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Ti-substituted zeolite Beta: a milestone in the design of large pore oxidation catalysts

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The synthesis of titanium-containing zeolite Beta was first published in this journal in 1992 and has since proven to be groundbreaking in the development of large pore zeolites as heterogeneous catalysts with isolated Lewis acid sites. In this Viewpoint we will illustrate its significance for oxidation chemistry and heterogeneous catalyst design.

Of all titanium-containing zeolites, TS-1 with MFI topology is by far the most famous, and it is widely used industrially. It was the first zeolitic material reported in which titanium had been isomorphously substituted into the silicate framework resulting in isolated Ti sites in a zeolite matrix. Not long after its discovery, its remarkable properties as an oxidation catalyst were reported, showing exceptional activities and selectivities in liquid phase oxidation reactions with hydrogen peroxide. Among those first reported reaction types are hydroxylation of aromatics, oxidation of alcohols to the corresponding aldehydes and ketones, oxyfunctionalization of alkanes, epoxidation of olefins and ammoximation of cyclic ketones.¹⁻³ However, because of its medium pore 10-membered-ring (MR) channel system, the use of TS-1 is limited to the conversion of fairly small molecules. The discovery by Corma and co-workers of a titanium-containing zeolite Beta, with its more accessible large pore 12-MR channel system, substantially expanded the substrate scope for liquid phase oxidation with titanium zeolites.⁴ This first report on Ti-Beta described the synthesis of a zeolite, isomorphous to zeolite Beta, but with both titanium and aluminum isomorphously substituted in the framework. The obtained material showed a much higher activity in the oxidation of cyclododecane with hydrogen peroxide than TS-1, illustrating the effect of a more spacious environment.

The original Ti-Beta was prepared in a synthesis mixture containing both Al- and Ti- sources and OH⁻ as mineralizing anion. Though active and selective as an oxidation catalyst for alkanes, its performance was rather poor in the epoxidation of olefins. Unwanted ring-opening of epoxides by the solvent or water was problematic and was attributed to the hydrophilicity of the framework and to the presence of acid sites because of the aluminum. This stimulated researchers to search for an Al-free version of Ti-Beta. Several strategies were followed. Al-free Ti-Beta was, for instance, successfully synthesized in an OH⁻ medium by adding highly dealuminated Beta seeds (Si/Al > 1000) to the synthesis gel.⁵ The decrease in Al-content had a positive effect on the epoxide selectivity. When cyclohexene for instance – which is not able to enter the pores of TS-1 – is oxidized in methanol by Al-containing Ti-Beta, the main product is the monomethylglycol ether; if the reaction is carried out in acetonitrile with aluminum-free Ti-Beta, then the epoxide is the main product.^{6,7} Still, epoxide selectivities in general were lower for this Al-free Ti-Beta than for TS-1. This observation had first been ascribed to either an intrinsically higher acidity of the Ti or Ti-hydroperoxo sites in Beta compared to TS-1, or to the stronger adsorption of the formed epoxide on the Ti-site because of the more hydrophilic character. By performing the synthesis of Al-free Ti-Beta in fluoride media a nearly defect-free material was obtained with a surface that contained almost no silanol groups, making it highly hydrophobic. However, this highly hydrophobic Ti-Beta still shows a higher tendency for epoxide ring opening compared to TS-1, indicating that the influence of the zeolitic framework itself on the active Ti-species was crucial, rather than the presence of acid or defect sites.⁸ Furthermore, regardless of

the method of synthesis, acetonitrile remains the solvent of choice for Ti-Beta, while for TS-1, methanol is strongly preferred. This difference in catalytic performance and solvent dependency is now believed to be related to the different behavior of Ti-hydroperoxo species that are generated *in situ* and thus not only to the different physicochemical properties of the materials. An important consequence of the synthesis of a hydrophobic Ti-Beta is the expansion of the substrate scope to amphiphilic molecules like unsaturated fatty acids and esters. On a hydrophilic framework, these molecules would at best adsorb with their polar heads, which would make it very unlikely for the double bond to reach the active site. Although the pore system of Ti-Beta is more accessible than that of TS-1, it might still impose steric constraints when larger substrates are used, as illustrated by the oxidation of vinylcyclohexenes. The exocyclic double bond of limonene is preferentially oxidized, indicating that steric effects dominate over electronic effects. Other shape selective effects have been observed in the oxidation of silanes to silanols where the formation of disiloxanes is impeded due to steric constraints, or in the epoxidation of 3-alkyl-substituted cyclohexenes where an increase in *trans* selectivity is observed with increasing bulk of the substituent.⁹

Ti-Beta and especially the aluminum-free analogues are valuable additions to the field of epoxidation using aqueous hydrogen peroxide as the oxidant. In this field, many homogeneous catalysts are known to successfully catalyze epoxidation reactions with hydrogen peroxide for a wide variety of substrates. They show specific advantages in for instance enantioselectivity or in the production of acid-sensitive epoxides. In addition, an active and non-toxic catalyst that is used in low concentrations, like some of the recent Mn or Fe systems, does not need to be removed from the product, though this could compromise the stability of the epoxide or derived product.¹⁰⁻¹² Nevertheless, some of these homogeneous epoxidation systems have their own specific disadvantages.¹³ Tungsten-based catalysts often require phase-transfer agents or even chlorinated solvents. Manganese- and iron-containing chelates are based on complex nitrogen-containing ligands and require organic additives. Rhenium-based catalysts allow production of acid-sensitive epoxides but they are toxic and nitrogen-containing aromatic bases are needed to achieve high yields. Heterogeneous catalysts for epoxidation with H₂O₂ often rely upon the immobilization of homogeneous metal complexes.¹⁴ For example, anionic tungsten-based complexes can be electrostatically bound to anion-exchange resins or layered double hydroxides and Mn-triazacyclononane complexes can be covalently attached to silica. These immobilized systems are usually less active than their homogeneous analogues and leaching can occur. From industrial viewpoint, fully inorganic materials are preferred. Layered double hydroxides are basic enough to catalyze the nucleophilic epoxidation of α,β -unsaturated carbonyls and when used in combination with excess amounts of nitriles or amides they can give high yields for unfunctionalized olefins. Different forms of alumina can epoxidize even unfunctionalized olefins with moderate yields when anhydrous hydrogen peroxide is used with high catalyst loadings.¹⁵ Considering the limitations of the described systems, the merits of (aluminum-free) Ti-Beta as epoxidation catalyst become clear. It is a fully inorganic heterogeneous catalyst with high hydrogen peroxide efficiency; it requires no additives and it is able to epoxidize linear and cyclic alkenes, monoterpenes, (methyl esters of) fatty acids, unsaturated alcohols and α,β -unsaturated carbonyls with moderate to good selectivities. One has to add that the selectivities found in literature often correspond with low levels of conversion.

In the two decades following the discovery of Ti-Beta, much effort has been invested in the search for materials that have an even better accessibility for bulkier molecules but their epoxidation activities are in general inferior to that of Ti-Beta. ITQ-7 with ISV-topology is an example of another large pore three-dimensional structure in which titanium can be substituted.¹⁶

Titanium was also introduced into mesoporous silica materials such as Ti-HMS and Ti-MCM-41 in 1994.^{17,18} With this type of materials, high activities were obtained in the oxidation of 2,6-di-*tert*-butyl phenol, a molecule too large to fit into the pores of TS-1. However, these materials are usually hydrophilic structures that are poisoned by water. Better results are obtained if anhydrous organic peroxides are used as the oxidant or if the silanol-rich surface is modified with apolar organic groups. More recently, in an effort to combine the high accessibility of these high surface area mesoporous molecular sieves with the stability and incorporation of isolated Ti sites in zeolite frameworks, the potential of layered zeolite precursors and their related materials has been explored. For instance, delamination of the layered precursor of MWW has been used to obtain titanium containing zeolites either by grafting titanocene on the delaminated precursor in Ti-ITQ-2¹⁹ or by delaminating the Ti-containing precursor.^{20,21} Delamination has also been applied to the Ti-containing precursor of the FER-topology to obtain Ti-ITQ-6.²²

The report on Ti-Beta was not only the discovery of the first titanium containing 12MR zeolite. It was also the first time isomorphous substitution of silicon by another tetravalent cation was reported. This makes Ti-Beta the predecessor of other remarkable Lewis acidic materials such as Sn-Beta and Zr-Beta which both have intriguing catalytic properties. Their complementarity is illustrated in Fig.1. The activities of Ti-Beta, Sn-Beta and Zr-Beta in different types of oxidation reactions have been compared by the group of Corma.²³ Using a similar approach as for hydrophobic Al-free Ti-Beta and purely siliceous Beta – a fluoride containing synthesis gel but in this case with the addition of seeding crystals – Sn-Beta was synthesized and it appeared to be an active, stable and chemoselective catalyst in the Baeyer-Villiger oxidation of both saturated and unsaturated ketones. Complementary to Ti-Beta, it catalyzes the lactone formation from unsaturated ketones without forming the epoxide.²⁴ Other Lewis acid catalyzed reactions that can be performed with Sn-Beta include Meerwein-Ponndorf-Verley-Oppenauer (MPVO) reactions,²³ the formation of ethers from alcohols,²⁵ diastereoselective intramolecular carbon-carbon bond formation in the isomerization of citronellal to isopulegol²⁶ and the isomerization and conversion of various sugars.^{27,28} Importantly, this hydrophobic zeolite is stable in presence of even bulk water. Zr-Beta shows many similarities to Sn-Beta. It can be synthesized according to the same strategy as Sn-Beta, as was shown by Jaenicke and co-workers.²⁹ It also catalyzes MPVO-reactions, diastereoselective citronellal isomerization but it is hardly active in Baeyer-Villiger oxidations.^{23,29,30} On the other hand it does catalyze the sulfoxidation of diphenyl sulfide, a reaction that can also be performed by Ti-Beta.

The large scale application of these promising catalysts is significantly hampered by their synthesis in fluoride media, long crystallization times and the limited amount of Sn or Zr that can be incorporated. Finding alternative routes for the synthesis of these materials is imperative. An encouraging example in this direction has been published for Sn-Beta by the group of Hermans, using solid state ion-exchange on dealuminated Beta crystals.³¹ Furthermore, acquiring more insight into transition-metal containing active sites in zeolitic materials by computational studies³² and novel characterization techniques³³ may provide crucial information which is needed to develop new materials with enhanced performance.

In conclusion, the initial publication of Ti-Beta by Cambor and colleagues can be considered as an important stepping stone in bringing heterogeneous catalysis to the field of oxidation of fine chemicals. As first report of isomorphous substitution of silicon by another tetravalent cation, this paper lies at the base of the development of other Beta zeolites with catalytic properties complementary to that of Ti-Beta and the success of Ti-Beta itself as epoxidation catalyst incited the scientific community to explore other large pore materials as heterogeneous epoxidation catalysts.

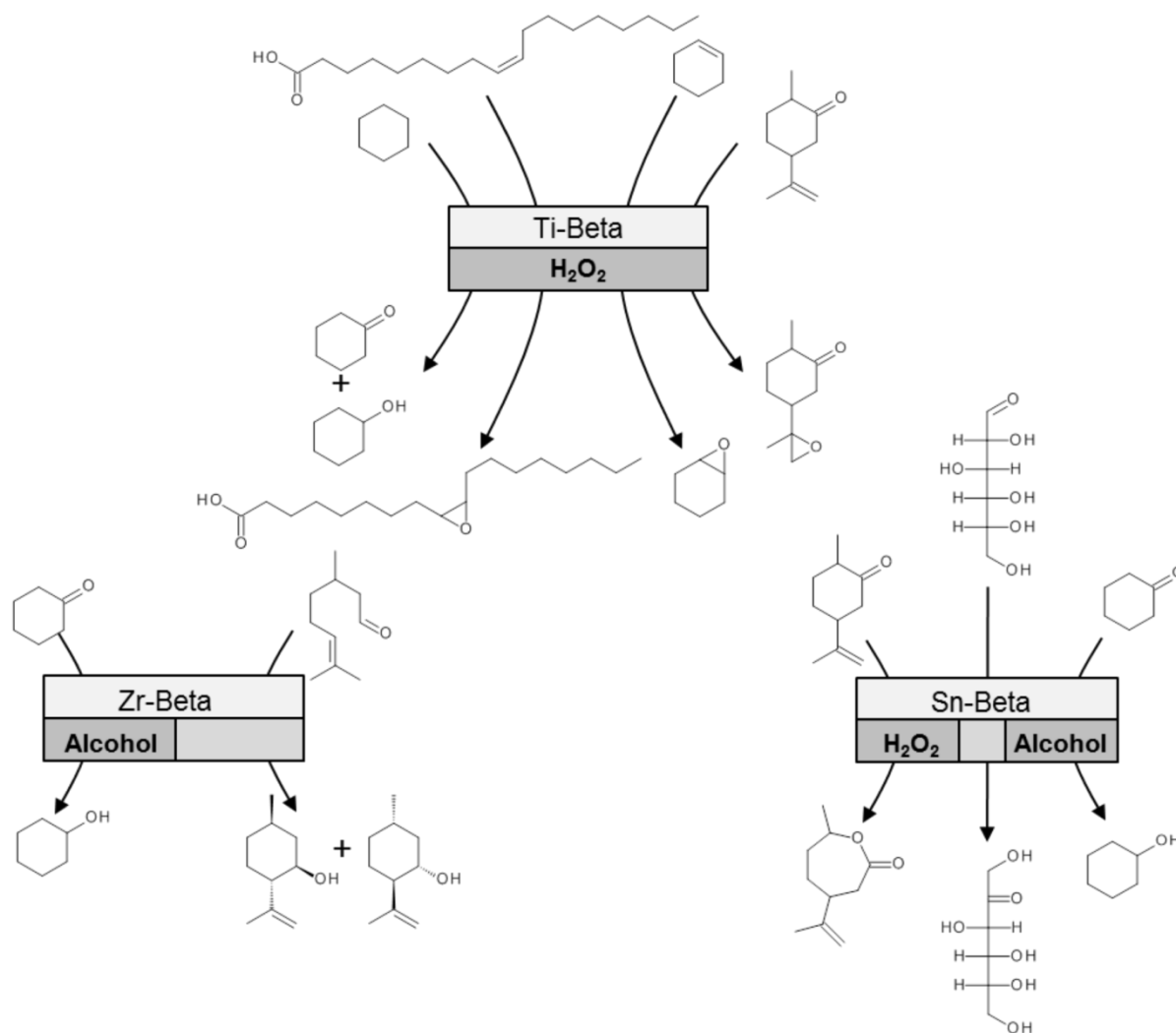


Fig. 1 Non-exhaustive overview of chemical transformations characteristic of MIV-substituted Beta zeolite catalysts.

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Notes and references

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