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Peculiarities of Sn-Beta and potential industrial applications

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Abstract

In the search for new environmentally friendly processes Sn-Beta has been developed as a heterogeneous catalyst. Its reactivity is different from similar materials, i.e. titanium containing molecular sieves. The origin of its singularity is described by means of density functional theory (DFT), in situ IR spectroscopy of deuterated acetonitrile and catalytic studies. All results point to a bi-functional active site that involves a Lewis acid tin centre and an adjacent oxygen atom capable to accept hydrogen bonding from water or hydrogen peroxide. The catalyst may be employed for Baeyer-Villiger oxidations taking part in multi-step synthesis of industrial interest, achieving more than 10,000 turnovers per tin centre.

Keywords: Bi-functional site; Heterogeneous catalysis; Solid Lewis acid; Tin-Beta zeolite

1. Introduction

The development of new environmentally friendly chemical processes is an urgent need and therefore new active, selective and recyclable catalysts are required. In this sense, heterogeneous catalysts can be an excellent option. Thus, a selective heterogeneous catalyst should possess isolated and well defined single sites [1,2]. With respect to solid Lewis acid catalysts, the discovery of Ti-silicalite (TS-1) as a catalyst for a series of oxidation reactions and its successful industrial implementation represented an important breakthrough [3,4]. This material can selectively catalyse reactions such as alcohol and alkane oxidation, olefin epoxidation, aromatics hydroxylation, and cyclohexanone ammoximation, among others, being its catalytic activity associated to the presence of isolated tetrahedral Ti(IV) atoms in framework positions.

Titanium has also been incorporated into the framework of larger pore 12-membered ring zeolites [5,6] and into mesoporous molecular sieves to overcome the pore restrictions of TS-1 [7]. An important development was the synthesis of aluminium-free titanium Beta zeolite in fluoride medium [8] not only because of the interesting adsorption and catalytic properties of the resulting material but also because it opened the possibility for introducing other Lewis acid metals into the zeolite framework. Thus, isolated tetrahedral tin sites were achieved in zeolite Beta [9] and characterized by ^{119}Sn MAS NMR [10] and EXAFS spectroscopy [11]. This material, namely Sn-Beta, has singular activity for the Baeyer-Villiger (BV) oxidation of cyclic ketones [12], and aromatic [13] and α,β-unsaturated [14] aldehydes, as well as for the cyclisation of citronellal to isopulegol (cyclic carbonyl-ene reaction) [15] and Meerwein-Ponndorf-Verley-Oppenauer redox reactions [16,17]. Similar catalytic activity for the last two reactions was obtained when zirconium was incorporated in the Beta structure by the fluoride synthesis procedure [18,19].

When Sn-Beta was applied to the BV oxidation of cyclic ketones in the presence of hydrogen peroxide, titanium containing zeolites were the well-established standard for oxidation reactions in the presence of hydrogen peroxide, but showed no activity for BV oxidations. On the contrary, Sn-Beta was active for BV oxidation and the other reactions named above, all of them involving a carbonyl compound. In this manuscript, we will summarize the peculiarities of the Sn-Beta active sites, with respect to titanium containing molecular sieves, as they have been studied by spectroscopic characterization, density functional theory (DFT) calculations and catalytic activity. Finally, a potential industrial application of the catalyst will be discussed.

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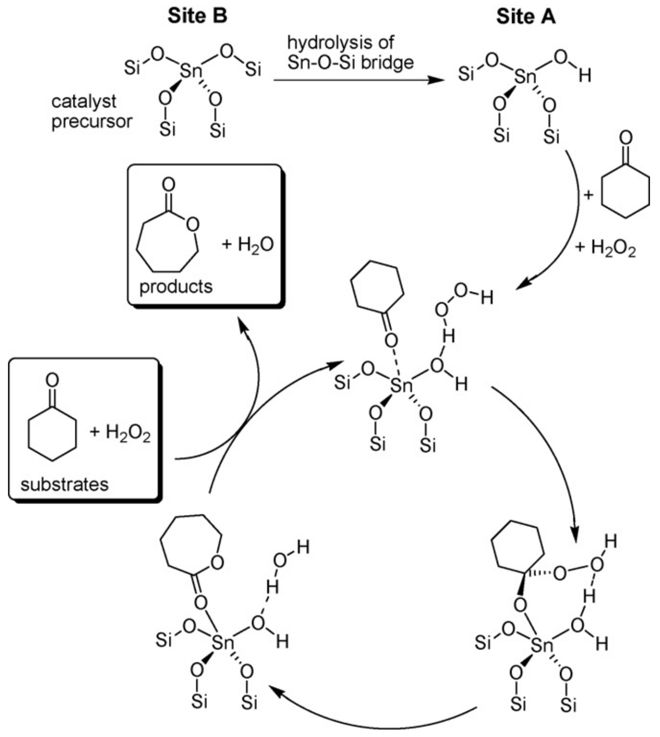
2. Nature of the catalytically active site

It was believed, in a first approximation, that the catalytically active species of Sn-Beta for BV oxidations was tetrahedrally coordinated framework Sn (site B, Scheme 1). A deeper study combining spectroscopic, mechanistic and kinetic experiments indicate that the active site was associated to the presence of partially hydrolyzed framework Sn centres (sites A) that combined a Lewis acid site (Sn) and an adjacent basic site on the oxygen atom of the Sn–OH group formed upon hydrolysis. The presence of this acid-base pair was required to propose the BV oxidation mechanism given in Scheme 1. There, in the first step, cyclohexanone is coordinated to the Lewis acid tin centre, as established before [10,12], and the second centre should bind to a hydrogen peroxide molecule building up the ‘‘loaded complex’’ (Scheme 1) [20]. In the corresponding spatial arrangement, the oxygen atom to be inserted is placed on the line of approach for the nucleophilic attack of the activated carbonyl group. Oxygen transfer and rearrangement are the next steps, followed by product desorption.

First evidences for this bi-functional active site were of theoretical nature [21]. When the mechanism of the Baeyer-Villiger oxidation with hydrogen peroxide was studied by means of DFT calculations it was found that, indeed, the tin atom of site B can coordinate cyclohexanone. The organic molecule acts as Lewis base and the tin centre as Lewis acid accepting the electron density from that. Hereby, the most important donor-acceptor interaction occurs between the HOMO of the adsorbed molecule and the LUMO of the catalyst, which is a combination of the four $\sigma^*_{\mathrm{Sn-O}}$ anti-bonding orbitals. This interaction implies a lengthening of the four Sn–$\mathrm{O_{framework}}$ distances that is difficult in the rigid zeolite framework. Much more favourable adsorption conditions were detected for the site A involving a flexible OH group. The calculated adsorption energy raised from -1.6 to -9.7 kcal mol^{-1} and the distance between the carbonyl oxygen and the tin centre decreased from 2.89 to 2.43 Å for cyclohexanone adsorbed to site B and site A, respectively. These theoretical results were indicative and site A can be claimed as active site for the BV oxidation. However, as the conclusion was based on a model zeolite cluster, experimental evidence on the presence of sites A and B and the correlation between the concentration of sites A and catalytic activity was required.



Scheme 1. Mechanism of the Baeyer-Villiger oxidation of cyclohexanone with hydrogen peroxide catalysed by Sn-Beta [20].

With the aim to get some spectroscopic evidence on the presence of the different Sn-sites, an in situ IR spectroscopy experiment was designed [22]. Deuterated acetonitrile was chosen as adsorbate since it can differentiate Lewis acid sites of different strength, by monotoring its ν(C≡N) stretching vibration in IR spectroscopy [23–26]. DFT calculations on coordinated deuterated acetonitrile show site A as a strong Lewis acid site with an adsorption energy of -9.2 kcal mol^{-1} versus -0.3 kcal mol^{-1} for site B. The distances r(Sn–N) were in line with 2.64 and 2.38 Å for site A and B, respectively, and the nitrile bond prolonged to 1.156 and 1.153 Å. The latter values correspond to a change in the ν(C≡N) stretching vibration of 53 and 43 cm^{-1} with respect to the gas phase value, and these shifts should be measurable experimentally.

Indeed, when the in situ IR spectrum of acetonitrile adsorbed on Sn-Beta was recorded four bands in the 2260–2340 cm^{-1} region associated with the ν(C≡N) stretching vibration could be observed (Fig. 1). The bands at 2316 and 2308 cm^{-1} are associated with acetonitrile coordinated with Lewis acid sites and IR bands at 2276 and 2268 cm^{-1} are due to acetonitrile coordinated to silanol groups and physisorbed acetonitrile, respectively. The two bands assigned to acetonitrile coordinated to the Lewis acid sites, 2316 and 2308 cm^{-1}, correspond

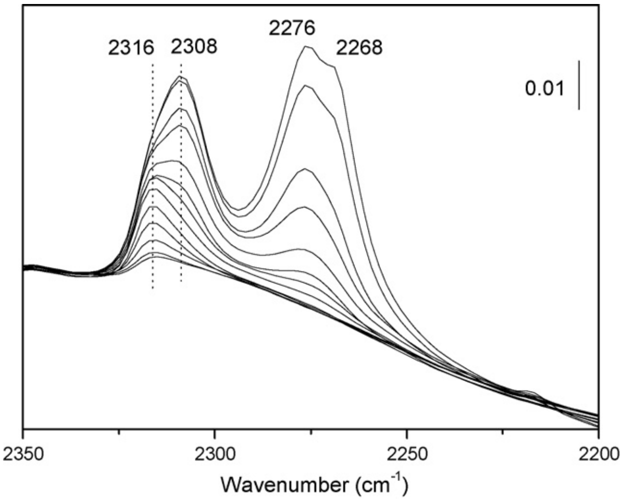


Fig. 1. IR spectra of deuterated acetonitrile adsorbed on Sn-Beta zeolite at increasing acetonitrile coverage [22].

to shifts of the stretching vibration of 51 and 43 cm^{-1} in good agreement with the calculated values.

It is clear that the 2316 cm^{-1} band should correspond to the stronger sites since the influence on the nitrile bond is stronger and, consequently, the shift of the stretching band larger (cf. also the results of the DFT calculations). This could be confirmed additionally by the kinetics of acetonitrile desorption at 25 °C and 10^{-4} Torr, monitored by IR spectroscopy [22], in where the band at 2308 cm^{-1} decreased much faster than the one at 2316 cm^{-1}.

Now, for the first time we had in hands a sensitive and fast spectroscopic method for the characterization and differentiation of the tin sites of Sn-Beta. The ^{119}Sn MAS NMR spectroscopy measurements were not appropriate for this purpose since they had to be done on samples enriched with ^{119}Sn that are obtained by a modified synthesis sequence. Furthermore, they required an average analysis time of 2 days with considerable background noise and, therefore, this technique is less sensitive to distinguish among different species.

In order to analyse the influence of the post-synthesis treatment on the number of strong sites, the ‘‘in situ’’ IR spectroscopy of acetonitrile was used to characterize a series of samples that were obtained from a calcination study. In the calcination of the same catalyst precursor in a quartz tubular reactor at 580 °C different amounts of water (up to 4 vol%) were added to the air flow. The resulting samples showed a different catalytic activity being the best ones those activated in presence of water. This already let us suppose that the water helps to hydrolyze bonds in the zeolite and that the best samples should be richer in site-A-type tin centres, i.e. those inducing a shift to 2316 cm^{-1} when adsorbing deuterated acetonitrile. Indeed, when the initial rate of the Baeyer-Villiger oxidations were correlated with the number of centres that correspond to the IR bands at 2316 cm^{-1} (sites A) a linear dependence could be detected (Fig. 2). Furthermore, the observed straight line goes very close to the origin indicating that almost all catalytic activity is created by this type of site. When the same correlation is made for the centres that correspond to the IR band at 2308 cm^{-1} (sites B) a random distribution is obtained without any clear trend (Fig. 3). From the combination of the four studies, i.e. DFT calculations, IR spectroscopy of adsorbed acetonitrile, activation of the catalyst in presence of different amounts of water and the catalytic activity in the Baeyer-Villiger oxidations, it can be concluded that the active species of the Sn-Beta catalyst is a bi-functional $(–SiO)_3SnOH$ centre.

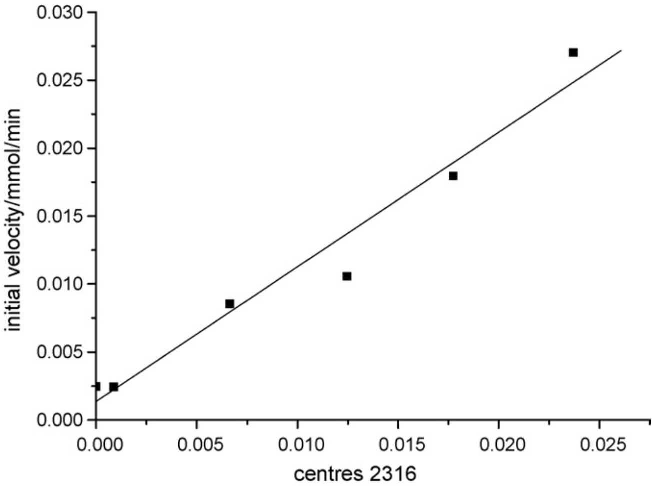


Fig. 2. Initial rate of the Baeyer-Villiger oxidation of adamantanone vs. intensity of the 2316 cm^{-1} IR band of deuterated acetonitrile adsorbed onto Sn-Beta zeolite [22].

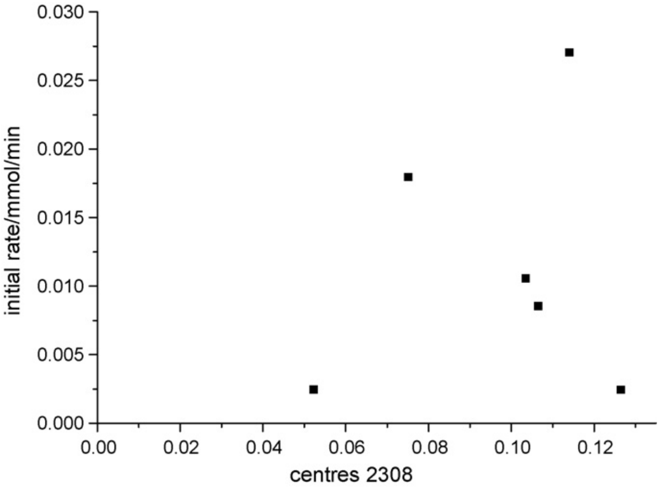


Fig. 3. Initial rate of the Baeyer-Villiger oxidation of adamantanone vs. intensity of the 2308 cm^{-1} IR band of deuterated acetonitrile adsorbed onto Sn-Beta zeolite [22].

It is interesting to notice that around 80% of the tin incorporated in the zeolite framework is present as tin atom coordinated to four framework silyloxy groups. This species is found to be catalytically in-active and may be converted by hydrolysis into the active $(–SiO)_3SnOH$ centre, i.e. the catalyst performance can still be improved by a more appropriate activation procedure.

Further experimental evidence for the existence of a bi-functional $(–SiO)_3SnOH$ centre was achieved through a kinetic study of the catalytic Baeyer-Villiger oxidation of cyclohexanone with hydrogen peroxide by applying the initial rate methodology [21]. In preliminary experiments it was found that water competes with cyclohexanone for coordination to the Lewis acid centre, and with hydrogen peroxide for coordination to the oxygen of the Sn–OH group. Therefore its coordination, without deprotonation, to the tin centre has been considered in the kinetic model. Being the hydrogen peroxide molecule very similar to water, an analogous behaviour with respect to the tin centre, i.e. a coordination without deprotonation, could be expected. In an analogous study for ε-caprolactone a linear relationship was obtained between the inverse of the initial reaction rate and the initial lactone concentration that indicated that it can adsorb on one of the centres, presumably on the tin atom. However, as the ε-caprolactone concentration is zero at the beginning of the reaction and the initial rates were considered, its concentration was not included in the kinetic equation. From all these considerations the following initial rate equation was derived:

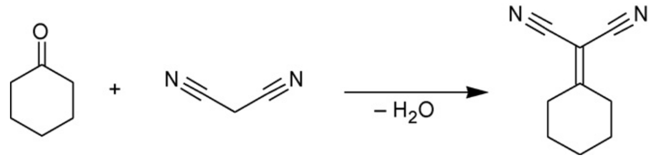
$$r_0 = \frac{k[\mathrm{CH}]_0[\mathrm{HP}]_0}{(1 + K_\mathrm{a}[\mathrm{CH}]_0 + K_\mathrm{b}[\mathrm{CH}]_0 + K_\mathrm{c}[\mathrm{WA}]_0)(1 + K_\mathrm{d}[\mathrm{HP}]_0 + K_\mathrm{e}[\mathrm{WA}]_0)} \quad (1)$$

where r_0 is the initial reaction rate, $[\mathrm{CH}]_0$ the initial concentration of cyclohexanone, $[\mathrm{HP}]_0$ the initial concentration of hydrogen peroxide, $[\mathrm{WA}]_0$ the initial concentration of water, k the rate constant is k_0 $[\mathrm{S}]_0$, K_a the adsorption constant of cyclohexanone at the tin centre, K_b the adsorption constant of hydrogen peroxide at the tin centre, K_c the adsorption constant of water at the tin centre, K_d the adsorption constant of hydrogen peroxide at the oxygen centre, and K_e is the adsorption constant of water at the oxygen centre.

To verify this initial rate equation three different experimental conditions were chosen and the initial rates were calculated by dividing conversion by reaction time at levels of conversion below 10% [21]. A good fit of the experimental results to the derived equations has been observed. Furthermore, the experimentally obtained activation energy of 11 kcal mol^{-1} was close to the one calculated (14.8 kcal mol^{-1}) using a cluster model of site A and considering the energy difference between the transition state of the rearrangement step and the reactants complex. In summary, the experimental results of the kinetic study were in accordance with a bi-functional site composed of a Lewis acid site that coordinates cyclohexanone but also water and hydrogen peroxide and an adjacent site, the Sn–OH oxygen atom, capable of hydrogen bonding to water and hydrogen peroxide. These results coincided perfectly with DFT calculations on a cluster model of site A.

A further experimental evidence for the presence of the basic centre in the bi-functional active site was searched for by carrying out a typical base catalysed reaction, i.e. the condensation of ketones with malononitrile (Scheme 2) [20]. This type of reaction has been often used to characterize basic sites of solid materials [27] and does not require strong basicities. Furthermore, it has been reported that the product of interaction of acid and basic sites of aluminium oxide is able to catalyse the reaction, although with a high amount of catalyst (350 wt%) [28]. Only half of the amount of catalyst was needed when $\mathrm{AlPO_4}$-$\mathrm{Al_2O_3}$, a material with similar characteristics, was used [29].

When equimolar amounts of cyclohexanone and malononitrile were mixed in the presence of Sn-Beta, the desired product, i.e. cyclohexylidenemalononitrile, was observed in 46% yield after 6 h reaction time (Table 1, entry 1) [20]. The catalytic action of the tin centre is evident when this result is compared to the 4% conversion obtained with the all-silica zeolite Beta (entry 2). However, not only the presence of tin is necessary but also a singular site geometry. Tin oxide, finely dispersed over all silicon zeolite Beta, does not improve much the catalytic activity of the all-silica zeolite, neither do tin centres of Sn-Beta samples that were calcined in absence of water and are supposed to involve almost exclusively tin centres of the type B.



Scheme 2. Condensation of cyclohexanone with malonitrile.

Table 1
Condensation of cyclohexanone with malononitrile catalysed by different Beta zeolites [20]

Entry	Catalyst	Yield (%)	Selectivity (%)
1	Sn-Beta	46	99
2	Si-Beta	4	99
3	Si-Beta/$\mathrm{SnO_2}$	7	99
4	Sn-Beta[a]	2	99
5	Al-Beta[b]	10	10[c]

Yield and selectivities towards cyclohexylidenemalononitrile given after 6 h reaction time in toluene solvent at 100 °C.

[a] Sn-Beta calcined in the absence of any water to avoid the formation of sites A.

[b] Synthesized in a fluoride medium; Si/Al ratio 100.

[c] Main product is the aldol condensation product in 80% selectivity.

A further proof for the requirement of a basic adjacent site comes from the comparison of the condensation reaction in the presence of Al-Beta. The latter is able to activate (protonate) a carbonyl group but does not have an adjacent (weakly) basic site. And indeed, only the same amount of cyclohexylidenemalononitrile product as for the all-silica zeolite Beta is observed (Table 1, entry 5). This let us to conclude that carbonyl activation alone is not enough to catalyse these Knoevenagel type condensations with malononitrile. In summary, this series of condensation reactions is a further proof of the bi-functional site of Sn-Beta, consisting of a Lewis acid tin centre and an adjacent weakly basic oxygen atom.

Now, with all these results in mind we can define the peculiarity of the Sn-Beta zeolite. DFT calculations on adsorbed acetonitrile and cyclohexanone, in situ IR experiments with deuterated acetonitrile adsorbed to the active sites, calcination experiments, kinetic studies and catalytic activity for several reactions, point towards a tin atom fixed into framework places by three framework silyloxy groups and one hydroxy group completing the coordination sphere. The geometry itself is not singular since similar ones have been proposed before for other metal atoms incorporated into a molecular sieve structure, even for titanium [30,31]. The paramount characteristic of the active site is the combination of this "site A" geometry with the nature of the LUMO orbital that is responsible for the Lewis acidity. The electron density received from a Lewis base is not located at the metal atom itself (the common case for Lewis acids) but it is distributed into the four $\sigma^*_{\mathrm{Sn-O}}$ anti-bonding orbitals. Thereby, the oxygen atom of the Sn–OH group gets a nucleophilic character and becomes capable to form hydrogen bonds, e.g. with water or hydrogen peroxide. In this way, a second basic centre is created adjacent to the Lewis acid tin centre and the combination of the two centres is responsible for the unique reactivity of tin-containing molecular sieves.

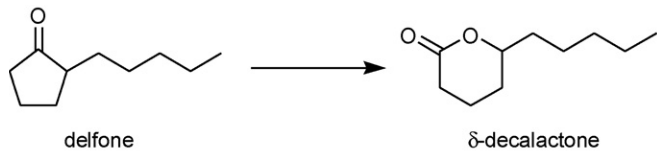
Although the characteristics of the tin centre is now quite well defined, it remains the question if a direct activation of hydrogen peroxide may occur. This is very unlikely for several reasons. None of the typical reactions for such metal-hydroperoxy species, e.g. epoxidation, has been observed for the oxidation system Sn-Beta/hydrogen peroxide. The coordination of hydrogen peroxide involving deprotonation, as it is generally proposed for the titanium species, is endothermic by 4.2 kcal mol^{-1} in the tin case and its formation possesses a relatively high activation barrier [21]. Furthermore, the activation of the oxygen atom to be transferred to double bonds can be clearly determined by DFT calculations in combination with a NBO analysis in the titanium model but not for the Sn-site [32]. These are, in our opinion, strong indications that a Sn–OOH species does not play any role in the reactions studied here.

3. Potential industrial application in the Baeyer-Villiger oxidation in fragrance and flavour industry

We have shown that Sn-Beta/hydrogen peroxide has the potential to substitute the classical oxidants, i.e. the peracids, for BV oxidations. At present, the oxidation of delfone(2-pentylcyclopentanone) to δ-decalactone(tetrahydro-6-pentyl-2H-pyran-2-one, Scheme 3) is carried out with peracetic acid producing, at least, a stoichiometric amount of acetic acid by-product. The resultant lactone has a creamy-coconut and peach-like aroma and is an important flavour constituent of many types of fruit, cheese and other dairy products. Furthermore, as it occurs with many fragrances, the two enantiomers have different aromas and the *R*-isomer is found preferentially in nature, and it is also the preferred one for practical uses. Industry takes this into account and has designed an asymmetric synthesis starting with enantiomerically enriched delfone. Organic peracids perform the Baeyer-Villiger oxidation involving a well-established retention of configuration so that the lactone is obtained with the corresponding enantiomeric excess introduced during the ketone synthesis.

Hence, Sn-Beta was tested for this Baeyer-Villiger transformation in a stirred reactor [33]. The desired lactone product was obtained in 86% yield when 107 g of delfone were stirred with 2.1 equivalents of hydrogen peroxide at 60 °C in the presence of 500 mg of Sn-Beta catalyst. It has to be noticed that the catalyst amount employed is only 0.5 wt%. The catalyst remains active for a long reaction time and turnover numbers (mol of substrate converted divided by mol of tin sites) of the magnitude of 10,000 have been achieved.

It has been assured that this catalytic version also retains the configuration of the migrating asymmetric carbon atom. Thus, when the enantiomerically enriched delfone was oxidized, the lactone product had exactly the same enantiomeric excess as the one obtained by peracid oxidation [33]. This demonstrated clearly that Sn-Beta/hydrogen peroxide is an environmentally friendly alternative to the commonly used organic peracids, even in asymmetric synthesis. Instead of a stoichiometric amount of carboxylic acid waste, water is produced as by-product from the oxidant.



Scheme 3. Oxidation of delfone to δ-decalactone.

4. Conclusions

Sn-Beta zeolite is an unique catalyst for BV oxidations owing to the combination of the geometry of its active site with the nature of the LUMO orbital. In this arrangement a second adjacent centre is created that may form a hydrogen bond or that may be protonated. Evidences for this bi-functional sites have been obtained from a combination of DFT calculations, in situ IR spectroscopy and catalytic activity studies.

Sn-Beta zeolite can be employed in different type of reactions that involve the activation of a carbonyl group. It has been used as catalyst for the Baeyer-Villiger reaction in multi-step asymmetric syntheses. Hereby, more than 10,000 cycles have been achieved per tin centre for the production δ-decalactone, a process being now scaled up by Takasago company. The catalyst can be separated easily by filtration due to its heterogeneous nature and the by-product produced from the oxidant is only water.

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