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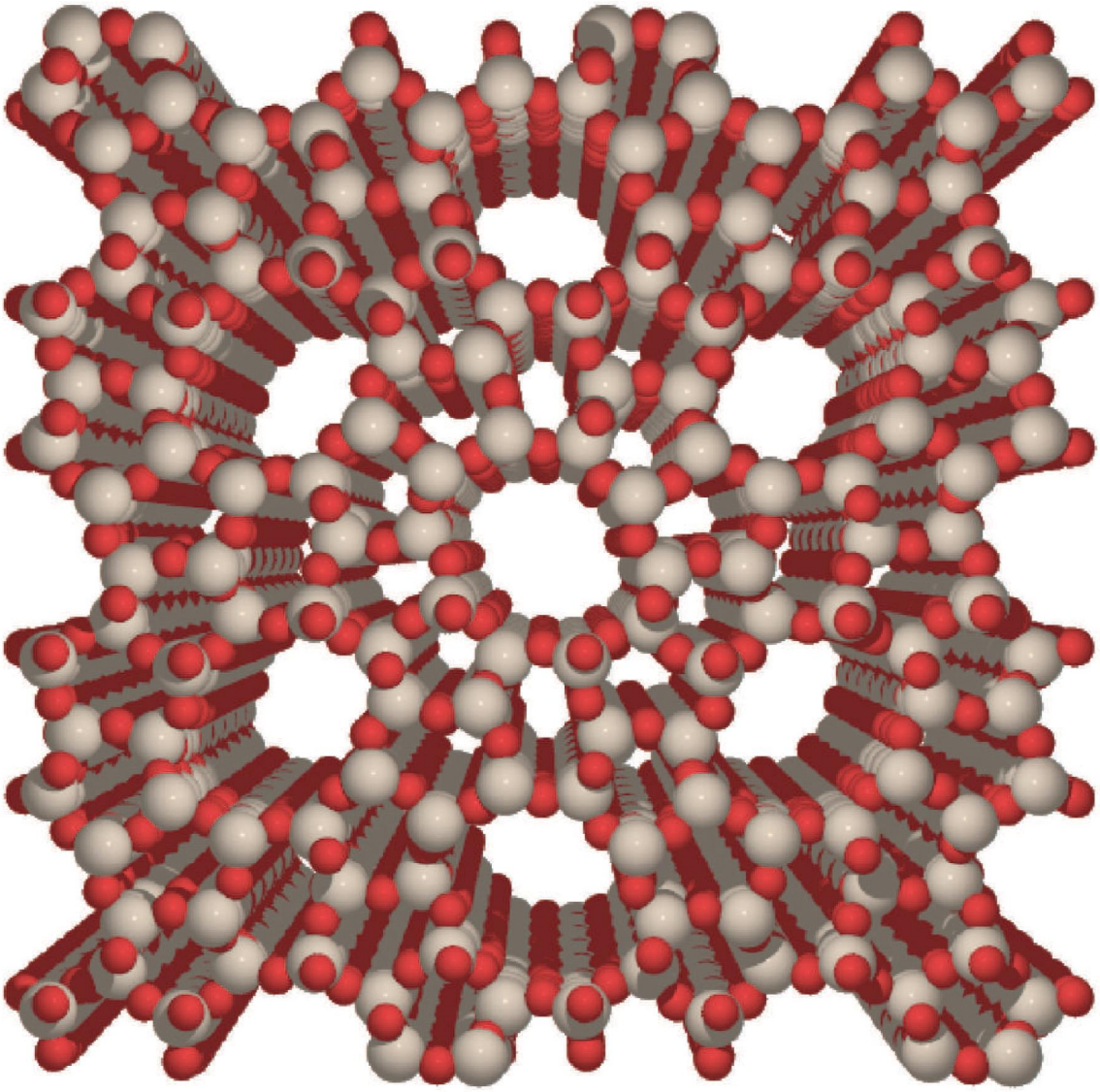


Discovery and Perspectives of Zeotype Sn-Beta

Industry Rumors: Regulation Spurs More Innovation and Competition in Polyolefin Catalysts...

Discovery and Perspectives of Zeotype Sn-Beta

By Søren Tolborg, MScEng, Esben Taarning, PhD and Martin S. Holm, PhD

1. Introduction

Zeolites are well-known in the catalyst community due to their great many uses; most notably, fluid catalytic cracking (FCC) and as a hydrocracking catalyst. Sn-Beta belongs to a class of materials called zeotypes which are closely related to zeolites; but there is a fundamental difference between a conventional zeolite and Sn-Beta. A zeolite is Brønsted acidic (a proton donor) whereas Sn-Beta is a solid Lewis acid (an electron acceptor). Naturally, this will give the materials completely different catalytic properties even though the siliceous crystalline structure hosting the metals can be identical.

Sn-Beta is a zeotype material containing tin as the catalytically active metal, and it has been a substance of interest for several academic research groups during the last decade. The crystalline material has pronounced Lewis acidity properties, attributable to the discrete tin sites, as well as a microporous network. These two features are responsible for the catalytic properties of the material. The shape selectivity induced by this microporosity can serve as a hindrance for reactions of large substrates, while Sn-Beta has sufficiently large pores to be an active catalyst in a range of industrially relevant reactions. This has sparked an interest to fully understand the properties of this zeolite-like material.

Sn-Beta catalyzes selective oxidation of a variety of organic substrates. The Bayer-Villiger (BV) oxidation is just one prime example among several, where Sn-Beta excels. BV oxidation is interesting because it is generally performed using expensive peracids—which makes a switch to a heterogeneous system using hydrogen peroxide welcome as a cheaper alternative. Sn-Beta has also shown interesting capabilities within Meerwein-Ponndorf-Verley-Oppenauer (MPVO) redox reaction and recently even within selective etherification.

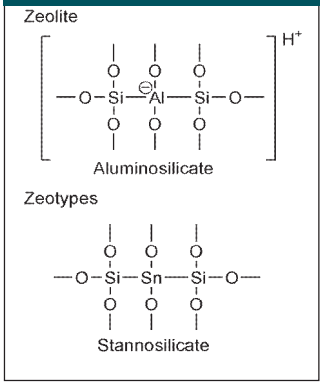
A new portfolio of catalysts for the emerging biorefinery sector is under development and Sn-Beta is an example of one such material. Although the use of Sn-Beta is far from restricted to the field of carbohydrate conversion, it is within this area that some new and exciting pathways resembling biological conversions have been found. Conventional zeolite catalysis in this area has focused on the Brønsted acidic conversion of sugars targeting furanic compounds such as furfural and hydroxymethylfurfural (HMF). In contrast, Lewis acidic materials such as Sn-Beta catalyzes the activation of the carbonyl functionality of the monosaccharide sugars leading to isomerization, and in some cases further fragmentation and conversion. Tin atoms homogeneously distributed as catalytically active sites in the Beta structure are not so different from the active site of an enzyme. The site has a single atom as the redox active center and a very distinct and rigid local microenvironment surrounding it, potentially forcing the reactant into activated states. These striking properties of materials like Sn-Beta have led to the nickname Zeozyme as a contraction of Zeolite and Enzyme. Indeed, Sn-Beta is bridging what is possible through biological reaction paths and heterogeneous catalysis which could be one reason why the material has attracted general interest.

In spite of these interesting properties Sn-Beta has not yet been commercialized. We will here provide details as to why we believe Sn-Beta deserves more than anonymity and why we find it likely that Sn-Beta will eventually find industrial application. Interesting parallels within the discovery of Sn-Beta's very successful zeotype predecessor titanium silicalite-1 (TS-1) will be drawn.

2. Isomorphous Substitution in Zeolites

In zeolites, connected tetrahedra of SiO_4 and $[AlO_4]^-$ give the conventional zeolitic system a charge imbalance, which is compensated for by external cations (e.g., H^+, NH_4^+, Mg^{2+}). When the material does *not* consist both of aluminum and silicon (but is still of a crystalline, zeolitic structure), it is denoted a zeotype material. A zeotype is thus structurally identical to a given zeolite, but the active metal is not aluminum but a hetero-element such as tin or titanium. Examples of other important zeotype materials include aluminumphosphates (i.e., AlPOs) and silicoaluminophospates (i.e., SAPOs). **Figure 1** shows how the active sites in Sn-Beta are different from the active site in a zeolite. By inserting a Lewis acidic metal atom (e.g., tin, titanium, zirconium) into the zeolite framework, a Lewis acidic catalyst is obtained. Although only a small amount of tin (a few wt%) can be incorporated in the structure, the atomic distribution of these hetero-elements in the structure makes for an ideal single-site heterogeneous catalyst, creating a catalyst in which every single embedded hetero-atom is an active site.

Figure 1. Illustration of the metal incorporation into a zeolite and the zeotype Sn-Beta, respectively.



The class of zeotype materials in which Sn-Beta belong is relatively new, with the first synthesis of a Lewis acidic zeotype dating back only 30 years. Since the initial discovery, several zeotype materials have been prepared with new and unique catalytic properties, though catalytic applications have had varying degrees of success. One material, TS-1, quickly made it to industrial application, while

other materials served as stepping stones toward the next generation of zeotype materials having superior properties.

2.1. TS-1, the Famous Predecessors of Sn-Beta

The discovery of titanium silicalite-1 (TS-1) was made little more than 30 years ago when the Taramasso group filed a patent, making them the first to successfully prepare a zeotype material.[1] They managed to substitute a small but significant percentage of the silicon atoms in the framework by the likewise tetravalent titanium. TS-1 was not only the first isomorphously substituted zeolitic material; it was also applied industrially after only a handful of years, making it the first big success within zeotype catalysts. So far the same rapid success and application has been eluding Sn-Beta for more than 15 years.

Titanium silicalite-1 (TS-1) has the MFI crystal structure, making it isomorphous to the widely used zeolite ZSM-5. It was discovered that TS-1 possessed exceptional catalytic properties utilizing hydrogen peroxide for the epoxidation of olefins and the oxidation of alcohols to aldehydes and ketones. As mentioned, industrial application very rapidly followed its discovery. The first plant using the titanosilicate catalyst was operational by 1986 in Italy, producing 10,000 tons/year of diphenols (catechol and hydroquinone) by hydroxylation of phenol with hydrogen peroxide (see **Figure 2a)**. More plants followed in the subsequent years producing cyclohexanone oxime by ammoximation of cyclohexanone, and propylene oxide by epoxidation of propylene, see **Figure 2b** and **Figure 2c**, respectively.[2] Cyclohexanone oxime is a vital intermediate in the production of Nylon-6, and propylene oxide is used in the production of polyurethane plastics and propylene glycol.

Despite the rapid industrial success of the TS-1 catalyst, the tin-containing equivalent Sn-MFI was synthesized approximately 10 years later, but has received very little attention. After being prepared in 1994 by the group of Ramaswamy, Sn-MFI showed promising results in the oxidation of ethylbenzene to acetophenone, actually yielding better results than TS-1 at similar conditions (**Figure 3**).[3]

The discovery of Ti-Beta occurred in 1992, when the group of Camblor *et al.* prepared a titanoaluminosilicate with the Beta structure.[4] It was later prepared without aluminum in the structure but unfortunately the synthesis required the use of hydrofluoric acid (HF).[5] Although the use of HF did yield an aluminum- and defect-free catalyst, it also marked the departure from the road toward an industrially feasible synthesis.

One of the main advantages of introducing titanium into the Beta framework as compared to the MFI framework was the much larger pore size shown in **Figure 4**. The vast majority of catalytic sites in a zeolite/zeotype are present within the zeolite structure so one of the main limitations of using TS-1 is the small pore size in the MFI (4.7 Å), which limited substrates to relatively small compounds. In reactions where TS-1 was not restricted by size limitations, it was generally far more active than Ti-Beta. An example of a difference in selectivity between the two titanium-containing catalysts can be seen in **Figure 5**.

Figure 2. Overview of industrial processes involving TS-1 yielding a) diphenols from phenol, b) the cyclohexanone oxime from cyclohexanone and c) propylene oxide from propylene.[2]

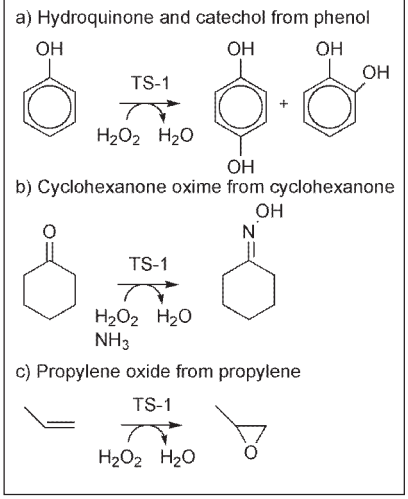


Figure 3. Oxidation of ethylbenzene to acetophenone over TS-1 and Sn-MFI.[7]

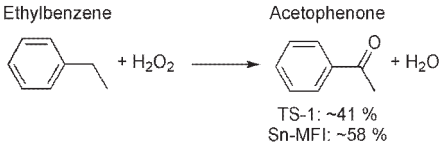


Figure 4. Graphic visualization of the respective sizes of the pore systems in the MFI and Beta zeolite.

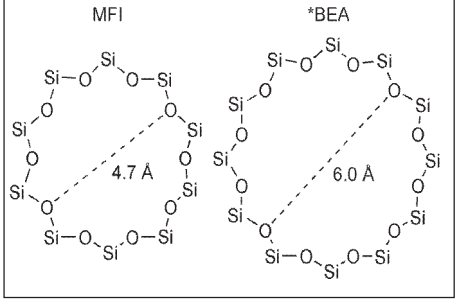
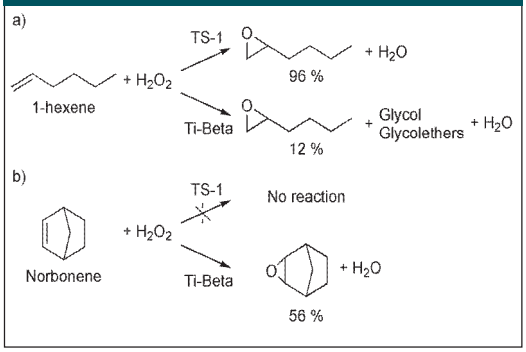


Figure 5. Epoxidation of 1-hexene (a) and norbonene (b) with TS-1 and Ti-Beta.[6]



With TS-1, 1-hexene was selectively converted into the epoxide, whereas Ti-Beta formed several byproducts caused by consecutive reactions of the epoxide with water and the formed glycol (**Figure 5a**).[6a] However, when a bulkier product was targeted, such as the epoxide of norbonene (**Figure 5b**), no reaction was observed with TS-1, whereas Ti-Beta could successfully form the epoxide.[6b]

3. The Remarkable Versatility of Sn-beta

An indirect route to prepare Sn-Beta was published in 1997 in a short communication from the group of Ramaswamy, marking another significant but relatively unnoticed step forward within the field of zeotype catalysts.[7] The catalytic oxidation capabilities using hydrogen peroxide of Sn-Beta especially were noted by the group, as they reported excellent selectivities in the oxidation of mesitylene, as shown in **Figure 6**.

Figure 6. Oxidation of mesitylene using Sn-Beta.[7]

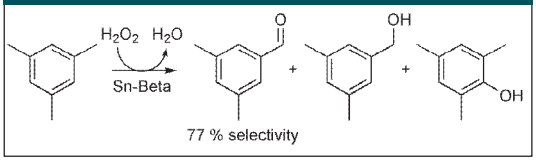
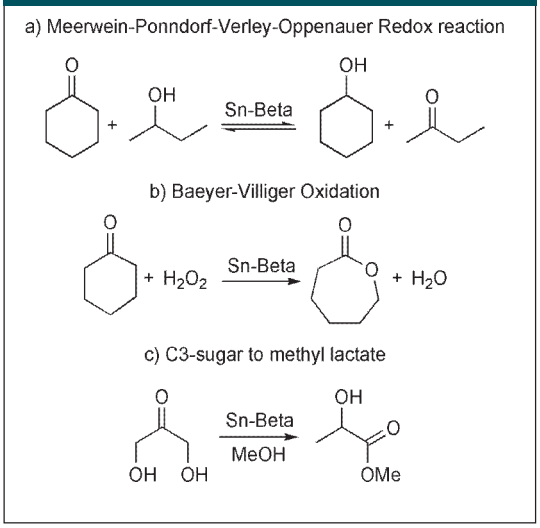


Figure 7. Various reactions catalyzed by Sn-Beta.[8,9]



Awareness of Sn-Beta did not rise until it was prepared by the group of Corma and shown to be an excellent catalyst for the important Baeyer-Villiger oxidation.[8] The Baeyer-Villiger oxidation converts a ketone to an ester as shown in **Figure 7b**. Previously this reaction was performed with expensive peracids, but the Corma group was able to use the much cheaper hydrogen peroxide catalyzed with Sn-Beta while still obtaining a remarkably high selectivity. Like the case of TS-1 some 20 years earlier, Sn-Beta was shown to be an active and selective catalyst in a number of industrially important reactions in the following years. However, in contrast to TS-1, the preparation of Sn-Beta is time-consuming and requires hydrofluoric acid which renders industrial application very difficult. This is likely one of the reasons why Sn-Beta in its current form has remained an interesting material for academic research but lacked the breakthrough into industrial application.

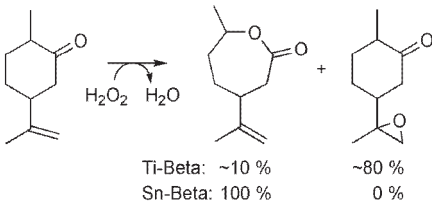
Ti-Beta and Sn-Beta, both being Lewis acidic catalysts, could be expected to be active in the same type of chemical transformations. This is indeed true but it's not the full picture. The activity and selectivity of the two materials have been compared in a number of industrially relevant reactions, including Baeyer-Villiger (BV) oxidation and Meerwein-Ponndorf-Verley and Oppenauer (MPVO) redox chemistry (listed in **Figure 7**). A significant difference in activity was seen in almost all cases and often Sn-Beta proved to be the most active catalyst.

In the selective reduction of cyclohexanone with 2-butanol (**Figure 7a**) both catalysts selectively formed cyclohexanol; however, at the chosen reaction conditions the conversion of Ti-Beta was only 6% compared to 95% for Sn-Beta.[10] The same difference in activity was observed for the oxidation of cyclohexanone to the corresponding lactone (**Figure 7b**) with a conversion of 4% and 42% for Ti-Beta and Sn-Beta, respectively. It has been suggested that the difference in activity between Ti-Beta and Sn-Beta is caused by a difference in the Lewis acidic strength of the active site. Tin, as the stronger Lewis acid, has at least been shown by FT-IR experiments to coordinate stronger than titanium to the carbonyl functionality of cyclohexanone.

Perhaps even more interesting, a selectivity difference between the two catalysts was found when converting a substrate that could be oxidized into either a lactone or an epoxide (**Figure 8**). It was found that whereas the Ti-Beta primarily produced the epoxide, Sn-Beta selectively formed the lactone.[11] This particular reaction shows how Sn-Beta is not just an improved version of Ti-Beta with higher activity, but that the two solid Lewis acids have complementary selectivities, adding further versatility to the zeotype catalyst portfolio.

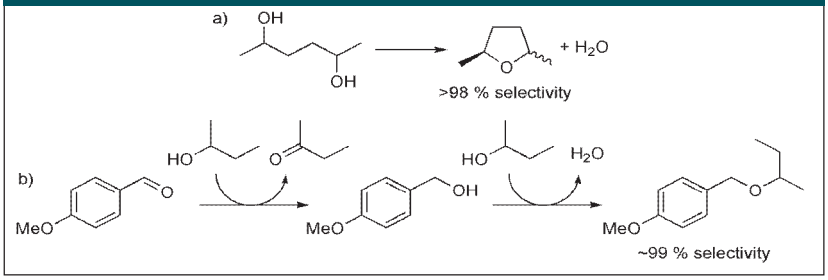
In another study by Boronat et al., Ti-Beta was found to be inactive in the BV and MPV of cyclohexanone but active in the epoxidation of octene, the exact opposite activities were found for Sn-Beta.[12] In the same study it was shown that the oxidation of diphenyl sulfide to the corresponding sulfoxide and sulfone proceeds far better with Ti-Beta than with Sn-Beta. This underlines that these two seemingly similar Lewis acidic catalysts can perform quite differently in catalysis.

Figure 8. Reaction of dihydrocarvone with H_2O_2 catalyzed by Sn-Beta and Ti-Beta forming predominantly the lactone and the epoxide, respectively.[11]



Continually Sn-Beta is shown to be active in new reaction types. In 2007 it was reported that Sn-Beta catalyzes the formation of ethers from a number of different alcohols with high selectivity. In addition it was elegantly shown (**Figure 9c**) how an aldehyde could be etherified with isobutanol, when Sn-Beta initially catalyzed an MPV reduction of the aldehyde to the alcohol using isobutanol as the reducing agent followed by an etherification also with isobutanol. In the same paper by the Corma group Sn-Beta was also used to prepare the cyclic 2,5-dimethyltetrahydrofuran (DHMF) by selective dehydration (**Figure 9a**).[13] Though this kind of reaction normally could be done using a simple Brønsted acidic catalyst, using a zeotype could result in improved selectivities to certain products due to the known shape/size restraints of such materials. Additionally, issues regarding substrate or product stability towards a homogeneous acid could potentially be avoided.

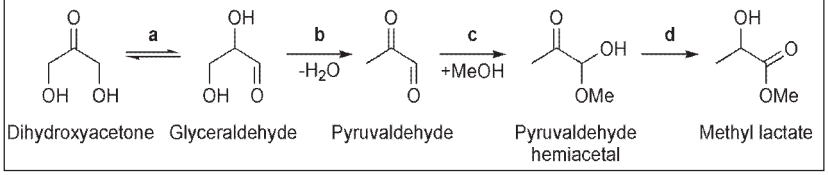
Figure 9. Etherification reactions using Sn-Beta.[13]



2009 marked the introduction of Sn-Beta in the field of biomass conversion with an article by Taarning *et al.* converting small sugars into methyl lactate over zeotype materials (Ti-Beta, Zr-Beta and Sn-Beta).[9] Methyl lactate is an ester of lactic acid, which can be used in the production of poly lactic acid (PLA); a compostable bio-plastic. A significant difference in activity between Ti-Beta, Zr-Beta and Sn-Beta was observed within carbohydrate conversion. For the conversion of C_3-sugars (dihydroxyacetone and glyceraldehyde) to methyl lactate, Ti-Beta is hardly active at temperatures below 80 °C, giving only a yield of 2 %, whereas Sn-Beta forms >99 % methyl lactate at the same conditions (**Figure 7c**).[9] Nonetheless, Ti-Beta becomes active and forms methyl lactate selectively at elevated temperatures which hints that the catalyst can indeed catalyze this type of reactions but does so in a different temperature regime potentially due to differences in Lewis acid strength. With C_5- and C_6-carbohydrates, Sn-Beta was likewise capable of forming methyl lactate possibly through a retro-aldol fragmentation of the sugars though in more modest yields (up to 68 %).[14]

Several sequential steps are believed to be involved in the formation of methyl lactate from sugars (**Figure 10**). Interestingly, it was observed that similar yields of methyl lactate are obtained when reacting different sugar epimers. This was explained by the fact that Sn-Beta actually catalyzes the isomerization of sugars (**a, Figure 10**). The mechanism has been investigated and shown to consist of a 1,2-hydride shift through the simultaneous coordination of the ketone and hydroxyl group of the sugar with the tin-site.[15] As a result, pyruvaldehyde is formed from both C_3-sugars through a dehydration reaction (**b, Figure 10**), not unlike what takes places during etherification as Sn-Beta was shown above to catalyze. Pyruvaldehyde forms the hemiacetal in the presence of an alcohol solvent (**c, Figure 10**). Finally, methyl lactate is formed through an intramolecular MPV-type redox reaction similar to the 1,2-hydride shift during the initial isomerization (**d, Figure 10**). It thus appears that Sn-Beta is capable of sequentially catalyzing a cascade of reactions resulting in modest to very high yields of methyl lactate depending on the complexity of the starting carbohydrate substrate. This versatility in choice of substrate could prove to be an important advantage over the much more substrate specific enzymatic systems.

Figure 10. Tentative reaction steps involved in the formation of methyl lactate from C_3-sugars (dihydroxyacetone or glyceraldehyde) through a) isomerization, b) dehydration, c) acetalization and d) 1,2-hydride shift.[9]



Sn-MFI has received some attention in comparison with Sn-Beta within sugar isomerization. Sn-MFI is active as an isomerization catalyst and can convert C_3- and C_4-sugars but the 10-ring microporosity makes it barely active for hexose isomerization (glucose to fructose) due to size limitations. Conversely, Sn-Beta is capable of isomerizing all of the monomeric sugars.[16] An important isomerization reaction—such as the production of high fructose corn syrup (an important sweetener used in the US) from glucose—could theoretically be made using a Sn-Beta catalyst instead of an enzyme to obtain the equilibrium distribution of glucose-fructose-mannose.

4. The Catalytically Active Tin Site

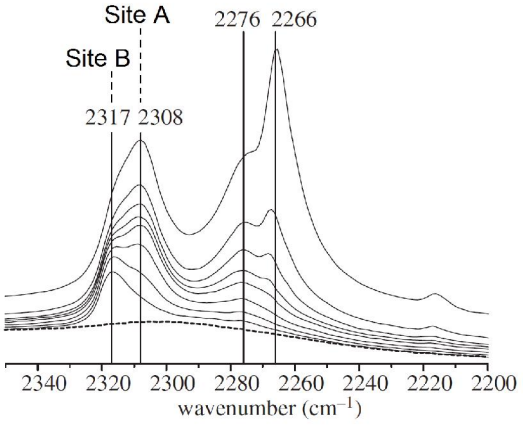
There has been much speculation as to the nature of the active site in Sn-Beta, since its discovery 15 years ago. Little is still known about the catalytic site and why it shows such high Lewis acidic strength compared with other isomorphously substituted zeotype materials. The main focus over the years has been to find a correlation between the tin-site present and the catalytic performance of the material. It is well-established that tin is found in at least two different coordinating environments in the framework (**Figure 11**).[17]

Figure 11 shows that site A can be described as one silicon atom in the framework being substituted with one tin atom. The same is the case for site B, but in that case one Si-O bond has been hydrolyzed. The idea that the active sites are to be found in two different forms is not new within the field of isomorphous substitution. Approximately 20 years ago, Millini described the titanium analogues in TS-1.[18] In addition, Ti-Beta also was found to contain these two distinct hydrophilic sites.[19]

Figure 11. Site A and Site B which both are present in the Sn-Beta catalyst.[17]

The study of the two sites has been done using a battery of methods (e.g., probe-molecule infra-red spectroscopy (IR), solid-state nuclear magnetic resonance (MAS-NMR) and computational studies. **Figure 12** shows how the probe-molecule acetonitrile coordinates to the different active sites in Sn-Beta and reveals that two distinctly different sites exist. From ^{119}Sn NMR, two distinct tin bands could be detected and, in addition, by coupling the tin measurement with ^{1}H NMR, it was shown that one of the two bands have hydrogen in its immediate area of coordination (i.e., the Sn-O-H in Site B).

Figure 12. Probe-molecule infrared spectroscopy of Sn-Beta. Acetonitrile coordinating to Site A and B can be seen. Adapted from.[20]



It is interesting to note that the hydrolyzed sites have been described as both detrimental *and* beneficial in the literature. Removal of the hydrolyzed site (site B) in Ti-Beta increased activity in the epoxidation of cyclohexene. The positive effect was mainly attributed to a decrease in the hydrophilic surroundings of the metal, leading to higher selectivity towards the epoxide. For Sn-Beta, the hydrolyzed site is believed to be the most active site in Sn-Beta. In a recent series of publications it has been argued that the bi-functionality of the Lewis acidic tin-site adjacent to a basic oxygen (on the hydroxyl) is essential to the catalytic activity of Sn-Beta and that these sites can be obtained through hydrolysis of the material.[17]

5. Future of Sn-Beta

A new catalyst can catch general interest for a number of reasons. It can either be highly selective in established and important chemical transformations, or it can catalyze novel and relevant reactions. Sn-Beta is capable of doing both. However, to date it has not been raised to an industrial level.

New characterization tools need to be developed for scientists to be able to make accurate structure-activity correlations for Sn-Beta. It is extremely important to be able to quantify the active sites in a catalyst and today this is difficult to do on a Sn-Beta sample. Temperature programmed desorption of ammonia is the standard method used to determine the number of active sites present in a zeolite catalyst. However, this technique cannot be used on Sn-Beta because ammonia does not bind strongly enough to the tin sites. Acetonitrile and diethyl ether are being investigated as alternative adsorbents and luckily the preliminary results looks promising.[21] The use of hydrofluoric acid in the synthesis of Sn-Beta has undoubtedly limited the interest in the material and possibly hindered the break-through into industrial application. Recently, the Hermans group has shown that Sn-Beta can be prepared in a simple and elegant post synthesis treatment of commercially de-aluminated zeolite Beta.

The technique involves thorough acidic de-alumination. This treatment removes aluminum from the zeolite, creating vacancies in the lattice while leaving the Beta framework intact. This initial step is then followed by the introduction of a suitable tin-source by physical mixing followed by calcination, resulting in catalytically active Sn-Beta. Catalytic testing of the material showed comparable results for the BV oxidation and triose to alkyl lactate conversion as obtained for conventionally prepared Sn-Beta.[22] The simplicity and scalability of this method has brought new industrial potential into the field of Sn-Beta. It is going to be very interesting to follow the impact of this discovery and see if this can facilitate the application of Sn-Beta in the industry.

One concern of the catalytic system using Sn-Beta is the long-term stability of the framework. Several groups have shown that Sn-Beta can be used for several cycles without a drop in activity. However, when operating for thousands of hours the strain of the catalyst in a liquid phase system is immense. TS-1 is successfully used industrially today with some regeneration of the catalyst needed, but after 25 years the catalyst is still sold commercially, despite having shown some stability issues.[23]

These days we see plenty of startup companies focusing solely on the biological angle of biomass conversion through enzymatic or fermentation strategies, but often these same target compounds can be formed through alternate routes using a heterogeneous

catalyst such as Sn-Beta. This is the case for lactic acid and the isomerization of sugars. Sn-Beta is in many ways bridging the gap that has been created between the biological and 'chemical' route of converting biomass-derived substrates into useful chemicals. As heterogeneous catalysts have always played an essential role in the chemical industry, Sn-Beta is a key candidate for a future catalyst in the industrial production of biomass-derived chemicals. With the proper catalyst portfolio, the chemical industry could have the luxury of choosing between the two complementary conversion technologies—catalytic and bio-chemical—depending on economy, selectivity, activity, and stability in the desired processes.

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