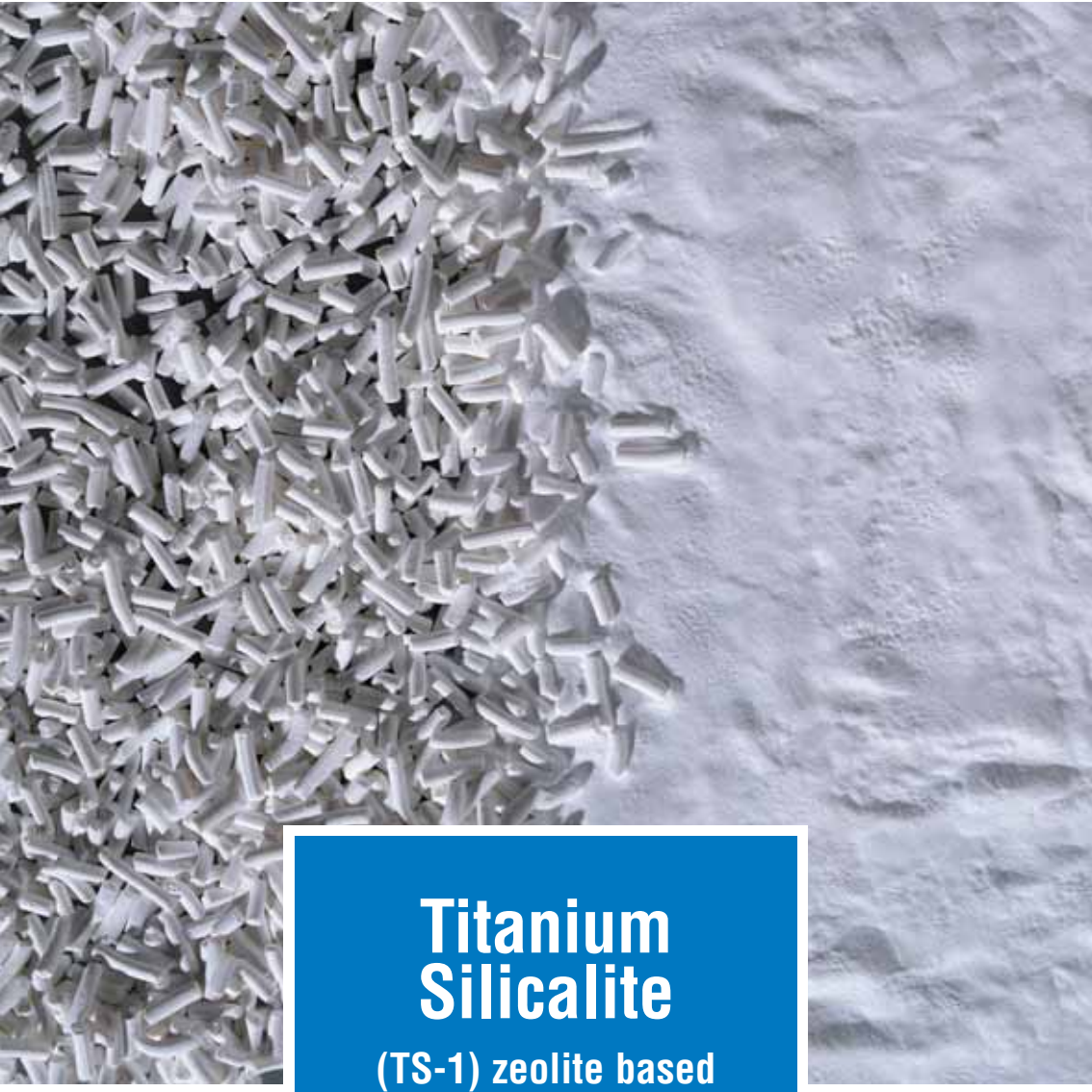


Titanium Silicalite

(TS-1) zeolite based

Proprietary catalyst

eni

polimeri europa

POLIMERI EUROPA CATALYSTS NOW AVAILABLE FOR LICENSING AND SALES

Licensing

Proprietary process technologies

Phenol and derivatives
PBE-1 Zeolite catalyst based Cumene *
Phenol, Acetone, Alphamethylstyrene *
Isopropyl Alcohol Acetone hydrogenation *
Isopropyl Alcohol to Cumene *
PBE-1 Zeolite catalyst
TS-1 Titanium silicalite catalyst based Ammoximation

DMC and derivatives
Dimethylcarbonate
via Carbon Monoxide and Methanol *
Dimethylcarbonate / Diphenylcarbonate *

Polyethylene
LDPE
HDPE
EVA

Styrenics
PBE-1 and PBE-2 Zeolite catalyst based Ethylbenzene
Styrene monomer
GPPS
HIPS
EPS
ABS continuous mass polymerization
SAN

Elastomers
e-SBR
s-SBR
SBS / SB / LCBR
Polybutadiene

Proprietary catalyst technologies

Titanium silicalite
PBE-1 Zeolite
PBE-2 Zeolite

* Co-licensing in cooperation with Lummus Technology

Polimeri Europa

Polimeri Europa – the petrochemical company of Eni – manages the production and marketing of Basic Chemicals, Polyethylene, Elastomers and Styrenics.

With its 17 production sites throughout Europe and a widespread sales network, Polimeri Europa can present itself to the intermediates, thermoplastic resins and elastomers market as a sound and comprehensive supplier whose key strength is its integration. From raw materials to production plants, from research laboratories to technology, through to the interface with the market which can turn to a single source with the certainty of finding solutions to its requirements not only in terms of products, but also in terms of assistance and service. Thanks to the definition of the e-commerce and the logistic portal express, Polimeri Europa can offer to its customers the opportunity to use their tailored made e-shopping and logistics.
Saving time and money.

On the basis of its first hand experience, Polimeri Europa can also license its proprietary production technologies aiming to satisfy the even more specific customers needs.

Polimeri Europa's commitment to quality, improvement and innovation continues, as does its pledge to promote sustainable growth with regard to the community and the environment.

General information

Titanium Silicalite (TS-1) catalyst, one of the most important innovation in heterogeneous catalysis over the last decades, is a high performances composite material specifically designed for industrial oxidation reactions with hydrogen peroxide. TS-1 is the result of long-term research within Eni group associated with direct Polimeri Europa (former EniChem) experience in industrial oxidation reactions. The unique performances of the catalyst are due to the specific features of isolated Ti active sites, able to efficiently promote activity and selectivity in oxidation reactions with hydrogen peroxide, while not isolated Titanium, such as segregated TiO_2 "Anatase like" phase, is inactive for these reactions.

Applications

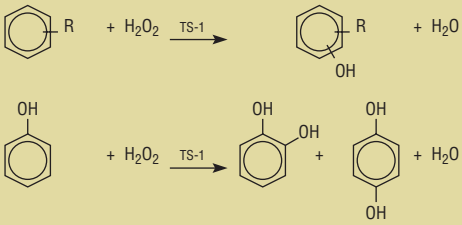
TS-1 catalyst exhibits unique activity and selectivity in several oxidation reactions of organic substrates carried out with dilute hidrogen peroxide at mild reaction conditions, with water as a major byproduct. High coordination ability of Ti^{IV} sites associated to the hydrophobicity of silicalite structure, spatial selectivity and random distribution of Ti^{IV} sites are responsible of this remarkable and unusual catalytic activity. Since its discovery TS-1 has been using in several chemical reactions, some of them also applied at industrial scale. Frequently TS-1 catalysis has completely opened new chemical ways replacing older technologies suffering from several drawbacks like wastes byproduct production as well as stronger reaction conditions.
Up to now TS-1 has been using in diphenols, cyclohexanone oxime and propylene oxide industrial production. Due to the peculiar features of this unique material it is strongly believed that other catalytic applications in fine, intermediates and base chemical industry are still unexplored and ready to be implemented.

Main physical properties

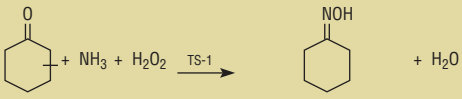
Physical form	
Extrudate	for fixed bed reactors
Microspheres	for slurry reactors
ABD	
Extrudate	650 kg/m^3
Microspheres	600 kg/m^3
Packaging	
Extrudate	200 liters drums
Microspheres	100 liters drums

SOME OF TS-1 PROVEN APPLICATIONS

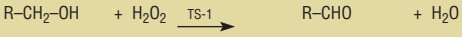
Aromatic hydroxylation



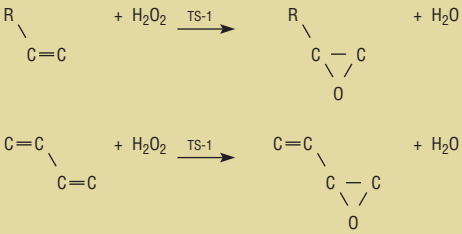
Ammoximation of cyclohexanone to the oxime



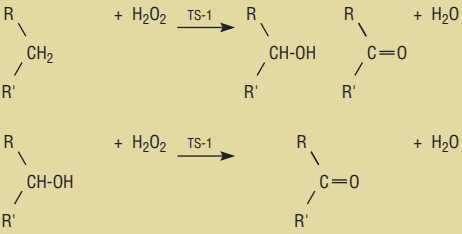
Primary alcohols oxidation to aldehydes



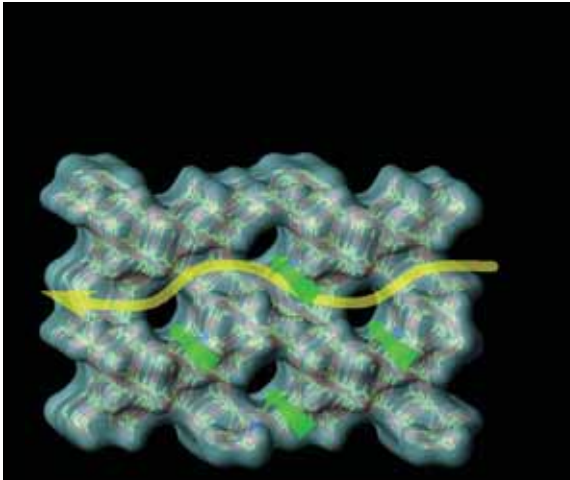
Olefin epoxidation



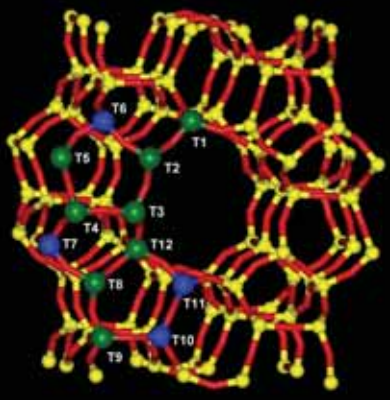
Alkane oxidation



PROPERTIES



Two channels system in TS-1 zeolite



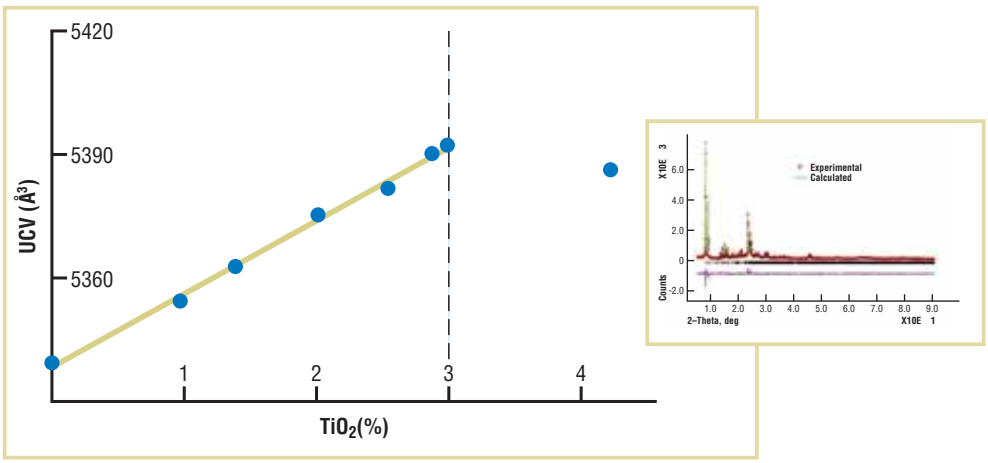
The 12 independent sites with Ti location (blue)

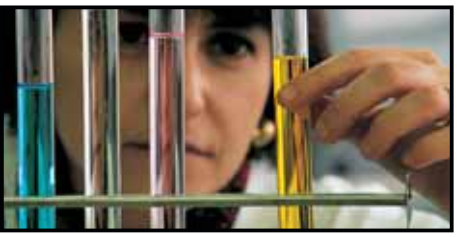
Titanium Silicalite is a crystalline zeotype material in which tetrahedral [TiO_4] and [SiO_4] units are arranged in a MFI structure. Owing to this structure TS-1 shows a three-dimensional system of channels having molecular dimension of 5.1-5.6 Å and which constitutes the zeolitic micropores of the material. Two main sub-system, sinusoidal one and the straight one, are present. 12 independent tetrahedral sites are present in the zeolite lattice. Some of them are probably preferred for Ti sites location.

The presence of Ti sites, with respect of pure MFI Ti-free Silicalite, leads to a regular change in Unit Cell Volume (UCV) occurring with the introduction of Ti^{IV}.

The correlation between UCV and Ti applies up to approx. 3% (as TiO_2) of Ti loading, after which the correlation starts to be no longer valid, clearly indicating an upper limit for Ti^{IV} insertion in the zeolite framework.

Linear correlation between Ti content vs. UCV

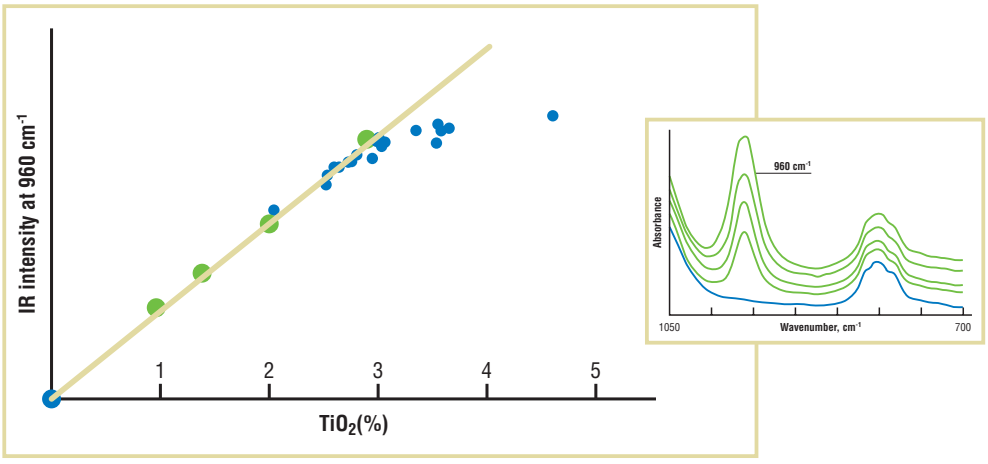




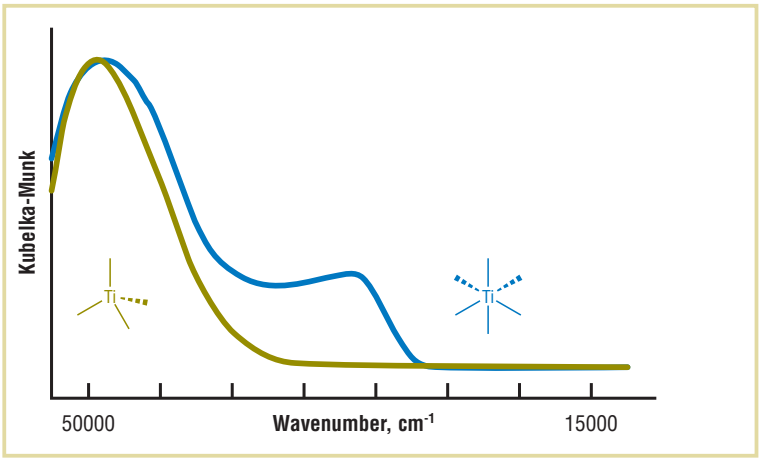
Clear evidences of the presence of Ti atom in TS-1 can be obtained from the IR band at 960 cm^{-1}, which is considered as a "fingerprint" for framework Ti atoms in tetrahedral or nearly tetrahedral coordination.

Also DRS UV-Vis band at approx. 50,000 cm^{-1} is very informative about tetrahedral coordination of Ti atom, being assigned to the Ligand to Metal Charge Transfer from Oxygen to Titanium in the isolated 4-fold coordinated [TiO_4] unit. Octahedral [TiO_6] units of TiO_2 "anatase like" phase, not active for oxidation reactions with hydrogen peroxide, are clearly detected as a band near to 30,000 cm^{-1}.

FTIR: linear correlation between Ti content vs. 960 cm^{-1} band intensity



DRS UV-Vis: tetra- and hexa- coordinated Ti

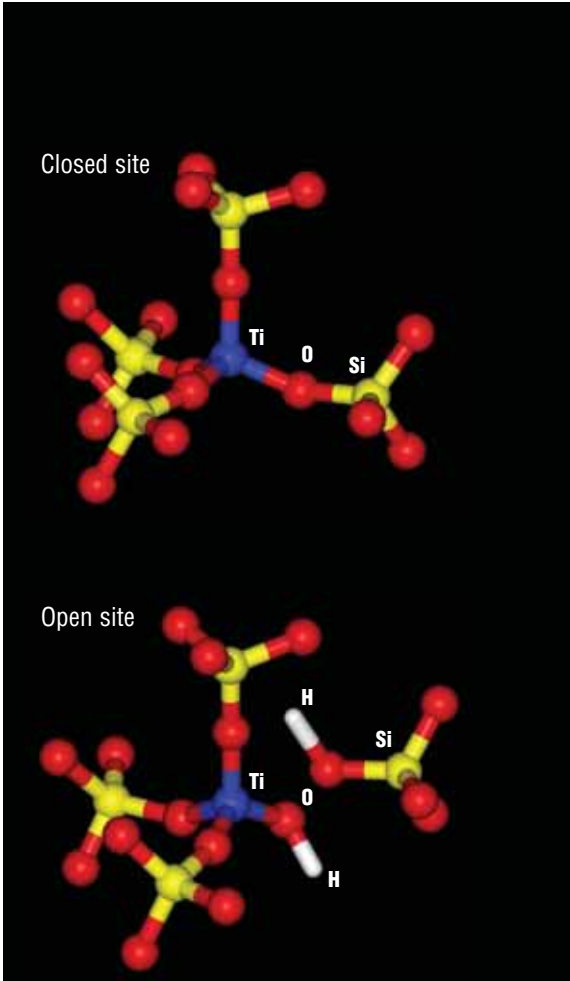


TS-1 zeolite crystals:
typical "blackberry" morphology

The real chemical nature of Ti species in TS-1 catalyst is made by the so-called perfect "closed" $Ti(OSi)_4$ tetrahedral site. The existence of some defective "open" $Ti(OSi)_3(OH)$ sites have been proposed based on extensive EXAFS study on well manufactured TS-1 samples.

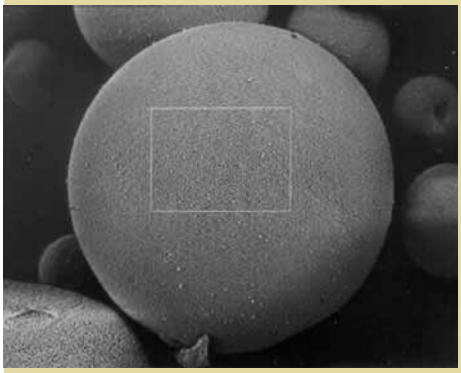
TS-1 zeolite crystals morphology also plays an important role for catalytic applications as configurational diffusion regimes of reactants and product through zeolite material are strongly affected by crystals morphology. The pure and "well manufactured" TS-1 crystals, the active phase in TS-1 catalyst, have the typical "blackberry" morphology associated to the high Ti loading.

Pure TS-1 zeolite crystals, due to their low dimension, are normally binded to form larger TS-1 catalyst particles whose shape and dimension depend on the required application.
Extrazeolite features, like porosity and mechanical strength, have been optimized for TS-1 catalyst final use in CSTR, where microspheres are conveniently used, or PFR where extrudate are preferred.

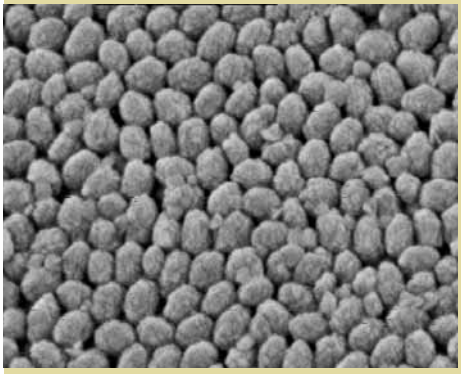


"Closed" and "open" tetrahedral Ti sites

Microsphere of TS-1 catalyst



TS-1 zeolite crystals binded on the microsphere TS-1 catalyst surface



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Responsible Care

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07/2009