text{ cm}^{-1}$  may be attributed due to Sn–O vibration bands. The intensity of the band is not large, as is to be expected, because the tin content of the catalyst is only 1.5% (wt.) (Table 1).



Fig. 1. IR spectra of Sn(salen)Cl<sub>2</sub> complex (a) and Sn(salen)-NaY (b).



Fig. 2. Diffuse reflectance UV-vis spectra of Sn(salen)Cl<sub>2</sub> (a) and Sn(salen)-NaY (b).

#### 3.2.2. UV-vis spectroscopy

The electronic spectra of the Sn(salen)Cl<sub>2</sub> complex and Sn(salen)-NaY have been measured in the solid state (Fig. 2). As shown in Fig. 2a the spectra of the Sn(salen)Cl<sub>2</sub> complex have an highly intense absorption peak at *ca*. 340 nm and have a weak absorption peak at *ca*. 460 nm. A blue-shift of absorption band at a lower wavelength of *ca*. 410 nm is observed in case of Sn(salen)-NaY, clearly indicating that the in-plane ligand field around the metal ion is becoming stronger upon immobilization of the complex in NaY matrix than it was in its un-immobilized state. This type of blue-shifting is quite common in case of transition metal complexes immobilized in zeolite matrices; the distortion results in increased catalytic activity by facilitating the dissociation of axial ligands, thereby increasing the attack of a nucleophile [60].

#### 3.2.3. XRD studies

X-ray powder diffraction measurements have been carried out for Sn(salen)-NaY and free NaY zeolite; the results are shown in Fig. 3. Comparison of the XRD pattern of Sn(salen)-NaY with the standard pattern of NaY shows no appreciable change in peak positions of the diffraction lines of the mother zeolite. This indicates that the crystallinity of the zeolitic matrix remained intact upon immobilization of the [Sn(salen)]<sup>2+</sup> complex moiety. However, the relative intensities of some of the diffraction lines may undergo slight changes because of immobilization.

#### 3.2.4. <sup>119</sup>Sn Mössbauer spectroscopy

Mössbauer spectra of Sn(salen)-NaY obtained at 80 K are shown in Fig. 4. Mössbauer spectra can be helpful in acquiring information



Fig. 3. X-ray diffraction (XRD) patterns of NaY (a) and Sn(salen)-NaY (b).

of the co-ordination environment of the tin metal ion. From the spectra only a weak positive isomer shift (IS) value of 0.15 mm/s with low quadrupole splitting (OS) value of 0.27 mm/s is obtained. The quadrupole splitting (OS) of a Mössbauer line is caused by the interaction between an electric field gradient in the material and the nuclear quadrupole. The very low QS value means that in this complex, tin is surrounded by all highly electronegative elements (nitrogen and oxygen). Many complexes of tin halides were studied, but the complexes with donor ligand atoms O, S, N usually show no resolvable QS value. When differences in bond-polarity are small, as in these complexes and also in the stannates and Sn-M compounds (M=Group IV element), it is not surprising that the quadrupole splittings lie below the resolvable limit of 0.4-0.5 mm/s [61-64]. The small QS value again stands for the fact that the two nitrogen donor atoms of salenH<sub>2</sub> ligand must be in the cis positions of octahedron. There are quite a number of previous reports of organotin complexes for which the geometry of the complexes was assigned on the basis of OS values of Mössbauer spectra [65.66].

Here again, if the ligands are identical, the isomeric shift decreases on increasing the co-ordination number [64]. In six co-ordinated state, as the electronegativity of the atoms bound to tin increases, the isomer shift value decreases because of diminution of s-electron density at the tin nucleus [64]. In the present case, tin is bound to two nitrogen and four oxygen atoms, all of them highly electonegative. So, the small value of IS can be explained by considering the octahedral geometry of the immobilized complex.



Fig. 4. The Mössbauer spectra of Sn(salen)-NaY.



Fig. 5. 223.66 MHz <sup>119</sup>Sn CP-MAS NMR spectra of Sn(salen)-NaY.

Further, the low value of IS can be accounted for the geometry of the salenH<sub>2</sub> ligand, which suggests that the two nitrogen donors of the ligand must be in *cis* position of the octahedron. It is known that a *cis* octahedral complex will have a lower IS value than the corresponding *trans* isomer.

#### 3.2.5. <sup>119</sup>Sn NMR spectroscopy

The <sup>119</sup>Sn NMR spectroscopy was carried out on Sn(salen)-NaY. The solid-state <sup>119</sup>Sn NMR spectroscopy experiments do give information about structural and crystallographic asymmetric units and local symmetry including shielding tensor components. Tin has three isotopes (I = 1/2), of which <sup>119</sup>Sn is most commonly studied because of its slightly higher magnetic moment and appreciable natural abundance of 8.58%. <sup>119</sup>Sn NMR spectroscopy can be applied to the study of solids using magic-angle spinning (MAS), often together with cross polarization (CP) to give high-quality spectra. The shielding anisotropy (SA) is often also large, and its size can give an indication of the co-ordination at the <sup>119</sup>Sn center [67]. Here the spectrum as shown in Fig. 5 features a sharp singlet at  $\delta = -560$  ppm which is in close proximity with the corresponding value reported earlier for similar type of tin (IV) complexes [68]. The <sup>119</sup>Sn NMR chemical shift value suggests that tin is in octahedral geometry. In the spectrum, a single center band was found, indicating that there is only one type of tin present in the catalyst. It is expected that, upon immobilization, aggregation of tin nuclei will not occur, resulting in only monomeric tin complexes. This type of octahedral tin complex has previously been used for catalytic activity in the coupling of  $CO_2$  and propylene oxide [68].

From Mössbauer spectra and NMR spectra, it can be concluded that tin in the Sn(salen)-NaY has an octahedral environment in the zeolite matrix. The salen ligand might be occupying the coordination sites of the basal plane while two oxygen atoms from zeolite matrix occupy the axial positions. UV–vis spectra show that, upon immobilization, the in-plane ligand field becomes stronger, the axial ligands concomitantly being weaker [68], which may facilitate the removal of the one axial ligand by ketone in the intermediate stage of the reaction (Scheme 1).



**Criegee adduct** 

Scheme 1. Proposed mechanism for Baeyer-Villiger oxidation reaction using tert-BuOOH in the presence of Sn(salen)-NaY catalyst.

#### 3.3. Catalytic reactions

Catalytic Baeyer-Villiger oxidation reactions over Sn(salen)-NaY were studied with a series of cyclic ketones using tert-BuOOH as an oxidant to produce lactones with remarkable selectivity and good yield. The reactions were carried out in 1,4-dioxane at two different temperatures (70 °C and 90 °C). The kinetic profiles of the reactions are given in Fig. 6, while the results of the reactions are reported in Table 2. No induction period was observed in any of the reactions. Reactions generally began with relatively fast rates but tend to level off rather quickly. 2-adamantanone was oxidized with tert-BuOOH in 1,4-dioxane at 90 °C using Sn(salen)-NaY affording the required product with excellent conversion 100% (Table 2). For cyclohexanone, 75% conversion to  $\varepsilon$ -caprolactone (selectivity >90%) and for cyclopentanone 100% conversion to  $\delta$ -valerolacton (selectivity >99%) are achieved. Cyclopentanone shows a higher conversion rate than cyclohexanone in Baeyer-Villiger oxidation probably due to the formation of a six member ring that relives the ring strain. Substituted cyclohexanone also shows better conversion, as we can see; for 2-methylcyclohexanone and 4-methylcyclohexanone lactone production is 80% and 85% respectively, with >99% selectivity. Sn-catalyzed Baeyer-Villiger oxidation of cyclohexanone under heterogeneous condition has been previously studied by different groups (Table 3). Sn-MCM-41 shows only 36% conversion of cyclohexanone oxidized by H<sub>2</sub>O<sub>2</sub> [51]. Again Sn- $\beta$  shows 52% conversion of cyclohexanone with 98% lactone selectivity using  $H_2O_2$  (35 wt.%  $H_2O_2$  in  $H_2O)$  as an oxidant [23]. Using the same oxidant with Sn-palygorskite, Lei et al. achieved only 16% conversion of cyclohexanone with 90% selectivity [20]. A conversion of 30% to  $\varepsilon$ -caprolactone has been achieved with H<sub>2</sub>O<sub>2</sub> using Sn-doped hydrotalcite (Sn/HT) catalyst prepared by ion-exchange technique [16]. It is noteworthy that only cyclohexanone shows a slightly lower selectivity towards lactone (90%) in our study. Similar observations were also reported earlier [16,18,20]. Pillai and Sahle-Demessie [16] ( $\varepsilon$ -caprolactone selectivity > 95%), and Lei et al. [20] ( $\varepsilon$ -caprolactone selectivity 90%) have also observed that, apart from cyclohexanone, all the other ketones showed 100% lactone selectivity in the Baeyer-Villiger oxidation. In our case, the side product in Baeyer-Villiger oxidation of cyclohexanone was identified to be adipic acid. To verify if adipic acid is the side product of oxidation of cyclohexanone, we subjected  $\varepsilon$ -caprolactone to the Baeyer–Villiger reaction under the same condition as those of the ketone. The  $\varepsilon$ -caprolactone showed 8% conversion to adipic acid, but the substituted caprolactones remained inactive. The presence of substituents seems to affect the cleavage of C-O bond, but the reasons for this unusual behavior of cyclohexanone and  $\varepsilon$ -caprolactone are still unclear and require separate investigation. We have also performed the mass-balance study based on GC analysis for the Baeyer-Villiger oxidation of cyclohexanone. The mass-balance was close to  $98 \pm 1\%$  (Fig. 7).

The efficacy of  $H_2O_2$  as an oxidant has also been examined under the same heterogeneous reaction conditions where cyclo-

## Sectors Sn(salen)-NaYa Sn(salen)-NaY, tert-BuOOH Lastona

1,4-dioxane, Heat						
Substrate	Reaction time (h)	Reaction temp. (°C)	Product	Conversion <sup>b</sup> (wt.%)	Selectivity <sup>b</sup> (wt.%)	$TOF^{c}(h^{-1})$
	<b>)</b> 20	90	o	100	>99	51
<b></b> 0	12	70	o	100	>99	158
°	24	70	° °	75	90 <sup>d</sup>	50
CH3	24	90	O CH <sub>3</sub>	80	>99	47
O CH <sub>3</sub>	24	90	O CH <sub>3</sub>	85	>99	50

<sup>a</sup> Reaction conditions: ketone (1g); catalyst (50 mg); tert-BuOOH (2 mL); 1,4-dioxane (5 mL).

<sup>b</sup> Percentage of conversion and product selectivity were determined using Varian CP-3800 gas chromatograph equipped with an FID detector and a CP-Sil 8 CB capillary column.

<sup>c</sup> Turn over frequency = moles converted/(mol of active site × time).

<sup>d</sup> Remaining product is adipic acid.

hexanone conversion was only *ca*. 30%. Hence, under such reaction conditions *tert*-BuOOH is proved to be better oxidant. The effects of organic solvents like acetonitrile, chlorobenzene, nitrobenzene, and 1,4-dioxane in Sn(salen)-NaY catalyzed Baeyer–Villiger oxidation reaction of cyclohexanone have been studied. The results of this study are given in Table 4. Although all the solvent systems

show 100% lactone selectivity, 1,4-dioxane shows the best conversion of cyclohexanone. Increase of reaction temperature to  $75 \,^{\circ}$ C increases the conversion of cyclohexanone to 39% and 15% for the solvents acetonitrile and nitrobenzene, respectively. But further increases in reaction temperature showed no remarkable effects on the conversion of cyclohexanone.

#### Table 3

Heterogeneous Baeyer–Villiger oxidation of cyclohexanone catalyzed by Sn-containing catalysts.

Catalyst	Conversion (%)	TON <sup>a</sup>	ε-Caprolactone selectivity (%)	Ref.
Sn(salen)-NaY <sup>b</sup>	75	1210	90	This study
Sn-doped hydrotalcite <sup>c</sup>	30	119	>95	[16]
P-PAMAM-HBA (2.0G)-Sn(II) <sup>d</sup>	70	-	100	[17]
Aminomethyl polystyrene resin supported tin (PS-Sn) <sup>e</sup>	56	147	85	[18]
Sn-palygorskite <sup>f</sup>	16	26	90	[20]
Montmorillonite supported SnCl <sub>2</sub> <sup>g</sup>	100	166	100	[22]
Sn-MCM-41(9% SnO <sub>2</sub> ) <sup>h</sup>	36	12	97	[51]

<sup>a</sup> TON = moles converted/mol of active site.

<sup>b</sup> Cyclohexanone (10.2 mmol), *tert*-BuOOH (0.016 eq.), catalyst (50 mg), 1,4-dioxane (5 mL), 70 °C, 24 h.

<sup>c</sup> Cyclohexanone (12.5 mmol), catalyst (250 mg), 30% H<sub>2</sub>O<sub>2</sub> (0.1 eq.), acetonitrile (10 mL), 80 °C, 4 h.

<sup>d</sup> Cyclohexanone (0.1 mmol), 30% H<sub>2</sub>O<sub>2</sub> (2 eq.), catalyst (3 mg), 1,2-dichloroethane (3 mL), 70 °C, 15 h.

 $^{\rm f}$  Cyclohexanone (0.1 mmol), 30%  $\rm H_2O_2$  (1.5 eq.), catalyst (3 mg), 1,4-dioxane (3 mL), 70  $^{\circ}$ C, 24 h.

<sup>h</sup> Cyclohexanone (1.2 mmol), H<sub>2</sub>O<sub>2</sub> (35 wt.%) (0.003 eq.), methyl-tert-butylether (MTBE) (4 mL), catalyst (50 mg), 56 °C, 6 h.

e Cyclohexanone (0.1 mmol), H<sub>2</sub>O<sub>2</sub> (1.5 eq.), catalyst (4 mg), 1,4-dioxane (3 mL), 90 °C, 24 h.

 $<sup>^{\</sup>rm g}\,$  Cyclohexanone (0.1 mmol), 30%  $\rm H_2O_2$  (2.0 eq.), catalyst (3 mg), 1,4-dioxane (3 ml), 90  $^{\circ}$ C, 24 h.



**Fig. 6.** Reaction profile for the Baeyer–Villiger oxidation of a series of cyclic ketones using *tert*-BuOOH in the presence of Sn(salen)-NaY catalyst. (Reaction conditions: ketone (1 g); Sn(salen)-NaY (50 mg); *tert*-BuOOH (2 mL); 1,4-dioxane (5 mL), heat).



**Fig. 7.** Mass-balance for the Baeyer–Villiger oxidation of cyclohexanone. (Reaction conditions: cyclohexanone (1 g); Sn(salen)-NaY (50 mg); *tert*-BuOOH (2 mL); 1,4-dioxane (5 mL), 70 °C).

Table	4
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RIAVAR_VIIIIGAR AV	$v_1 d_1 + t_1 o_1 o_1 o_1 o_1 o_1 o_1 o_1 o_1 o_1 o$	welohov mono	in variance	organic colvente
Dauvu = v mizu = 0	$\lambda (u a (u $	venune anone	III various	Ulganne Sulvents.

Solvent	Cyclohexanone conversion (wt.%)	Selectivity of $\varepsilon$ -caprolactone (%)
Acetonitrile	37	>99
Chlorobenzene	25	>99
Nitrobenzene	12	>99
1,4-dioxane	75	90

 $^a$  Reaction conditions: cyclohexanone (1 g),  $tert\mbox{-BuOOH}$  (2 mL), Sn(salen)-NaY (50 mg), solvent (5 mL), 70  $^\circ$ C, 24 h.

Table 5

Comparison o	f catalytic activity	of Sn(salen)Cl <sub>2</sub> ª, Sn-NaY	<sup>o</sup> , and Sn(salen)-NaY <sup>b</sup> .
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Substrate	Catalyst	Conversion (wt.%)	Selectivity (wt.%)
Cyclohexanone	Sn(salen)Cl <sub>2</sub>	Not detectable	-
	Sn-NaY	9	98
	Sn(salen)-NaY	37	>99

 $^a\,$  Reaction condition: 1 g of substrate, 2 mL of tert-BuOOH, 2.9 mg of catalyst, 5 mL of acetonitrile, 70  $^\circ$  C, 24 h.

<sup>b</sup> Reaction condition: 1 g of substrate, 2 mL of *tert*-BuOOH, 50 mg of catalyst, 5 mL of acetonitrile, 70 °C, 24 h.

To test the efficacy of Sn(salen)-NaY catalyst in Baeyer–Villiger reaction over Sn-NaY and Sn(salen)Cl<sub>2</sub>, a comparative study has been undertaken (Table 5). It is clearly observed that Sn(salen)-NaY is a better catalyst both in conversion and selectivity over NaY and Sn(salen)Cl<sub>2</sub> under comparable conditions. The solvent for this comparison was chosen as acetonitrile, because the polarity of acetonitrile is ideal to dissolve Sn(salen)Cl<sub>2</sub> and *tert*-BuOOH. However, even in 1,4-dioxane, Sn(salen)Cl<sub>2</sub> did not show any catalytic activity.

Jing et al. reviewed the recent developments in research of Sn-containing catalysts used in Baeyer-Villiger oxidation [69]. Sn(IV) phosphonates have been shown to be highly active catalysts for Baeyer-Villiger oxidation with H<sub>2</sub>O<sub>2</sub> (30%) in a solvent free condition [70]. The surface area and pore sizes of these systems can be controlled and tuned over a wide range. Yoshida et al. developed an environmentally benign Baeyer-Villiger oxidation using fluorous catalysts [71].  $Sn[N(SO_2-n-C_8F_{17})_2]_4$  was the most effective catalyst for lactonization of 2-adamantanone. The fluorous tin(IV) catalyst was recyclable up to the 4th cycle reaction with high conversion and selectivity. It was also found that the Florous Biphasic System reaction displayed better selectivity than a single-phase system. Furthermore, fluorous amide catalysts were more active than the corresponding triflate catalysts [71]. 3% Sn ion-exchanged hydrotalcite exhibited superior activity at 30% conversion and 100% selectivity of liquid phase Baeyer-Villiger oxidation of admantonone using hydrogen peroxide  $(H_2O_2)$  as an oxidant and acetonitrile as a solvent [72].

Several other metals are found to be active in Baeyer-Villiger reaction under heterogeneous conditions. Redox molecular sieves, namely Mn-AlPO-36 and Co-AlPO-36 that are employed on the oxidation of ketones to lactones show high conversion rates. However, the reaction is carried out by peracids prepared in situ from sacrificial benzaldehyde and oxygen [73]. Palazzi et al. have anchored platinum complexes onto polymers to prepare heterogeneous Baeyer-Villiger oxidation catalyst [9]. Nanosized WO<sub>3</sub> particles supported on MCM-48 work as a highly efficient and selective heterogeneous catalyst for Baeyer-Villiger reaction. But the oxidant in this case is peracetic acid, and hydrogen peroxide turned out to be much less effective [74]. A nickel complex supported on a surface-functionalized silica gel is an active and selective heterogeneous catalyst for the liquid phase, room temperature Baeyer-Villiger oxidation of both cyclic and linear ketones using molecular oxygen and sacrificial benzaldehyde [75]. Bhaumik et al. demonstrated that the titanium silicate molecular sieve (TS-1) can act as an efficient catalyst for Baeyer-Villiger oxidation of cyclic and aromatic ketones under triphase conditions (solid catalyst along with two immiscible liquid reactants in the absence of any co-solvent), using dilute H<sub>2</sub>O<sub>2</sub> [76]. Magnesium-aluminium hydrotalcite is used as a catalyst in the Baeyer-Villiger oxidation of cyclic ketones with a mixture of 30% H<sub>2</sub>O<sub>2</sub> and benzonitrile as oxidant [77]. Tetrahedrally coordinated Fe<sup>3+</sup> was incorporated inside the framework of MCM-41 and the catalyst exhibits the highest activity for Baeyer-Villiger

oxidation of ketones using molecular oxygen and sacrificial benzaldehyde [78]. Recently, Steffen et al. reported the alumina catalyzed Baeyer–Villiger oxidation of cyclohexanone with hydrogen peroxide as oxidant [79]. Sever and Root proposed that the ketone substrate and the hydrogen peroxide oxidant both interact with the metal active site; thus  $Sn(IV) - H_2O_2$  directly participates in the addition reaction between hydrogen peroxide and acetone [80].

Leaching of the metal is a common problem in reactions in the liquid phase (particularly in those involving oxidation with peroxide by an effect of the chelating and solvolytic properties of the oxidant and products) [7,81]. Although no evidence of metal leaching during the Baeyer-Villiger reaction appears to exist, mesoporous catalysts containing titanium have been found to release some metal during the oxidation of alcohols with hydrogen peroxide; with tert-butylhydroperoxide as oxidant, however, the amount of titanium leached was minimal [81]. To test if the tin is leaching out from the catalyst during reaction, the reaction mixture was filtered out hot after the reaction is over and was subjected to atomic absorption spectroscopic analysis. The analyses show tin was absent in the filtrate. Besides, the filtered mixture did not show any catalytic activity toward oxidation reactions. Therefore, it is clear that tin is not leaching out from the catalyst during Baeyer-Villiger oxidations. The Sn(salen)-NaY catalyst has been recovered from the reaction mixture and has been reused successively three times under the same reaction conditions. The solid catalyst has been recovered by filtration after each reaction and has been washed thoroughly with 1,4-dioxane. The recovered catalyst is found to exhibit almost the same catalytic activity for cyclohexanone oxidation reaction by tert-BuOOH in every run: first run, cyclohexanone conversion = 75%, turnover = 1210; second run, cyclohexanone conversion = 74%, turnover = 1215; third run, cyclohexanone conversion = 75%, turnover = 1208. No induction period was observed in any of the reactions (Fig. 6).

#### 4. Conclusion

In summary, we have succeeded in immobilizing tin-salen moiety into NaY zeolite matrix through an *in situ* synthesis procedure. The complex undergoes noticeable distortion after immobilization and remained in an octahedral geometry. The resulting material was successfully employed in Baeyer–Villiger oxidation reactions using *tert*-BuOOH as oxidant. The catalyst showed remarkable activity, selectivity and high TON in Baeyer–Villiger oxidation reactions. Since such reactions are industrially important, the catalyst has some potential for commercial use.

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#### References

- [1] A. Baeyer, V. Villiger, Ber. Dtsch. Chem. Ges. 32 (1899) 3625-3627.
- [2] G.C. Krow, Org. React. 43 (1993) 251-798.
- [3] C.H. Hassall, Org. React. 9 (1957) 73-106.
- [4] C. Bolm, Adv. Catal. Process. 2 (1997) 43-68.

- [5] H. Heaney, in: S.D. Burke, R.L. Danheiser (Eds.), Handbook of Reagents for Organic Synthesis—Oxidizing and Reducing Agents, Wiley, 1999, pp. 84–89.
- [6] G.-J. Ten Brink, I.W.C.E. Arends, R.A. Sheldon, Chem. Rev. 104 (2004) 4105–4124.
- [7] C. Jiménez-Sanchidrián, J.R. Ruiz, Tetrahedron 64 (2008) 2011–2026.
- [8] G. Strukul, A. Varagnolo, F. Pinna, J. Mol. Catal. A 117 (1997) 413–423
- [9] C. Palazzi, F. Pinna, G. Strukul, J. Mol. Catal. A 151 (2000) 245–252.
- [10] R. Bernini, E. Mincione, M. Cortese, R. Saladino, G. Gualandi, M.C. Belfiore, Tetrahedron Lett. 44 (2003) 4823–4825.
- 11] J. Fischer, W.F. Holderich, Appl. Catal. A 180 (1999) 435–443.
- [12] A. Berkessel, R.M.M. Andrae, Tetrahedron Lett. 42 (2001) 2293–2295.
  [13] W. Hoelderich, J. Fischer, G. Schindler, P. Arntz, German Patent DE 19745442 (1999).
- [14] B. Notari, Adv. Catal. 41 (1996) 253-334.
- [15] K. Kaneda, S. Ueno, T. Imanaka, J. Mol. Catal. A 102 (1995) 135-138.
- [16] U.R. Pillai, E. Sahle-Demessie, J. Mol. Catal. A: Chem. 191 (2003) 93-100.
- [17] C. Li, J. Wang, Z. Yang, Z. Hu, Z. Lei, Catal. Commun. 8 (2007) 1202-1208.
- [18] Q. Zhang, S. Wen, Z. Lei, React. Funct. Polym. 66 (2006) 1278-1283.
- [19] C.-L. Li, Z.-W. Yang, S. Wu, Z.-Q. Lei, React. Funct. Polym. 67 (2007) 53-59.
- [20] Z. Lei, Q. Zhang, J. Luo, X. He, Tetrahedron Lett. 46 (2005) 3505-3508.
- [21] Z. Lei, Q. Zhang, R. Wang, G. Ma, C. Jia, J. Organomet. Chem. 691 (2006) 5767–5773.
- [22] Z. Lei, G. Ma, C. Jian, Catal. Commun. 8 (2007) 305–309.
- [23] A. Corma, L.T. Nemeth, M. Renz, S. Valencia, Nature 412 (2001) 423-425.
- [24] M. Renz, T. Blasco, A. Corma, V. Fornés, R. Jensen, L. Nemeth, Chem. Eur. J. 8 (2002) 4708–4717.
- [25] A. Corma, M.T. Navarro, M. Renz, J. Catal. 219 (2003) 242-246.
- [26] A. Corma, V. Fornés, S. Iborra, M. Mifsud, M. Renz, J. Catal. 221 (2004) 67-76.
- [27] A. Corma, S. Iborra, M. Mifsud, M. Renz, M. Susarte, Adv. Synth. Catal. 346 (2004) 257-262.
- [28] M. Boronat, P. Concepción, A. Corma, M. Renz, S. Valencia, J. Catal. 234 (2005) 111–118.
- [29] A. Corma, S. Iborra, M. Mifsud, M. Renz, J. Catal. 234 (2005) 96-100.
- [30] M. Boronat, P. Concepción, A. Corma, M. Renz, Catal. Today 121 (2007) 39-44.
- [31] A. Corma, S. Iborra, M. Mifsud, M. Renz, Arkivoc 9 (2005) 124-132.
- [32] M. Boronat, A. Corma, M. Renz, G. Sastre, P.M. Viruela, Chem. Eur. J. 11 (2005) 6905-6915.
- [33] J.-M. Brégeault, Dalton Trans. (2003) 3289-3302.
- [34] W. Zhang, J.L. Loebach, S.R. Wilson, E.N. Jacobsen, J. Am. Chem. Soc. 112 (1990) 2801-2803.
- [35] E.N. Jacobsen, Acc. Chem. Res. 33 (2000) 421-431.
- [36] E.N. Jacobsen, in: I. Ojima (Ed.), Catalytic Asymmetric Synthesis, VCH Publishers, New York, 1993, pp. 159–202.
- [37] T. Katsuki, Coord. Chem. Rev. 140 (1995) 189-214.
- [38] T. Uchida, R. Irie, T. Katsuki, Tetrahedron 56 (2000) 3501-3509.
- [39] C. Adhikary, R. Bera, B. Dutta, S. Jana, G. Bocelli, A. Cantoni, S. Chaudhuri, S. Koner, Polyhedron 27 (2008) 1556–1562.
- [40] T. Niimi, T. Uchida, R. Irie, T. Katsuki, Adv. Synth. Catal. 1 (2001) 79-88.
- [41] K.C. Gupta, A.K. Sutar, Coord. Chem. Rev. 252 (2008) 1420–1450.
- [42] S. Koner, Chem. Commun. (1998) 593-594.
- [43] P.K. Saha, B. Dutta, S. Jana, R. Bera, S. Koner, Polyhedron 26 (2006) 563–571.
- [44] M. Pereyre, J.-P. Quintard, A. Rahm, Tin in Organic Synthesis, Butterworth, Lon-
- don, 1987 (Chapter 4).
- [45] T. Hashiyama, Med. Res. Rev. 20 (2000) 485-501.
- [46] T. Mukaiyama, S. Kobayashi, in: B.M. Trost (Ed.), Stereocontrolled Organic Synthesis, Blackwell Scientific Publications, Oxford, 1994, pp. 37–65.
- [47] J. Harada, A. Kimura, S. Tagami, J.P. Watanabe, Idemitsu Kosan Co., Ltd., Japan, Patent Application, Japan, Kokai (1976).
- [48] J.F. Larrow, US Patent, 6448449, B2, 66 (2002).
- [49] Y.N. Belokon, A.A. Petrosyan, V.I. Maleev, T.F. Saveleva, A.V. Grachev, N.S. Ikonnikov, A.S. Sagiyan, Russ. Chem. Bull. 51 (2002) 2086–2089.
- [50] A.A. Kelkar, S.S. Tonde, S.S. Divekar, R.V. Chaudhari, Council of Scientific and Industrial Research, India, US Patent Application, U.S. Pat. Appl. Publ. (2002).
- [51] A. Corma, M.T. Navarro, L. Nemeth, M. Renz, Chem. Commun. (2001) 2190–2191
- [52] R.H. Holm, G.W. Everett, A. Chakravorty, Prog. Inorg. Chem. 7 (1965) 83–214.
- [53] A. Van den Bergen, R.J. Cozens, K.S. Murray, J. Chem. Soc. A (1970) 3060–3064.
- [54] F. Bedioui, Coord. Chem. Rev. 144 (1995) 39–68 (and references therein).
- [55] B. Dutta, S. Jana, R. Bera, P.K. Saha, S. Koner, Appl. Catal. A: Gen. 318 (2007)
- 89–94.
- [56] N. Herron, Inorg. Chem. 25 (1986) 4714–4717.
- [57] R.M. Silverstein, G.C. Bassler, Spectrometric Identification of Organic Compounds, John Wiley and Sons Inc., New York, 1963, pp. 55–56.
- [58] D.K. Dey, M.K. Das, H. Nöth, Z. Naturforsch. 54b (1999) 145-154.
- [59] R.M. Barrer, Hydrothermal Chemistry of Zeolite, Academic Press, New York, 1982.
- [60] R. Ganesan, B. Viswanathan, J. Phys. Chem. B 108 (2004) 7102-7114.
- [61] N.N. Greenwood, J.N.R. Ruddick, J. Chem. Soc. A (1967) 1679–1683.
- [62] J. Phillip, M.S. Mullins, C. Curran, Inorg. Chem. 7 (1968) 1895-1898.
- [63] H.A. Stockler, H. Sano, R.H. Herber, J. Chem. Phys. 45 (1966) 1182–1189.
- [64] R.V. Parish, R.H. Platt, J. Chem. Soc. A (1969) 2145–2150.
- [65] D.V. Naik, C. Curran, Inorg. Chem. 10 (1971) 1017-1020.
- [66] B.W. Fitzsimmons, N.J. Seeley, A.W. Smith, J. Chem. Soc. A (1969) 143–146.
- [67] R.K. Harris, S.T. Lawrence, S. Oh, V.G. Kumar Das, J. Mol. Struct. 347 (1995) 309–320.
- [68] H. Jing, S.K. Edulji, J.M. Gibbs, C.L. Stern, H. Zhou, S-B.T. Nguyen, Inorg. Chem. 43 (2004) 4315–4327.

- [69] H. Jing, J. Li, W. Dai, Y. Cao, K. Fan, Petrochem. Technol. 36 (2007) 200–204.
- [70] S. Kirumakki, S. Samarajeewa, R. Harwell, A. Mukherjee, R.H. Herber, A. Clearfield, Chem. Commun. (2008) 5556–5558.
- [71] A. Yoshida, X. Hao, O. Yamazaki, J. Nishikido, Molecules 11 (2006) 627-640.
- [72] Z. Yang, S.-E. Park, Diffus. Defect Data Part B: Solid State Phenom. 119 (2007) 163–166.
- [73] R. Raja, J.M. Thomas, G. Sankar, Chem. Commun. (1999) 525-526.
- [74] D.H. Koo, M. Kim, S. Chang, Org. Lett. 7 (2005) 5015-5018.
- [75] I.C. Chisem, J. Chisem (née Bovey), J.H. Clark, New J. Chem. (1998) 81–82.
- [76] A. Bhaumik, P. Kumar, R. Kumar, Catal. Lett. 40 (1996) 47-50.
- [77] R. Llamas, C. Jiménez-Sanchidrián, J.R. Ruiz, Tetrahedron 63 (2007) 1435– 1439.
- [78] T. Kawabata, Y. Ohishi, S. Itsuki, N. Fujisaki, T. Shishido, K. Takaki, Q. Zhang, Y. Wang, K. Takehira, J. Mol. Catal. A: Chem. 236 (2005) 99–106.
- [79] R.A. Steffen, S. Teixeira, J. Sepulveda, R. Rinaldi, U. Schuchardt, J. Mol. Catal. A: Chem. 287 (2008) 40–43.
- [80] R.R. Sever, T.W. Root, J. Phys. Chem. B 107 (2003) 10848-10862.
- [81] I.W.C.E. Arends, R.A. Sheldon, Appl. Catal. A: Gen. 212 (2001) 175-187.