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Advances in the synthesis of titanosilicates: from the medium pore TS-1 zeolite to highly-accessible ordered materials

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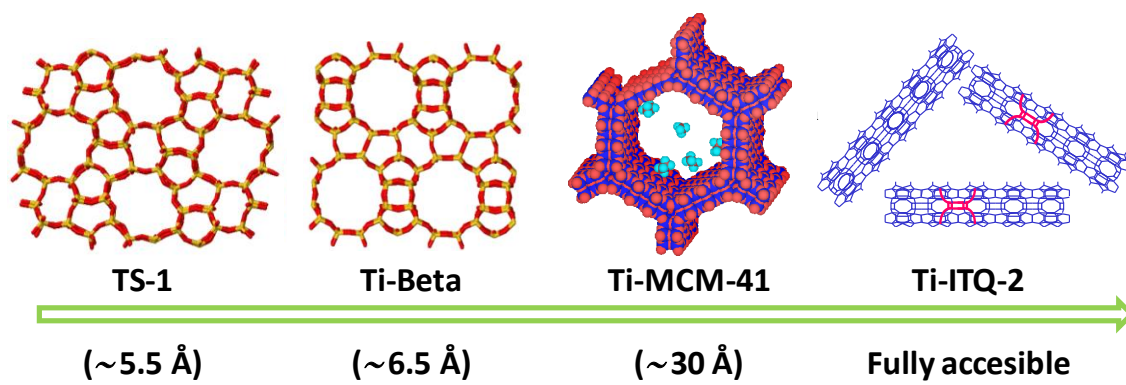
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Dedicated to Professor Takashi Tatsumi on his 65th birthday

Abstract

In the present review, we would like to cover the most fundamental advances achieved in the design of ordered titanosilicates since the earlier discovery of TS-1 reported by EniChem in the mid-eighties. The invention of the medium-pore TS-1 zeolite was a breakthrough, and this material has been applied as efficient catalyst in diverse industrial applications. However, its limited pore size (5-5.5 Å) offers diffusion limitations when working with large molecules. The design and preparation of open titanosilicates, such as large pore molecular sieves, mesoporous ordered materials, or layered-type zeolites will be described. The applicability of these titanosilicates to catalytic oxidation processes requiring bulky organic molecules will also be presented.

Graphical abstract



1.- Introduction

Traditionally, zeolites are defined as crystalline microporous aluminosilicates, whose structures are formed by tetrahedral T atoms (T = Si or Al) connected by O atoms.¹ The arrangement of these atoms creates crystals with regular microporosity and well defined pores and cavities.¹ The presence of aluminum atoms in tetrahedral coordination in the zeolitic framework creates negative charges, which can be balanced by organic or inorganic cations (such as alkali or alkaline-earth cations), as well as by protons.² The large ionic exchange capacity and the possibility to generate Brønsted acidity, offer them unique properties for cation exchange, adsorption, separation, or heterogeneous acid catalysis.^{1,3} However, chemical compositions other than aluminosilicates can be synthesized and heteroatoms such as B, Ge, Fe, V, Sn, Ti, Ga, among others, have been introduced in zeolite frameworks during the last thirty years.⁴ The presence of heteroatoms other than Al in the zeolitic walls permits to introduce other chemical properties to the zeolite, offering new opportunities for these microporous molecular sieves. Among the different heteroatoms introduced in framework positions, the titanosilicates are very interesting materials, as revealed by large number of synthesized titanosilicates and the large number of chemical reactions that they are able to catalyze.⁵ As seen in [Figure 1](#), the number of publications per year related to titanosilicates shows a continuous increase since the first reports in earlier 80s.

The isomorphic substitution of Ti(IV) species in the zeolitic framework does not introduce negative charges, as it occurs with aluminosilicates, and consequently, their potential applicability as Brønsted acid materials can be neglected. However, Ti can act as a Lewis acid which together with the hydrophobic character of silicates, can catalyze diverse oxidation reactions of hydrocarbons using hydrogen peroxide as oxidizing agent.⁶ Up to the discovery of TS-1 (Titanium Silicalite-1), most industrial processes for oxidizing hydrocarbons were performed using homogeneous catalysts or expensive organic hydroperoxides or peracids.⁷

Therefore, the discovery that TS-1 was able to epoxidize olefins and even alkanes, opened an intense research in the preparation of new titanosilicates polymorphs for their application in Lewis acid catalyzed reactions, including oxidations with H₂O₂ and organic peroxides.

TS-1 zeolite is the titanosilicate form of MFI, which possesses a bi-directional medium pore system (openings close to 5.5 Å).⁸ This material has been applied as catalyst in different chemical processes on industrial scale, such as phenol hydroxylation, cyclohexanone ammoximation or propylene epoxidation.^{5f,9} However, large molecules suffer severe diffusion restrictions through the medium pores of TS-1 zeolite, and new materials with larger accessibility were required. In this sense, several academic and industrial research groups have made efforts in the design of new or improved titanosilicates polymorphs. In the present review, we would like to highlight the most remarkable achievements in the preparation and optimization of titanosilicates with different pore topologies, covering from the medium pore TS-1 material to ultra-large pore ordered mesoporous materials.

2.- Medium pore TS-1 zeolite

As mentioned above, TS-1 was the first description of a titanosilicate zeolite presenting tetrahedral Ti atoms in framework positions.⁶ The high activity of medium-pore TS-1 material for different catalytic oxidations of hydrocarbons is attributed to the selective activation of H₂O₂ by isolated tetrahedral Ti species in the crystalline walls.^{5a} Indeed, the presence of tetrahedral Ti(IV) atoms in the framework can be easily recognized when the solids were characterized by ultraviolet-visible spectroscopy (UV-Vis) or by Fourier transform infrared spectroscopy (FT-IR). A UV-Vis band at 190-210 nm was assigned to the charge transfer of tetrahedral Ti species, while a band at 310-330 nm is attributed to extra-framework octahedral TiO₂.¹⁰ On the other hand, the signal centered at 960 cm⁻¹ in the FT-IR spectra is assigned to Ti species in framework positions.^{6a}

Since the former report on TS-1, many different synthetic protocols have been described for the synthesis of the titanasilicate form of silicalite.¹¹ These include different Si and Ti sources, organic structure directing agents (OSDA), and mineralizing agents (see [Figure 2](#)).^{5f} From the large number of preparations described in the literature, it is possible to find TS-1 materials with different crystal size, morphology, hydrophobic-hydrophilic properties, and titanium distributions along the crystals.¹² Perego et al. have nicely reviewed different TS-1 synthesis procedures, describing the effect of different synthetic variables on the physico-chemical properties of the final titanasilicate produced.^{5f}

Moreover, several catalytic reactions have been broadly studied using TS-1 as an efficient oxidation catalyst using H₂O₂ as oxidizing agent under mild conditions.^{5f,9} In this sense, TS-1 has been applied in the hydroxylation of aromatic compounds,¹³ epoxidation of alkenes,¹⁴ oxygenation of alkanes and alcohols,¹⁵ and ammoximation of ketones,¹⁶ among other processes.

The shape selectivity of TS-1 for oxidation reactions was first shown by Tatsumi et al.,¹⁷ when oxidizing different linear, branched and cyclic alkanes with TS-1 using H₂O₂ as oxidant (see [Table 1](#)).¹⁷ As seen there, hexane showed an oxidation turnover number seventeen times higher than cyclohexene, and branched alkanes showed negligible activities. The authors also observed a notable decrease in activity when the length of the linear alkane was above six carbon atoms, in clear relationship with their higher diffusion restrictions (see [Table 1](#)). Other reactions were performed in order to further study the shape-selective oxidation, as epoxidation of alkenes,¹⁸ or oxidation of unsaturated alcohols.¹⁹

In order to increase the framework Ti content in TS-1,²⁰ Tatsumi et al. presented that it could be improved if the hydrolysis rate of Ti alkoxide and silicate species were harmonized with nucleation and crystal growth rates. To do this, (NH₄)₂CO₃ was added as a crystallization-mediating agent in the synthesis media. This agent was able to reduce the crystallization rate

by lowering the pH. By doing that, Ti incorporation and crystallization rates were comparables, and the Si/Ti ratio can be decreased from 58 to 34, without formation of extra-framework Ti species.²⁰ Interestingly, this Ti-rich TS-1 showed improved activity for the oxidation of different organic substrates, such as 1-hexene or 2-hexanol.

3.- Large pore Ti-Beta zeolite and other large-pore titanosilicates

3.1.- Ti-Beta zeolites

It has been shown that TS-1 is an efficient catalyst in the selective oxidation of different organic substrates.^{5f} However, large organic molecules suffer severe steric restrictions through the relative small medium pores of TS-1 (~5.5 Å), precluding the use of this titanosilicate in chemical processes involving bulky molecules. At that point, the design of new titanosilicates presenting larger pores was highly desired.

The former descriptions related to large pore titanosilicates were the synthesis of Beta and Y zeolites, where Ti atoms were introduced by post-synthetic treatments using TiCl_4 .²¹ Nevertheless, those materials showed poor activities in the oxidation of phenol with H_2O_2 , probably because Ti atoms were not properly placed in framework positions.²¹

Corma et al. first reported the isomorphic substitution of Si by Ti in the Beta zeolite by a direct synthesis procedure.²² This new titanoaluminosilicate polymorph of Beta was more active catalyst than TS-1 for the selective oxidation of large molecules with H_2O_2 , revealing that large pore Ti-zeolites can also be efficient catalysts in the oxidation of bulky molecules (see [Table 2](#)). Deeper synthesis and characterization studies on the titanoaluminosilicate form of Beta, have allowed understanding the role of the different synthetic variables on the final Ti coordination, and consequently, on the catalytic activity for oxidation reactions.²³ For instance, the presence of alkali metal cations precluded the insertion of tetrahedral Ti species into the zeolitic framework, forming an inactive titanosilicate phase where Ti was in octahedral coordination.²³

As seen in Table 2, Ti-Al-Beta shows higher conversion per Ti site than TS-1 in the oxidation of cyclic olefins, which can be easily explained by the higher geometrical restrictions imposed by the medium-pore TS-1 zeolite. However, while high selectivities to the desired epoxides were achieved using TS-1 zeolite, the firstly synthesized Ti-containing Betas also contained Al in framework positions. This tetrahedral Al was responsible for the appearance of acidity in the Ti-Al-Beta that, in turn, was responsible for the lowering of epoxide selectivity by opening the epoxide ring (see Table 2).^{23b}

It was then clear that to increase the selectivity to the epoxide product using Ti-Beta during the oxidation of alkenes with H₂O₂, the number of acid sites in the microporous molecular sieve must be reduced. However, at that moment, it was believed that Ti-Beta zeolite could only be achieved in the presence of aluminum atoms, obtaining Si/Al ratios in the final Ti-Al-Beta lower than 150.²⁴ To afford the synthesis of Al-free Ti-Beta zeolite, Corma et al. developed a new and reproducible direct synthesis method based on seeding procedures.²⁵ The authors found that the addition of seeds of Beta in where the Al was eliminated by acid leaching, allowed to grow Al-free Ti-Beta.²⁵ As could be expected, the selectivity to the epoxide was strongly increased (see Figure 3), being possible to obtain Ti-Beta catalysts with activities much higher than TS-1 for the oxidation of bulkier hydrocarbons. However, the selectivity to desired products, such as epoxides, using Al-free Ti-Beta synthesized in OH⁻ media [Ti-Beta(OH)] following the above seeding methodology, was still low.

Rigutto et al. developed a different method to synthesize an Al-free Ti-Beta zeolite in OH⁻ media, based on the post-synthetic gas phase substitution of the boron atoms present in a B-Beta zeolite with TiCl₄.²⁶ These authors also observed a decrease in the epoxide selectivity when this Al-free Ti-Beta was tested for selective oxidation reactions using H₂O₂.²⁶

It was then realized that the Al-free Ti-Beta zeolites synthesized in OH⁻ media, had a large number of internal silanol groups since the organic structure directing agent (OSDA), TEA⁺, was

balanced by SiO^- groups, which yield to Si-OH after elimination of TEA^+ . The resultant samples were able to open the epoxides with H_2O_2 (aq).²⁵ Corma et al. decided to perform the synthesis in F^- media since in that case, TEA^+ molecules would be neutralized by F^- anions, and defect free Ti-Beta samples could be obtained.^{5c} The new samples presented completely different physico-chemical properties compared to any previously synthesized Ti-zeolites, such as high crystallinity, high hydrothermal stability, large hydrophobicity and large pores.^{5c,27} The catalytic benefits of the hydrophobic Al-free Ti-Beta were demonstrated in different selective oxidation reactions, such as the selective epoxidation of esters of unsaturated fatty oils (see Table 3), where Ti-Beta(F) shows higher activity and selectivity to the epoxide than Ti-Beta(OH).^{5c,28}

In addition to the above improved direct methods, other procedure to synthesize Ti-Beta based on dry-gel conversion (DGC) has been described.²⁹ Rao and Matsukata first reported the synthesis of high-silica Beta zeolite with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios higher than 900 by DGC methods.³⁰ Following this work, Tatsumi et al. were able to prepare the titanosilicate polymorph of Beta by the DGC, even in presence of alkali cations, observing that this large pore Ti-Beta sample also shows a large hydrophobic character.²⁹ The authors reported that the hydrophobic Ti-Beta-DGC performs better in terms of activity and selectivity than hydrophilic Ti-Betas in the oxidation of different hydrophobic substrates,^{29b,31} in agreement with previous results on the influence of zeolite Beta polarity on oxidation reactions.^{5c,27}

3.2.- Other large pore titanosilicates

Other large pore zeolites that have been successfully synthesized are Ti-ZSM-12,³² Ti-ITQ-7³³ and Ti-ITQ-17,^{5d} with a mono- and three-dimensional systems of pores, respectively.

Indeed, ZSM-12 is a mono-dimensional large pore zeolite enclosing a channel of 5.6×7.7 Å. Since this material was prepared within a broad range of Si/Al ratios in absence of alkali cations, the synthesis of its titanosilicate polymorph could be achieved.³² However, the catalytic activity observed using Ti-ZSM-12 zeolite was much lower than Ti-Beta. The relative

smaller micropore volume of mono-dimensional ZSM-12 compared to Beta can explain this different catalytic behavior.³²

The fluoride synthetic route under very concentrate gels reported by researchers at ITQ has allowed the preparation of several very open pure silica zeolites,³⁴ and particularly interesting, are the multi-dimensional large pore ITQ-7³⁵ and ITQ-17³⁶ zeolites. ITQ-7 is a three-dimensional large pore zeolite, presenting two straight large pore channels, and one sinusoidal channel running along the *c* direction, in a similar way to Beta zeolite.³⁵ Ti-ITQ-7 has been directly synthesized in their titanosilicate form following the fluoride route using 1,3,3-trimethyl-6-azonium-tricyclo[3.2.1.4^{6,6}]dodecane as OSDA, after being crystallized at 150°C for 12 days.^{33a}

The amount of tetrahedral Ti atoms in the zeolitic structure can be controlled in a broad range (from 0.3 to 1.14 %wt TiO₂). Ti-ITQ-7 materials show equivalent activities and selectivities for the oxidation of 1-hexene in H₂O₂ to those of aluminum-free Ti-Beta also synthesized in fluoride media, as expected by their similar framework topologies.^{33a}

Theoretical studies revealed that the incorporation of Ge atoms close to Ti sites in zeolitic structures containing double-four ring (D4R) cages results in a stabilization of the system thanks to the additional framework flexibility provided by GeO₄ units.³⁷ Therefore, Corma et al. attempted the synthesis of Ti-ITQ-7 by introducing Ge in the synthesis gel in order to accelerate the ITQ-7 crystallization and, at the same time, to study the Ge influence on the efficiency in the incorporation of Ti.^{33b} They observed that the incorporation of Ge drastically reduces the crystallization time of the titanogermaniumsilicate ITQ-7 to 12 hours instead of the 12 days required in absence of Ge. Interestingly, the efficiency in the incorporation of Ti was clearly improved from 17.1 to 51% when Ge atoms are present, resulting in materials with higher catalytic activity for the epoxidation of olefins with different molecular sizes.^{33b}

ITQ-17 is a very open structure presenting a three-dimensional straight large channel system (7.5x6.3 Å and 6.9x6.0 Å). The structure of the ITQ-17 corresponds to the polymorph C of Beta

zeolite (BEC), and it was first prepared as germanate³⁸ or silicogermanate³⁹ forms. Unfortunately, the titanogermaniumsilicate of ITQ-17 showed low hydrothermal stability and catalytic activity.^{5d} Nevertheless, it was thought that if a Ge-free Ti-ITQ-17 could be synthesized, this zeolite should improve the catalytic behavior of Beta zeolite, since the former should allow large molecules to diffuse better within the pores than in the case of Beta (notice that Beta zeolite has two straight channels, 6.6x6.7 Å, and one sinusoidal, 5.6x5.6 Å).

We finally achieved the preparation of the pure silica ITQ-17 polymorph under very specific conditions. The synthesis was done in the presence of a buffered media with hexafluorosilicate species and K⁺ cations using SDA1 as organic structure directing agent (see Figure 4a).³⁶ After achieving the synthesis of the pure silica polymorph of ITQ-17, the synthesis of the titanosilicate form was attempted under the same synthesis conditions. However, the presence of potassium cations precluded the insertion of Ti species in framework positions.^{5d} At this point, a further study by molecular modeling using different SDA1-related organics as directing agents (see Figure 4a) was performed in an attempt to find a most specific OSDA for the ITQ-17 that perhaps would allow the preparation under potassium-free conditions. From the different OSDAs (see Figure 4a), it was found that SDA9 extraordinarily directs the crystallization of the ITQ-17 in its titanosilicate form.^{5d} As hypothesized, Ti-ITQ-17 performed better in terms of activity and selectivity than Ti-Beta when large cyclic olefins, such as cyclooctene, were tested for selective epoxidation reactions (see Figure 4b).

4.- Ti-MWW zeolite and related expanded materials

The success in the synthesis of titanosilicate materials with large openings, such as Ti-Beta, encouraged the research of other stable titanosilicates to catalyze selective oxidation reactions of bulky organic substrates. In this sense, Tatsumi et al. nicely rationalized the synthesis of Ti-MWW,^{5e,40} and some related structures.⁴¹ MWW is obtained by the calcination of a lamellar precursor, forming a crystalline structure with two-dimensional sinusoidal 10-ring channels,

and an independent channel system comprised of supercages (0.7x0.7x1.8nm).⁴² Those supercages are converted in large pockets or cups in the external surface, which have been proved as the catalytic sites in different reactions, such as toluene disproportionation,⁴³ and benzene alkylation.⁴⁴ Therefore, the framework of MWW seems attractive for its application in oxidation reactions of bulky substrates.

Tatsumi et al. first reported the direct synthesis of Ti-MWW.^{5e,40} To do this, they modified the original synthesis procedure of the borosilicate ERB-1 described by Millini et al.,⁴⁵ introducing the required Ti in the preparative gel. In those preparations, the presence of boron is mandatory, since it is acting as structure-supporting agent in the MWW formation. After crystallization of the lamellar titanoborosilicate form of MWW, the sample was washed several times with a mineral acid in order to remove some boron atoms and extra-framework Ti atoms. The resultant sample was finally calcined to obtain the crystalline titanoborosilicate form of MWW. Depending on the synthesis conditions, the Si/Ti ratio in the final solids can be controlled from 17 to almost infinite, with most of Ti atoms being in framework positions.^{5e,40} Those Ti-B-MWW materials showed superior catalytic activity to TS-1 for the oxidation of alkenes, such as in the oxidation of 1-hexene with H₂O₂.⁴⁶

The presence of some boron atoms in the final zeolite can introduce weak Brønsted acidity, which would influence the product selectivities. To avoid the presence of boron, Tatsumi et al. reported the B-free preparation of Ti-MWW by a reversible structural conversion (see **Figure 5**).⁴⁷ The authors synthesized first the borosilicate form of MWW following the procedure described by Millini et al.,⁴⁵ and later, the calcined B-MWW material was deboronated by several acid treatments until removal of nearly all boron atoms, while creating defect sites. Finally, the achieved silicate was introduced into an autoclave with a source of Ti, an OSDA (piperidine or hexamethyleneimine), and water, with the aim to introduce Ti atoms in the framework vacancies created during the deboronation process. During those deboronation

and post-synthesis treatments, the MWW material suffers representative and reversible structural modifications, changing from the lamellar structure to the three-dimensional MWW form (see [Figure 5](#)). The specific catalytic activity and epoxide selectivity of bulky cyclohexene and linear allyl alcohols are clearly improved using the B-free Ti-MWW compared to the Ti-B-MWW prepared by direct synthesis. Those catalytic improvements were assumed as a result of the complete removal of the acidity associated to the presence of boron.

Interestingly, Tatsumi et al. have found that adjusting the Ti content above 80 in the synthesis and washing the as-synthesized solid under refluxing conditions before calcination, an expanded new titanosilicate molecular sieve with a structure similar to MWW-lamellar precursor, named Ti-YNU-1, was obtained.^{41,48} The retention of lamellar-like MWW-structure, which presents an expanded layer spacing (see YNU in [Figure 6a](#)), should offer an excellent accessibility to bulky molecules. Indeed, this expanded material shows much higher catalytic activities in the oxidation of different cycloalkenes compared to TS-1, Ti-MWW or even Ti-Beta (see [Figure 6b](#)).⁴⁸ Ruan et al. have studied Ti-YNU-1 structure by high-resolution transmission electron microscopy (HRTEM), powder X-ray diffraction (PXRD), and scanning electron microscopy (SEM), and they have found that Ti-YNU-1 has a 3-D connected MWW-like framework with larger spacing along the *c*-axes.⁴⁹ They proposed that Ti atoms are occupying the pillar sites (see [Figure 6a](#)), expanding the MWW layers, and creating new 12-ring pores.⁴⁹

Recently, Moliner et al. have optimized the synthesis preparation of this expanded titanosilicate MWW-related material.⁵⁰ The expanded titanosilicate Ti-YNU-1 material described by Tatsumi et al. required borosilicate ERB-1 as initial precursor.^{41,48} This borosilicate must be washed under reflux conditions with acid several times to obtain the boron-free precursor, since the presence of boron in the framework negatively influences the product selectivity.⁴⁷ In contrast, Moliner et al. have started from a pure silica MWW precursor, avoiding the presence of boron in the entire synthetic process and, more important, avoiding

the multiple acid treatments required for selectively remove B atoms.⁵⁰ To do this, a pure silica MWW zeolite was directly prepared, and this all-silica precursor was introduced with the Ti source and piperidine to obtain the expanded titanosilicate MWW-related material. As seen in **Figure 7**, the expanded Ti-MWW material [Ti-MWW-exp(1)] shows an improved catalytic activity compared to regular Ti-MWW in the selective epoxidation of bulky cyclohexene with H₂O₂.

5.- Multipore titanosilicates

The synthesis of zeolites containing interconnected pores of medium and large pores is a matter of potential interest since different diffusion rates of molecules along the channels with different dimensions may result in unique activities and selectivities.⁵¹ Three different titanosilicates can be found in the literature containing interconnected large and medium pores, such as Ti-SSZ-33,⁵² Ti-MCM-68,⁵³ and Ti-ITQ-39.⁵⁴

SSZ-33 is a borosilicate molecular sieve with a multidimensional pore system formed by intersecting 10- and 12-ring pores.⁵⁵ The preparation of the Ti-SSZ-33 material was achieved using post-synthetic treatments in order to carry out the isomorphic substitution of B by Ti atoms.⁵² Most of the Ti atoms were properly introduced in isolated framework positions, as revealed by Raman and DR-UV. This Ti-SSZ-33 material shows intermediate catalytic activities in different selective oxidation reactions when compared to TS-1 and Ti-Beta. These catalytic results are in agreement with the intermediate void volume of SSZ-33 between those of Beta and ZSM-5.⁵⁵

ITQ-39 is a new zeolite formed by the intergrowth of three different polymorphs, all of them with interconnected large and medium pores.^{51b,56} This material can be prepared under a broad range of synthesis conditions, even as pure silica form, in fluoride media and free of alkali cations.⁴⁵ The synthesis of the titanosilicate material was attempted under similar conditions to the pure silica polymorph, achieving a fully-crystalline Ti-ITQ-39 with all Ti atoms

in framework positions ($\sim 0.8\% \text{wt TiO}_2$). This material was tested for selective epoxidation of different substrates, and as occurred with Ti-SSZ-33, the catalytic activities were between those of Ti-Beta and TS-1.

Recently, Tatsumi et al. have reported the preparation of Ti-MCM-68.⁵³ MCM-68 is a multidimensional molecular sieve with a pore system comprised by a straight 12-ring channel interconnected with two independent twisted 10-ring channels.⁵⁷ Since this material can only be prepared under a very narrow range of synthesis compositions, its preparation by direct methods is difficult. Then, the preparation of Ti-MCM-68 was performed by post-synthetic procedures, using an acid treatment for dealuminating the sample followed by gas-phase Ti insertion.⁵³ As seen in Table 4, this Ti-MCM-68 shows superior activity for phenol oxidation using H_2O_2 as oxidant to other titanosilicates. This high activity and *para*-selectivity nature is attributed to the higher diffusivity in 12-ring over 10-ring pores and the absence of large cavities, respectively.⁵³

6.- Delaminated titanosilicates

The synthesis of crystalline zeolites with as extra-large pores ($>10 \text{ \AA}$) would be desired because they can combine large accessibility to bulky molecules and high hydrothermal stability thanks to the crystalline nature of the zeolitic walls.⁴ In the last years, several extra-large pore zeolites have been synthesized by carrying out their preparation in the presence of germanium atoms and fluoride anions under very concentrated gels.⁵⁸ Unfortunately, most of those extra-large pore zeolites in their germanosilicate form show low hydrothermal stability. Germanium atoms in framework positions tend to interact with water molecules, changing their coordination from tetrahedral to octahedral, and resulting in the zeolite structure collapse.⁵⁹

In an attempt to increase the accessibility to the catalytic sites while keeping the crystalline nature of zeolites, Corma et al. rationalized the preparation of delaminated zeolites by exploiting the layered nature of some zeolite precursors.⁶⁰ This approach involves the swelling

of the lamellar zeolite, such as the pure silica MWW precursor, using hexadecyltrimethylammonium as swelling agent, and finally, the thin crystalline layers are forced apart by sonication (see Figure 8).⁶⁰ This delaminated material, named ITQ-2, presents layers of 2.5 nm height and very large external surface area ($> 700 \text{ m}^2/\text{g}$).

Since the direct preparation of the titanosilicate form of MWW precursor is difficult, Ti was post-synthetically grafted on the surface of pure silica ITQ-2 using titanocene as Ti precursor.⁶¹ Interestingly, the resultant Ti-ITQ-2 materials keep similar textural and structural properties to the former ITQ-2 silicate. Ti-ITQ-2 was used as catalyst for the epoxidation of cyclohexene with *tert*-butyl hydroperoxide (TBHP) and performing high activities and selectivities were obtained. The authors observed that the higher the Ti content, the higher the catalytic activity.

An ITQ-2-related titanosilicate has been described by Tatsumi et al, called Del-Ti-MWW.⁶² In this work they delaminated the lamellar precursor of Ti-MWW, which was previously post-synthesized from highly deboronated MWW zeolite, avoiding the secondary grafting of titanocene on the external surface. Del-Ti-MWW shows improved TON for the epoxidation of bulky cyclic olefins, such as cyclooctene and cyclododecene.⁶²

Our group was also able to prepare a different delaminated titanosilicate, as Ti-ITQ-6.⁶³ The laminar precursor of ferrierite zeolite (PREFER) upon calcination produce the crystalline ferrierite zeolite, but this precursor can also be swollen and delaminated to obtain thin sheets of ITQ-6. In this case, the direct synthesis of the titanosilicate form of PREFER can be achieved, and therefore, its delamination allows the direct formation of Ti-ITQ-6.^{63a} This delaminated titanosilicate shows improved catalytic activity compared to large-pore Ti-Beta in the epoxidation of bulky norbornene, revealing that bulky molecules suffer less restrictions to diffusion in the delaminated material.^{63b}

Very recently, Ryoo et al. have developed a new synthetic methodology for the direct preparation of MFI nanosheets.⁶⁴ For this purpose, a novel di-quaternary ammonium-type

surfactant formed by a long-chain alkyl group (C₂₂) and two quaternary ammonium groups has been designed, where the diammonium section permits the crystallization of the zeolitic sheets and the long hydrophobic chain prevents the zeolite growth through the *b*-axis.⁶⁴

Approaching the synthetic route proposed by Ryoo et al., the preparation of MFI nanosheets in their titanosilicate form has been reported, achieving larger catalytic activities for the epoxidation of bulky olefins with H₂O₂.⁶⁵

7.- Mesoporous titanosilicates

The discovery of the ordered mesoporous family M41S by Mobil researchers in the 90s using ammonium surfactants as templates was an important achievement. These siliceous materials show uniform ultra-large pores (ranging 1.6-10 nm) and very large external surface areas.⁶⁶

Different ordered mesoporous materials can be achieved depending on the surfactant concentration in the preparative gels, obtaining hexagonal (MCM-41), cubic (MCM-48), or laminar (MCM-50) phases.⁶⁷ For instance, the formation of MCM-48 instead of MCM-41 is

favoured when increasing the surfactant/silica molar ratio to 1-1.5 values. We thought that the isomorphic substitution of Si by Ti in the walls of those mesoporous materials should offer unique opportunities for their application in the selective oxidation of bulky organic molecules.

Then, we first reported the synthesis of the ultra-large pore titanium silicate isomorphous to MCM-41 by direct synthesis.⁶⁸ This Ti-containing MCM-41 material showed regular 35 Å pore

diameters, and almost all Ti atoms were in the mesoporous framework in tetrahedral coordination, as revealed by DRS-UV and IR spectroscopy.⁶⁹ To show the benefits of Ti-MCM-

41 for the oxidation of bulky organic molecules, the catalytic activity of this mesoporous titanosilicate was tested for the epoxidation of norbornene using TBHP as bulky oxidant.⁶⁸

Higher conversions were achieved for Ti-MCM-41 compared to Ti-Beta and TS-1, clearly confirming the potential use of this material to oxidize bulky molecules in the productions of

fine chemicals. A similar Ti-containing mesoporous material called Ti-HMS was reported by Pinnavaia et al.⁷⁰

The synthesis of the titanosilicate form of the cubic structure of M41S, MCM-48, was described by Tatsumi et al by introducing large amounts of surfactant to silicon ratios (1-1.5).⁷¹ MCM-48 material has a three-dimensional channel system, while MCM-41 only shows one-dimensional channel. Therefore, it was expected that MCM-48 must be more resistant to pore blockage than MCM-41, and at the same time, may offer less diffusion restrictions. The authors reported that Ti-MCM-48 performs better than Ti-MCM-41 for the oxidation of cyclododecene, confirming the above expectations.⁷¹ A posterior communication also reported the synthesis of Ti-MCM-48, but in this case, was prepared using a much lower amount of the expensive surfactant (surfactant to silicon ratio in the synthesis gel of 0.2-0.3).⁷²

As reported before, the hydrophilic/hydrophobic nature of the catalyst surface affects to the catalytic activity and selectivity in liquid phase oxidations.⁷³ The presence of silanols groups at the external surface of the mesoporous materials results in the undesired ring opening of epoxides to form diols, especially when using H_2O_2 (aq) as oxidant. The amount of silanols can be decreased by post-synthesis silylation of the mesoporous materials with different organosilanes, such as trimethylsilane, increasing in this way the hydrophobicity of the catalyst.⁷⁴ Ti-MCM-41 and Ti-MCM-48 were treated with trimethylsilane, improving the catalytic activity in the oxidation of alkenes with H_2O_2 .⁷⁵ For instance, the turnover number (TON) was increased from 5 to 112 in the cyclohexene epoxidation by silylating Ti-MCM-41. However, the selectivity to the epoxide using those silylated titanosilicates was poor, reporting values lower than 20%.⁷⁵ In contrast, Corma et al. presented much higher selectivities to the epoxide when similar silylated Ti-MCM-41 catalysts were tested in the selective oxidation reaction of cyclohexene using TBHP as oxidant.⁷⁶ The authors found an increase in activity and selectivity to epoxide when the hydrophobicity of the catalysts, and consequently the surface

coverage with trimethylsilane groups, was increased (see **Figure 9**). A different strategy to reduce the number of silanol groups was the direct introduction of organosilanes, such as methylated silicons, in the synthesis gel.⁷⁷ Those organic-inorganic mesoporous materials also shows excellent activities and selectivities for the epoxidation of cyclohexene using TBHP due to their high hydrophobic nature.^{77c}

Finally, the synthesis of the mesoporous titanosilicate SBA-15 has also been described by direct or post-synthetic procedures.⁷⁸ SBA-15 is synthesized with a triblock copolymer as OSDA, and contains uniform mesopores (5-30 nm) with very thick walls, which results in a mesoporous material with high hydrothermal stability.⁷⁹ Ti-SBA-15 shows similar catalytic activities to Ti-MCM-41 in different oxidations reactions of bulky molecules, but interestingly, it presents improved thermal stability and lower leaching of Ti-species when treated with boiling water.^{78a}

8.- Conclusions

As it can be observed, important advances have been achieved in the design of titanosilicate materials with different pore architectures since the former discovery of medium-pore TS-1 zeolite by ENI researchers.

TS-1 zeolite was the first heterogeneous catalyst for the selective oxidation of organic compounds with H₂O₂, being applied as industrial catalyst in diverse chemical processes. Taking this material as reference, other open titanosilicates have been rationalized following different synthetic methodologies based on “one-pot” or post-synthetic approaches. Those open materials have shown extraordinary catalytic properties for selective oxidation reactions of bulky organic molecules.

The ability of tuning the textural properties of those open titanosilicates, either directing the formation of large hydrophobic crystals or attaching organic groups to the external surfaces,

strongly improve their catalytic behavior. For instance, hydrophobic titanasilicate materials clearly improve the product selectivity for selective epoxidation of olefins.

Up to now, open titanosilicates have been used as efficient green heterogeneous catalysis for the synthesis of bulky organic molecules in fine chemistry. However, in the last years, it has been shown that different open metallosilicate zeolites, and particularly titanosilicates, can be applied as potential heterogeneous catalysts in biomass transformations. The specific interactions of isolated catalytic sites in framework positions with different functional groups (such as alcohols or carbonyls), which are present in most of the biomass substrates, combined with the excellent stability of those hydrophobic titanosilicates in presence of water, offer new catalytic perspectives in biomass-derived processes for those materials.

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Figure 1: Number of scientific reports per year related to titanosilicate materials (Source: SciFinder)

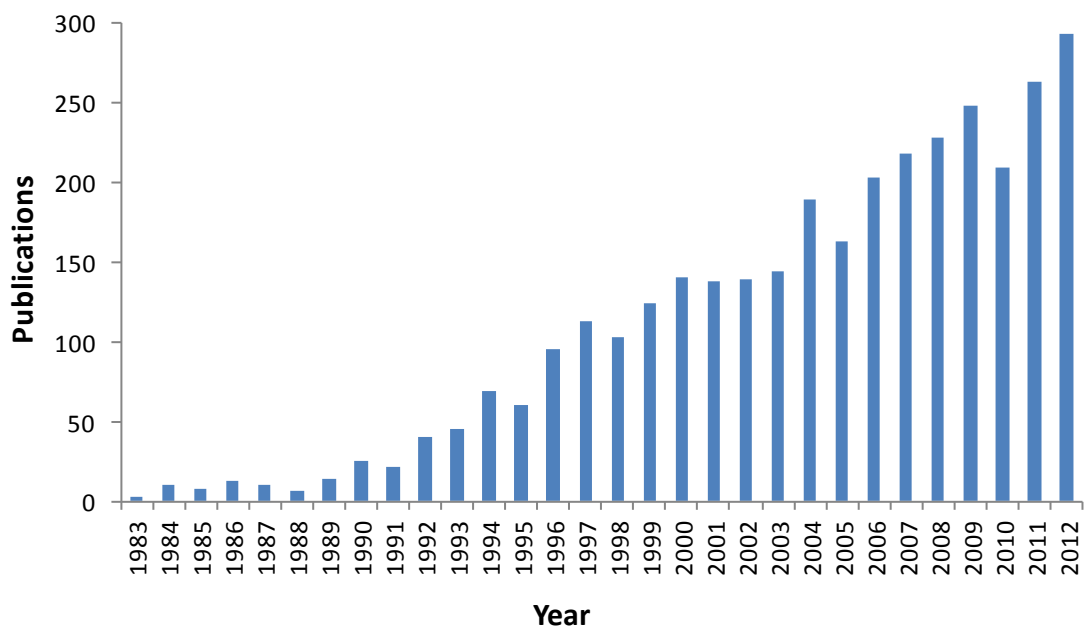


Figure 2: Large number of sources used in TS-1 preparation. Reproduced from ^{5f}.

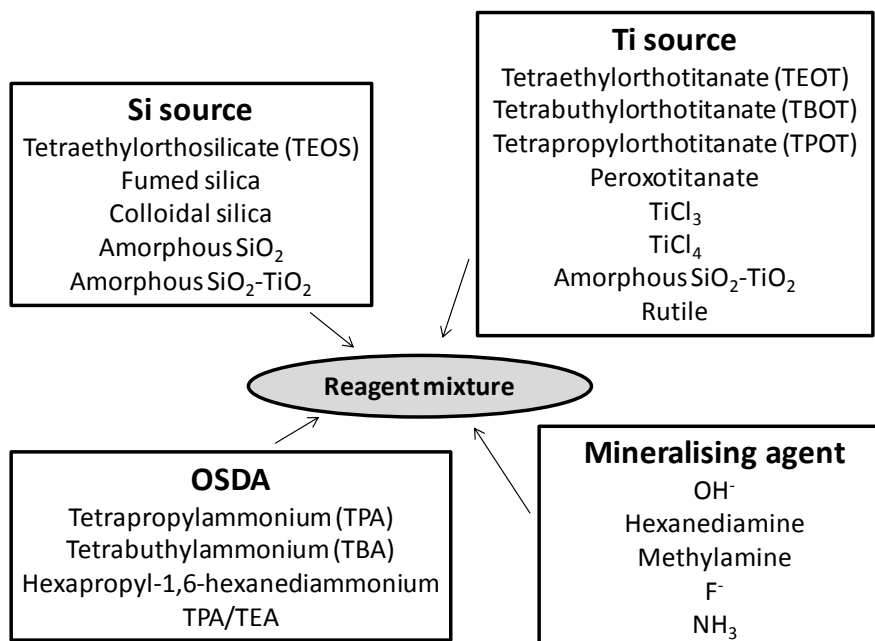


Figure 3: Selectivity to the epoxide product front conversion in the oxidation of hex-1-ene with H₂O₂ over Ti-Beta. The numbers correspond to the Si/Al ratio and Ti content (%wt TiO₂).

Reproduced from ²⁵.

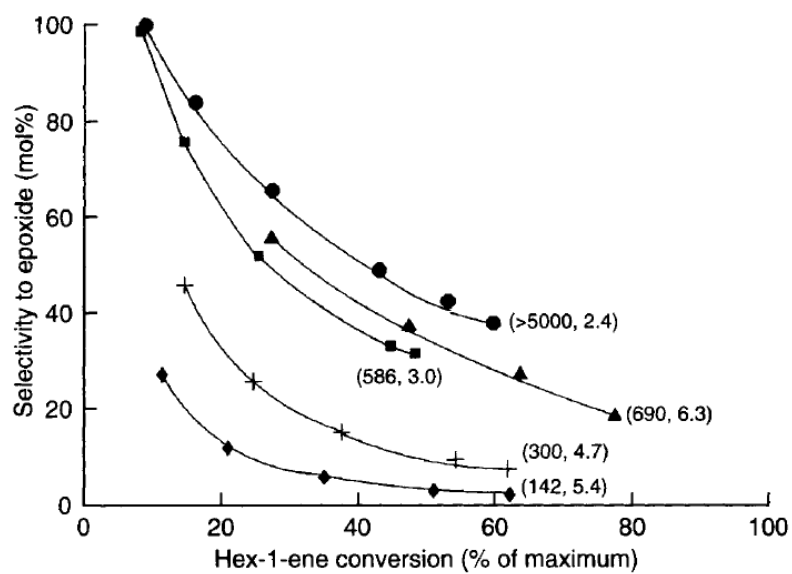


Figure 4: (A) Different OSDAs used in the synthesis of the Ti-ITQ-17. (B) Intrinsic activity of Ti-Beta and Ti-ITQ-17 on the epoxidation of different substrates with H₂O₂ (expressed as mmol alkene converted/mmolTi.h). Reproduced from ^{5d}.

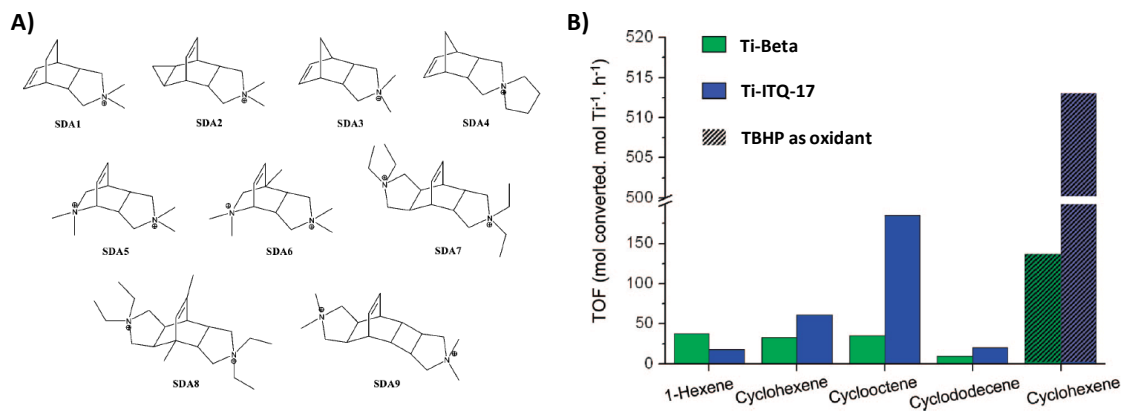


Figure 5: Rationalized methodology followed by Tatsumi et al. for the preparation of B-free Ti-MWW by a reversible structural conversion. Reproduced from [80](#).

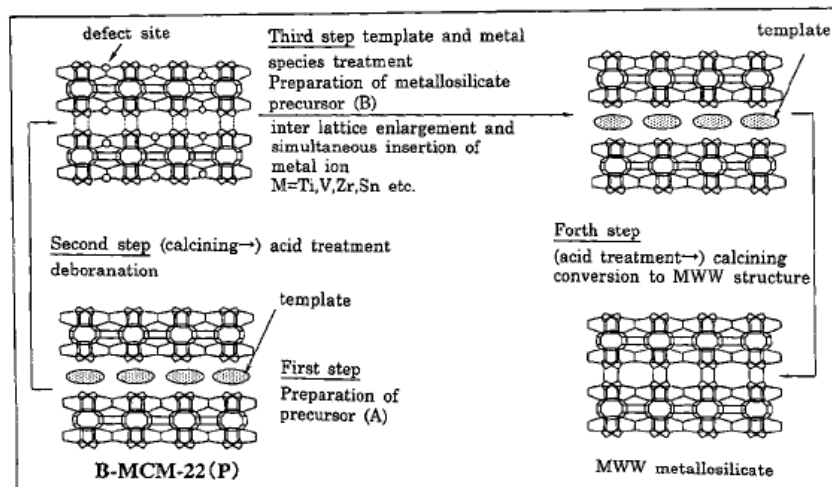


Figure 6: (A) Structures of MWW and YNU zeolites. Reproduced from ⁴⁹. (B) Turnover numbers for the oxidation of different sized cycloalkenes reported by Tatsumi et al.

Reproduced from ⁴⁸.

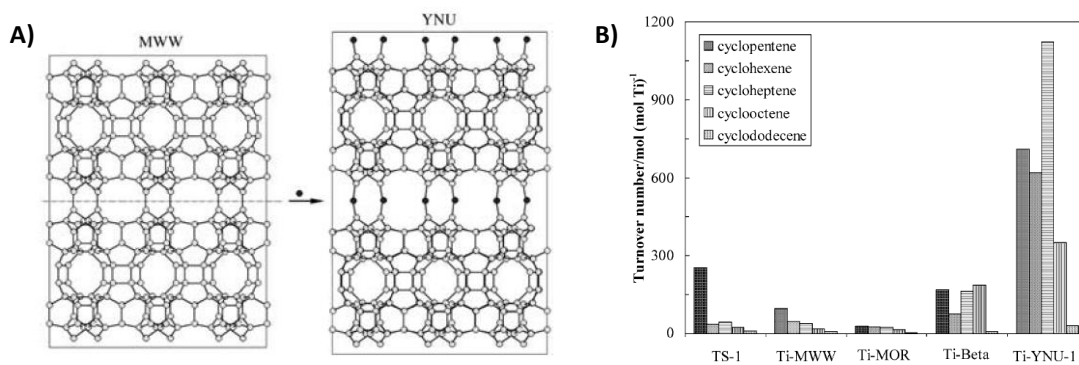


Figure 7: Catalytic activity of Ti-MWW and expanded Ti-MWW in the oxidation of cyclohexene with H_2O_2 reported by Moliner et al. Reproduced from ⁵⁰.

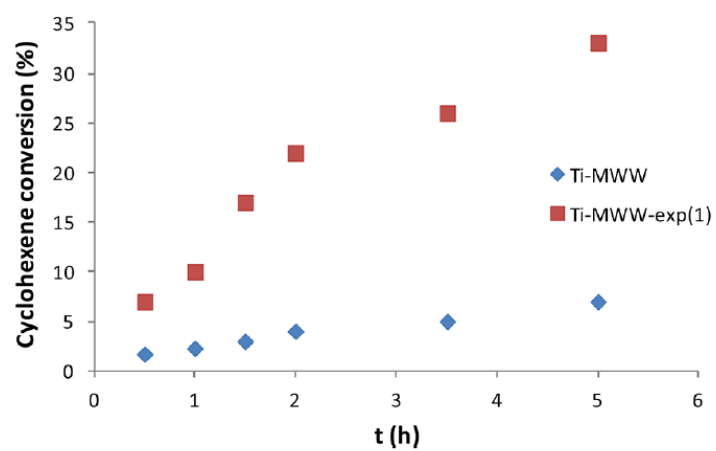


Figure 8: Scheme of the process followed to obtain the delaminated ITQ-2 zeolite.

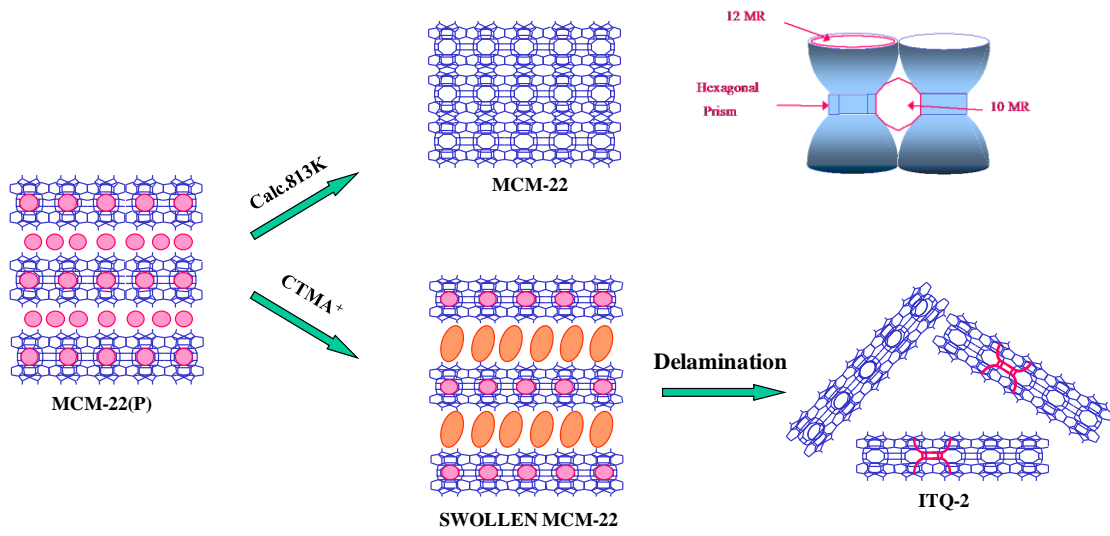
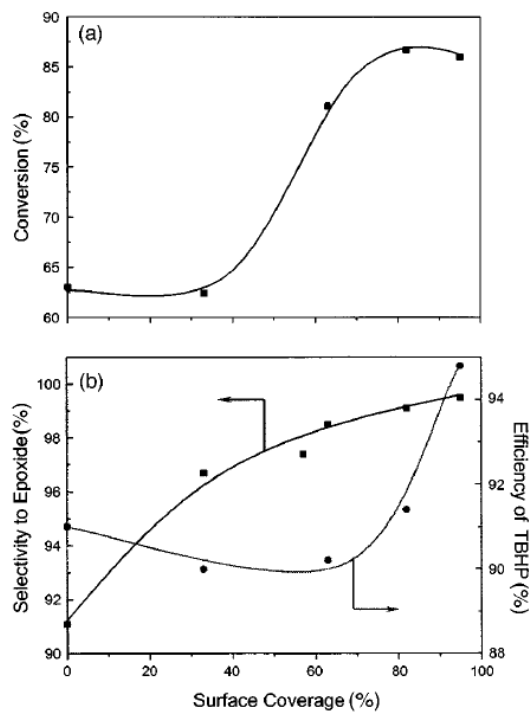


Figure 9: Catalytic activity (A) and selectivity to epoxide (B) in the selective oxidation of cyclohexene with TBHP using Ti-MCM-41 materials at different degree of silylation.

Reproduced from [76](#).



Tables

Table 1: Results of the oxidation of different alkanes with TS-1 using H₂O₂ reported by

Tatsumi et al.¹⁷

Substrate	Turnover number (mol/mol Ti)
Hexane	7.0
Cyclohexane	0.37
2-Methylpentane	0.24
3-Methylpentane	0.26
2,2-Dimethylbutane	0
Heptane	4.5
Octane	0.50
Nonane	0.10

Table 2: Results on the selective oxidation of different olefins over Ti-Al-Beta and TS-1.Reproduced from ^{23b}.

Olefin	Catalyst	Reaction time (h)	Turnover (mol/mol Ti)	Selectivity (mol%)		
				Epoxide	Glycol	Glycolethers
1-Hexene	TS-1	3	50	96	--	4
	Ti-Al-Beta	3	12	12	8	80
Cyclohexene	TS-1	3	1	100	--	--
	Ti-Al-Beta	3.5	14	--	--	100
1-Dodecene	TS-1	3.5	110	77	23	--
	Ti-Al-Beta	3.5	87	--	100	--
Cyclododecene	TS-1	4	5	66	34	--
	Ti-Al-Beta	3.5	20	80	20	--

Table 3: Catalytic results of Ti-Beta(OH) and Ti-Beta(F) in the epoxidation of methyl oleate with H₂O₂. Reproduced from ^{5c}.

Catalyst	%wt TiO ₂	Conversion (%mol)		Selectivity	
		Methyl oleate	H ₂ O ₂	Epoxide	H ₂ O ₂
Ti-Beta(F)	2.2	81.2	96.6	95.1	55.7
Ti-Beta(OH)	3.3	27.6	97.5	80.2	17.8

Table 4: Catalytic results of Ti-MCM-68 in the oxidation of phenol with H₂O₂. Reproduced

from ⁵³.

Yields (%)

Catalyst	Si/Ti	TON	Total	Hydroquinine	Catechol	Para/ortho ratio
Ti-MCM-68	67	307	69.1	55.5	13.6	4.1
TS-1	43	166	57.5	29.1	27.2	1.1
Ti-Beta	45	5	1.7	0.3	0.7	1.4
Ti-MWW	42	11	4.0	0.6	2.1	0.9

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