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Original Citation:

Availability:

This version is available <http://hdl.handle.net/2318/1685603> since 2019-09-18T10:58:53Z

Published version:

DOI:10.1002/tcr.201800108

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by

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The Chemical Record 18 (2018) 1-19

DOI: 10.1002/tcr.201800108

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Ti-based catalysts and photocatalysts: characterization and modeling[†]

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[†] To the memory of Prof. Gilberto Vlaic, passed away on May 18th, 2018. He was a pioneer in EXAFS spectroscopy applied to catalysis and mentor of CL. He contributed to the first works of our research group concerning TS-1 and including XAS data, here reviewed.

This perspective article aims to underline how cutting-edge synchrotron radiation spectroscopies such as extended X-ray absorption spectroscopy (EXAFS), X-ray absorption near edge structure (XANES), high resolution fluorescence detected (HRFD) XANES, X-ray emission spectroscopy (XES) and resonant inelastic X-ray scattering (RIXS) have played a key role in the structural and electronic characterization of Ti-based catalysts and photocatalysts, representing an important additional value to the outcomes of conventional laboratory spectroscopies (UV-Vis, IR, Raman, EPR, NMR etc.). Selected examples are taken from the authors research activity in the last two decades, covering both band-gap and shape engineered TiO₂ materials and microporous titanosilicates (ETS-10, TS-1 and Ti<C->AlPO-5). The relevance of the state of the art simulation techniques as a support for experiments interpretation is underlined for all the reported examples.

1. Introduction

Titanium is the 9th most abundant element in the Earth crust, making up about 0.62^{8%} of it, and is the 4th most abundant metallic element, after aluminum, iron, and magnesium. It was discovered in 1791 in England by Reverend William Gregor and independently rediscovered in 1797 by the German chemist Heinrich Klaporth, who named it after the Titans of Greek mythology. Titanium is rarely found as native metal in nature and it occurs primarily in minerals like rutile, ilmenite, leucoxene, anatase, brookite, perovskite, in titanates and several iron ores.^[1]

Titanium dioxide (TiO_2) is the most common titanium compound, since it constitutes about 93--96% of rutile and 44--70% of ilmenite ores, which are the two primary sources of titanium. TiO_2 is abundant, inexpensive, chemically stable and harmless. It has been used since ancient times as white pigment, thus its safety toward humans and environment is historically guaranteed. In catalysis, titania is widely used as support, for both noble metals^[2] and metal oxides^[3] based active phases.

Scientific studies on its photoactivity have been reported since the early part of the 20th century:^[4] already in 1921, Renz reported the partial reduction of titania upon sunlight illumination in the presence of organic compounds.^[5] However, the interest in this material raised considerably after the publication in Nature, in 1972, of the famous paper by Fujishima and Honda about water photoelectrolysis.^[6] Nowadays, more than 10000 articles concerning TiO_2 are published per year.

The most common oxidation states of titanium are 4+ and 3+, giving rise to a large variety of compounds with even more abundant fields of application. Among these, catalysis covers a relevant role and several (photo)catalytically active materials find in titanium their active center. In most of Ti-based catalysts, titanium is found as Ti^{4+} , because of the superior stability of such oxidation state at ambient (i.e. oxidative) conditions. Ti^{4+} can be incorporated in extended phases (TiO_2), as well as in low-dimensionality or even isolated sites in proper matrixes,^[7] e.g. allowing $\text{Ti}-\text{C}->\text{O}-\text{C}->\text{Ti}$ nanowires in ETS-10^[8] or isolated tetrahedral Ti to be formed in Ti-zeolites such as TS-1^[9] The latter material has been first synthesized in the EniChem laboratories in the '80s and has been thoroughly studied in the last 30 years: some milestones in its characterization will be discussed in the following sections. Upon the discovery of TS-1, several analogous materials presenting isolated Ti sites have been synthesized by different laboratories, including Ti-zeolites with different framework topologies (such as: Ti- β ,^[10] Ti-MWW,^[11] Ti-STT,^[12] Ti-CHA,^[13]) and Ti-doped ordered mesoporous silicas (such as: MCM-41, MCM-48, SBA-15 etc.)^[14]

Ti^{3+} is naturally less common, however materials based on this oxidation state are routinely exploited in the field of polymerization reactions, such as the well-known Ziegler-Natta catalysts.^[15]

Moreover, a particular chemical environment surrounding the Ti centers can lead to the simultaneous presence of Ti in both the 4+ and 3+ oxidation states. This is the case of Ti-substituted

aluminophosphates (Ti-C-AlPO),^[16] where the peculiar composition of the zeotype framework allows both Ti^{4+} (generating Brønsted acidity) and Ti^{3+} (leading to Lewis acidity) to be generated.

Beside the oxidation state of the active centers, also the surface modification of Ti-materials can have an impact on the catalytic activity, e.g. the hydrophobicity generated by silylation treatments. Yamashita and coworkers demonstrated the effectiveness of such surface treatments over different Ti-based materials toward the conversion of organic molecules in aqueous environments, as the photocatalytic abatement of water pollutants by TiO_2 /zeolite composites,^[17] the ammoximation of cyclohexanone on TS-1,^[18] or the epoxidation of cyclooctene over Ti-SBA-15.^[19] All these modified catalysts showed superior conversions retaining the selectivity of the pristine materials, thanks to the increased hydrophobicity (i.e. affinity to the substrates) of their surfaces.

Among the wide variety of materials presented above, this perspective paper focuses on the Ti^{4+} based ones. In Section² we will focus on two aspects which have recently attracted increasing research efforts: i) the synthesis of visible light active TiO_2 nanomaterials^[20] (Section^{2.1}); and ii) the study of facet-dependent properties of TiO_2 nanoparticles^[21] (Section^{2.2}). Section³ is devoted to three important microporous titanosilicates where Ti^{4+} is found in confined structures: ETS-10,^[8] TS-1^[9] and Ti-C-AlPO -5^[22] (Sections, 3.1, 3.2 and 3.3, respectively).

In the characterization of such Ti-based catalysts^[9b,10,14e,14j,23] and photocatalysts,^[24] cutting edge synchrotron radiation spectroscopies^[25] including extended X-ray absorption spectroscopy (EXAFS),^[26] X-ray absorption near edge structure (XANES),^[27] high resolution fluorescence detected (HRFD) XANES,^[28] X-ray emission spectroscopy (XES)^[29] and resonant inelastic X-ray scattering (RIXS)^[29b,30] played a key role, by making accessible insights otherwise unreachable through conventional laboratory spectroscopies (UV-vis, IR, Raman, etc). Beside these invaluable experimental findings, parallel computational studies facilitated their interpretation and rationalization on both functionalized titania^[31] and titanosilicates.^[32] Thereby, in the following section, computational insights will be discussed too.

2. TiO_2

Titanium dioxide (TiO_2) is the most common titanium compound and occurs naturally in three crystalline forms: rutile, anatase and brookite. Rutile is the most abundant polymorph, but anatase is the most stable form for small nanoparticles,^[33] thus it is the most used in photocatalysis. In both anatase and rutile structures, the basic building blocks are chains of TiO_6 octahedra, where each Ti^{4+} ion is surrounded by an octahedron of six $\text{O}^{2-\text{M}-}$ ions. The two polymorphs differ in the distortion of each octahedron and in the assembly pattern of the octahedra chains.^[34]

Titanium dioxide is employed in a wide range of applications, e.g as white pigment, as gas sensor, as a corrosion-protective coating, in electric devices, in catalysis, in solar cells, in cosmetics and to increase biocompatibility of bone implants.^[21a,35] Concerning heterogenous catalysis, it is widely used as catalyst support, owing to its high chemical and thermal stability with outstanding resistance towards corrosion in different electrolytic media.^[36] However, the most important application of TiO_2 is in photocatalysis. In the last years increasing research efforts have been devoted to develop visible light active TiO_2 nanomaterials and to investigate the role of different TiO_2 crystal facets in determining the nanoparticles (NPs) photocatalytic activity:^[4,37] both aspects will be discussed in detail in the next sections.

2.1. Visible Light Active TiO_2 Photocatalysts

According to its wide band gap (3.2^{++eV} for anatase and 3.0^{++eV} for rutile), pristine TiO_2 mainly absorb ultraviolet photons, which represent only the 5% of the solar spectrum. To extend the spectral response of pure TiO_2 to visible light different approaches have been proposed, including the doping with metal impurities or non-metal atoms, the preparation of oxygen-deficient TiO_2 nanomaterials and the coupling with narrow band gap semiconductors.^[21a,21c,24k,38]

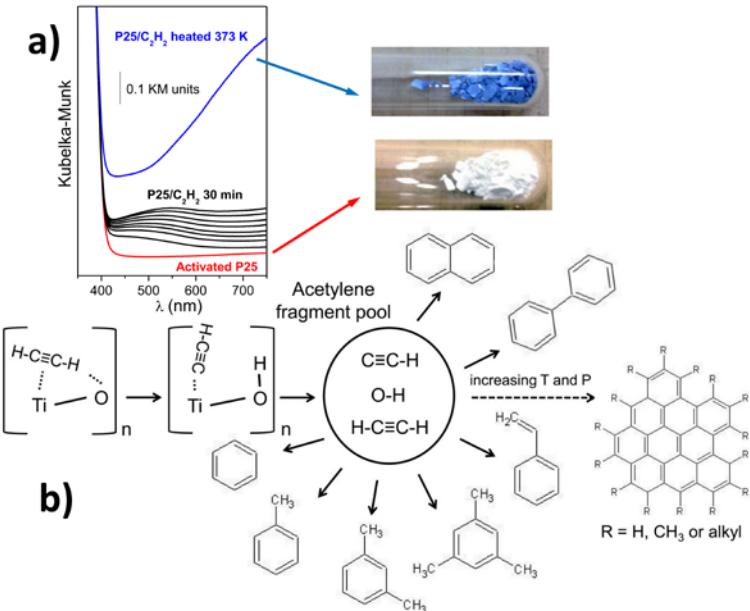
Concerning doping with non-metals, N is one of the most commonly employed elements. The first study of photocatalytic degradation of organic compounds using N-doped TiO_2 was published at the beginning of the century.^[24f] The origin of the visible light activity of N-doped TiO_2 has been very debated in literature, both from a theoretical and experimental point of view.^[20b,31a,39] In this context density functional theory (DFT) calculations have fundamentally contributed to elucidate the possible structural configurations of the dopants and the resulting electronic structure.^[31a,31b] Also the combination of different experimental techniques, like electron

paramagnetic resonance and X-ray photoelectron spectroscopy, provided crucial insights into this problem.^[24k] For instance, Giamello and coworkers employed electron paramagnetic resonance to show that in these systems surface electrons and, at lower extent, surface holes are formed due to the synergistic effect of visible (around 400^{nm}) and near-infrared components of light.^[40]

With respect to metal dopants, Au/TiO₂ systems have attracted increasing attention owing to the ability of Au NPs to improve the photocatalytic activity of pure TiO₂ by plasmon resonance energy transfer and generation of hot electrons, which can overcome the Schottky barrier at the metal/TiO₂ interface.^[41] In these materials, the use of characterization techniques based on synchrotron radiation was crucial to achieve a detailed description of the trapping sites and of the charge localization induced by excited carriers.^[42] In this regard, Boscherini and coworkers^[42b] combined X-ray absorption spectroscopy (XAS) and RIXS to provide atomistic insights into the electronic and structural localization of plasmonic-generated charges. In particular, they highlighted that part of the injected electrons survive longer, being captured at Ti sites concentrated near the surface.

The sensitization of the TiO₂ surface via chemisorbed or physisorbed dyes can increase the efficiency of the excitation process and allows visible light absorption to be effective.^[37b,37e,43] Nowadays, Ru-based complexes are the most widely employed dyes for photocatalytic applications,^[44] notwithstanding considerable drawbacks represented by their cost and low chemical stability. Other popular dyes, such as porphyrins,^[45] catechol,^[46] phthalocyanines,^[47] etc. are often toxic and easily undergo a self-degradation process in the reaction medium, that makes them unsuitable for durable applications in photocatalysis. In a recent study,^[48] we proposed a different strategy for surface sensitization based on cheaper carbon-based coloured dyes grown *in situ* on the TiO₂ surface. By combining electronic and vibrational spectroscopies with gas chromatography-mass spectrometry analysis, we showed that *in situ* oligomerization of acetylene is an effective way to synthesize polycyclic condensed hydrocarbons tightly anchored to the TiO₂ surface. The products obtained after oligomerization at 373^K have an intense blue color, being able to efficiently absorb visible light (Figure^{1<figr1>a}). We also described the reaction mechanism: at low pressure the reaction proceeds through surface adsorption of acetylene and cyclotrimerization to benzene, while at higher pressure ($P > 100\text{mbar}$) the adsorption step is followed by the

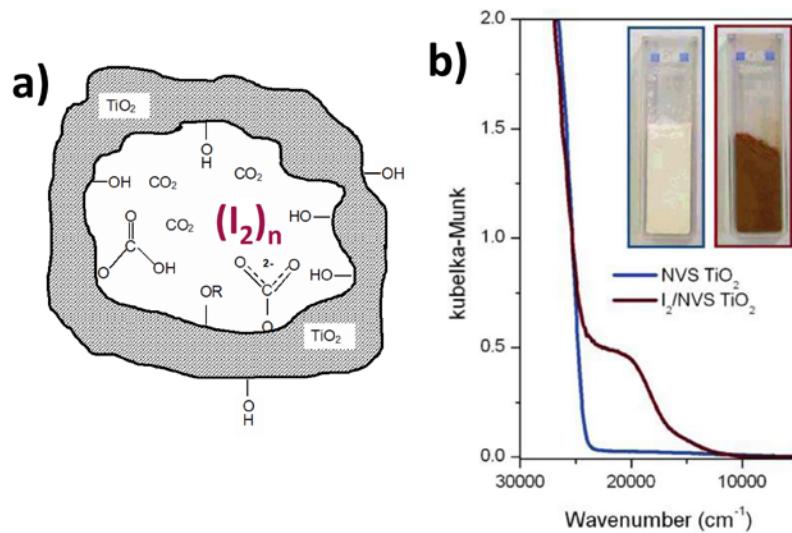
progressive formation of more complex oligomerization products containing an increasing number of conjugated double bonds (Figure⁴⁹b). These polycyclic condensed hydrocarbons can also represent intermediate steps toward the *in situ* synthesis of graphene layers on TiO₂ in very mild conditions.^[49]



Figure⁴⁹a a) UV-Vis spectra of the acetylene/TiO₂ system. Red curve: spectrum of pure activated TiO₂ P25. Black curves (from the bottom): spectra immediately after dosage of C₂H₂ (initial pressure 120 mbar) and at increasing contact times up to 30 minutes. Blue curve: after heating in acetylene atmosphere at 373 K for 30 minutes. The pictures in the right part of the figure illustrate the color change of the sample passing from pure activated TiO₂ to the final TiO₂/C₂H₂ system heated in acetylene atmosphere for 30 minutes at 373 K. b) Schematic representation of the reaction of acetylene on TiO₂ showing the first steps of the reaction (adsorption and dissociation of C₂H₂ on the oxide surface) and the main reaction products. Unpublished Figure reporting data published in ref.^[48]

Another original approach to extend the spectral response of TiO₂ proposed by our group took advantage on the synthesis, via a sol-gel route, of TiO₂ nanostructured materials with nanovoids containing encapsulated iodine species.^[50] The origin of the visible light activity of the material was ascribed to the presence of (I₂)_n adducts encapsulated in the nanocavities. These species coexist with partial combustion products of isopropoxide groups (see Figure²a) present after thermal treatment in air at 773 K of the hydrolyzed titanium isopropoxide precursor.

The $(I_2)_n$ adducts can efficiently absorb visible light (see Figure²b) to create electron-hole pairs which can subsequently migrate to the external surface of the semiconductor particles (i.e. where photocatalysis can take place). Being the iodine species encapsulated inside the TiO_2 nanovoids, these are not exposed to the reaction environment and are not subject to undesired degradation. Such system was about ten times more efficient than commercial TiO_2 P25 in the photodegradation of methylene blue under sunlight.



Figure² a) Pictorial representation of the nanovoids containing the partial combustion products of isopropoxide groups and the $(I_2)_n$ adducts. b) UV-Vis spectra of non-doped (NVS TiO_2) and I_2 -doped ($I_2/NVS TiO_2$) TiO_2 samples with nanovoids. The inset reports a color photograph of NVS- TiO_2 (left) and $I_2/NVS-TiO_2$ (right) samples. Unpublished Figure reporting data published in ref.^[50]

2.2. Shape Engineering of TiO_2 Nanoparticles

Crystal facet engineering of semiconductors nanoparticles, and in particular of TiO_2 , is emerging as an important strategy to finely tune their physicochemical properties, aiming to optimize their reactivity and selectivity.^[21b] For anatase TiO_2 the shape under equilibrium conditions, calculated using the Wulff construction, is a truncated tetragonal bipyramid, which mainly exposes $\{101\}$ facets. However, starting from the seminal paper by Yang *et al.*,^[51] increasing research efforts have been devoted to synthesize TiO_2 anatase nano-sheets (n-sh) which

maximize the presence of the minority basal {001} surfaces, that have been reported to show superior photocatalytic activity.^[52] The synthesis of TiO₂ n-sh requires the use of suitable adsorbates (commonly fluorides) to lower their surface energy.

In the last decade many papers have reported improved photocatalytic activity of TiO₂ n-sh, which was ascribed to the dominant {001} facets. Nevertheless, DFT calculations highlighted that, during the calcination procedure commonly performed to remove the fluorides employed in the synthesis, the {001} surfaces can easily undergo a (1×4) reconstruction, resulting in a weakly reactive surface.^[53] This theoretical prediction has been very recently confirmed by experimental studies.^[54] Therefore, the exact contribution of the {001} facets to the photocatalytic activity of TiO₂ n-sh is nowadays stimulating lively debates and even the dominant species at the surface are not yet fully determined. In this case, the use of experimental techniques able to investigate the physicochemical properties of the different TiO₂ surfaces and parallel theoretical modeling could significantly contribute to clarify the issue.

In this context, our group investigated several TiO₂ anatase and rutile samples using IR spectroscopy to study the surface properties and the processes occurring at the oxide surface during photocatalytic reactions.^[55] For instance, the use of adsorbed carbon monoxide as molecular probe^[25d,56] allowed us to obtain information at molecular level on the different exposed surfaces. Indeed, in the IR spectra, obtained for the adsorption of CO at 60^K on a TiO₂ sample (Figure^3<figr3>a), several signals can be observed, and most of these spectral features are related to the internal stretching mode of CO interacting with the Ti⁴⁺ surface sites. Since their electronic configuration is d^0 , only the electrostatic interaction^[57] and the σ bond formation with adsorbed CO is possible.^[23e,58] Therefore, its stretching frequency is directly linked to the electrophilicity, and thus to the Lewis acidity, of the surface Ti⁴⁺ centres located on extended surfaces, edges, steps and corners.^[59] Moreover, since the stretching frequency of adsorbed CO is also strongly influenced by the lateral interactions occurring in the adlayers,^[56c,60] it can give indirect information on the bidimensional packing of Lewis centres, and hence on the structure of the different adsorbing faces. Therefore CO is not only an excellent probe of the individual sites, but can also give information about faces distribution and particles morphology when the interpretation of the IR spectra is

supported by high-resolution transmission electron microscopy (HRTEM) images and parallel DFT calculations.^[31c-e,61]

In particular, Mino *et al.*^[61a,61b] assigned the different spectral features in the IR spectrum of CO adsorbed on Evonik (Degussa) TiO₂ P25 (Figure^{3<xfigr3>a}), a mixture of about 85% anatase and 15% rutile, showing that main spectral features of CO on TiO₂ P25 can be found separately in the pure anatase and rutile phases. This suggests that no apparent interaction between the anatase and the rutile components of TiO₂ P25 with formation of new peculiar structures characteristic of anatase-rutile junctions is observable. More recently, Deiana *et al.*^[31c] investigated shape-engineered TiO₂ anatase nanoparticles with well-defined bipyramidal shape, unequivocally confirming the assignment of the main peak in the IR spectrum to CO adsorbed on {101} facets.

The same approach was applied also to highlight the role of different anatase surface sites in the CO₂ adsorption and in the subsequent reactions.^[62] We showed that CO₂ is mainly adsorbed in linear form on the {101} facets, while the formation of a variety of surface carbonates is occurring at the {001} ones. The role of co-adsorbed water in the formation of surface bicarbonates was also assessed. Simulated spectra have been constructed by employing computed IR vibrational frequencies of the structures considered the most likely on the basis of the DFT results and systematically compared with the experimental spectra (Figure^{3<xfigr3>b}).

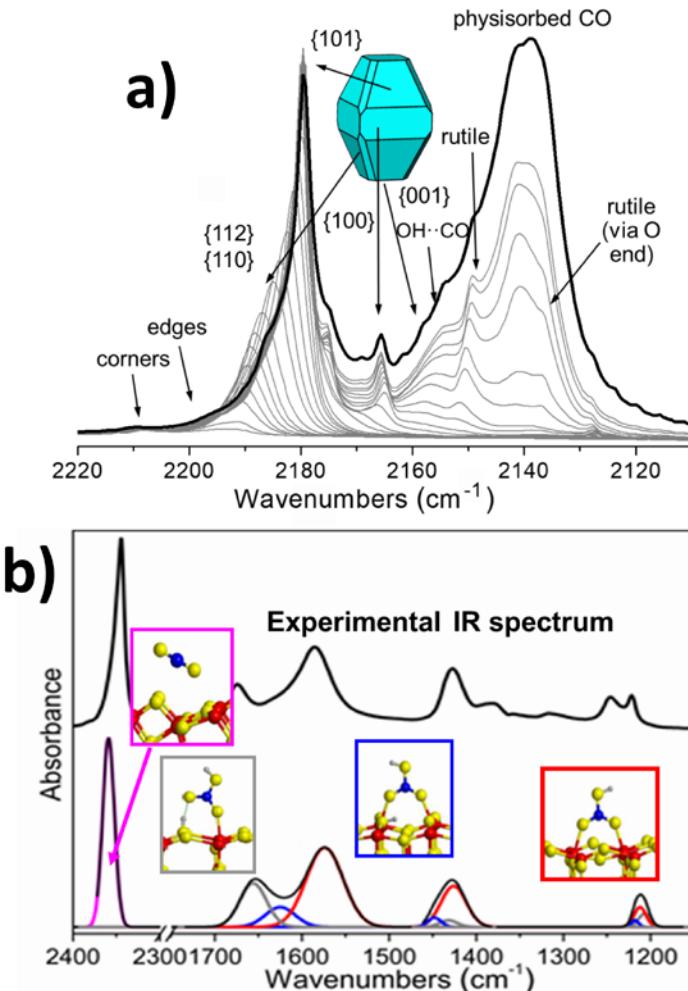


Figure 3 a) Assignment of the IR spectra of CO adsorbed at 60 K on TiO₂ P25. b) Comparison between experimental IR spectrum (black curve) of CO₂ adsorbed on anatase TiO₂ and simulated IR spectra constructed employing vibrational frequencies computed by DFT for different surface carbonates and bicarbonates. Unpublished Figure reporting data published in Refs.^[61a,62]

Other peculiar TiO₂ crystal shapes have been synthesized to obtain physicochemical properties optimized for specific reactions. For instance, our group developed the synthesis of nanostructured parallelly oriented TiO₂ micropillar arrays, either pure or implanted on a carbon matrix, obtained via controlled oxidation of hybrid carbonaceous precursors.^[63] These oriented systems show enhanced electron transport properties which can be useful for photocatalytic and energy conversion applications.

3. Microporous Titanosilicates

3.1. ETS-10

Engelhard Titanosilicate-10 (ETS-10) is a microporous crystalline material, belonging to the family of Ti-substituted silicates containing Ti^{4+} in octahedral coordination.^[64] Because of its inherently disordered nature, showing the presence of different polymorphs, conventional diffraction approaches could not be applied straightforwardly to determine its atomic structure. Indeed, Anderson *et al.* solved the structure of ETS-10 by combining the results from an impressive number of complementary experimental techniques and molecular modeling simulations.^[8a] They finally demonstrated that ETS-10 framework is composed of corner-sharing SiO_4 tetrahedra and TiO_6 octahedra linked through bridging oxygen atoms, and that two sets of perpendicular 12-ring channels having an elliptical cross-section with dimension $7.6\text{\AA}\times4.9\text{\AA}$. The TiO_6 octahedra forms linear - $\text{Ti}-\text{C}-\text{O}-\text{C}-\text{Ti}-\text{C}-\text{O}-\text{C}-\text{Ti}-$ chains running along both *a* and *b* crystallographic directions (Figure 4a). This model was successively confirmed by single crystal XRD,^[65] by periodic DFT^[320] and by Ti K-edge EXAFS.^[66]

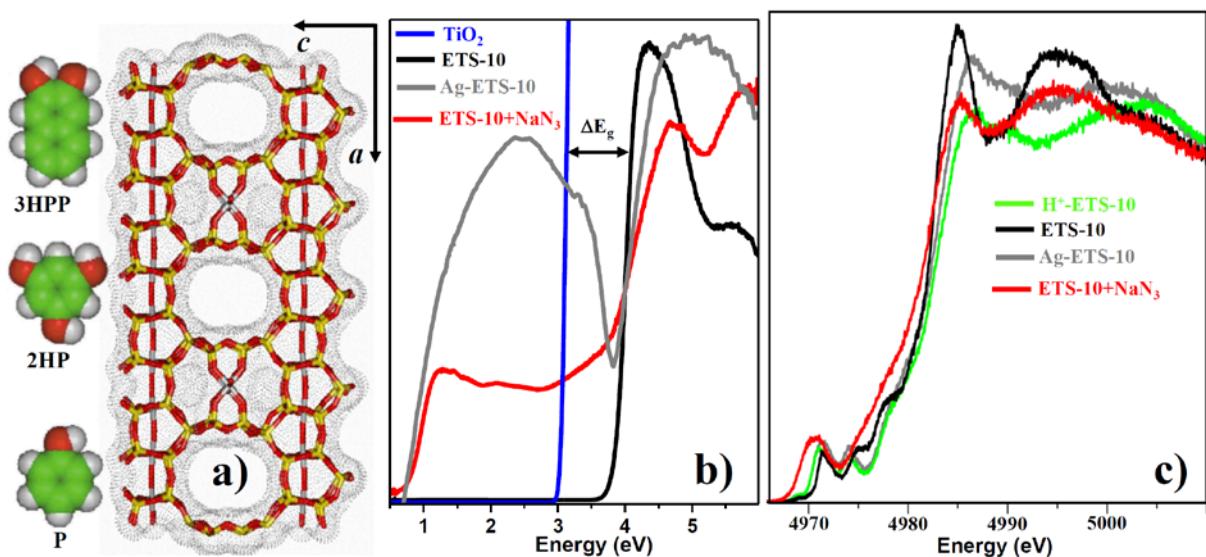


Figure 4 ETS-10. a) Sticks representation of ETS-10 structure viewed along *b* direction showing the $\text{Ti}-\text{C}-\text{O}-\text{C}-\text{Ti}-\text{C}-\text{O}-\text{C}-\text{Ti}-$ chains, running along *a* and *b* directions and the available free space in the channels running along the *b* direction is evidenced using Connolly algorithm. Ti, Si and O atoms are represented as grey, yellow and red sticks, respectively, while charge-balancing cations have been omitted for clarity. Among the three different aromatic

molecules reported on the left, only phenol (P) is able to penetrate inside the ETS-10 channels. b) UV-Vis spectrum of ETS-10 (black curve) compared with that of rutile bulk (blue curve). The shape of this spectrum reflects the DOS of the unoccupied valence states. The blue shift of the band gap (ΔE_g), with respect to bulk TiO_2 , is evidenced by the black arrow. Also reported are the spectra of the ETS-10 sample reduced with NaN_3 (red curve) and that of Ag-ETS-10 reduced in H_2 (gray curve). Previously unpublished figure reporting spectra published in Refs.^[8e,32n,67] c) HRFD Ti K-edge XANES spectra of ETS-10 and of treated ETS-10. Data collected at ESRF ID26 in collaboration with P. Glatzel and E. Gallo, reproduced with permission from Ref.^[68]

The most interesting structural peculiarity of ETS-10 consists in the presence of linear chains of TiO_6 octahedra, forming - $\text{Ti} < \text{C} > \text{O} < \text{C} > \text{Ti} < \text{C} > \text{O} < \text{C} > \text{Ti}$ - quantum wires embedded in a highly insulating SiO_2 matrix. Consequently, ETS-10 exhibits a semiconducting character, with an energy gap blue shifted by about $1^{\wedge\wedge}\text{eV}$ with respect to bulk TiO_2 due to quantum confinement effect,^[8c,8d] as confirmed by periodic one-dimensional DFT calculations.^[32n,32o] Such peculiarity makes ETS-10 a material able to photodegrade aromatic pollutants hosted at the pore opening of the particles, where surface $\text{Ti} < \text{C} > \text{OH}$ groups are present. Smaller molecules, like phenol, which are able to penetrate within the channels, are prevented from photodegradation owing to the absence of active titanol groups inside the porous system. Consequently, the combination of a microporous structure with a semiconductive electronic behavior makes ETS-10 an interesting material in the field of photocatalysis, because of its “inverse shape selectivity”.^[69] In particular, molecules of different steric hindrance like phenol (P), 1,3,5-trihydroxybenzene (3HP) and 2,3-dihydroxynaphthalene (2HPP), see Figure^{4<xfigr4>a}, are photo-degraded inside ETS-10 according to the following rate $\text{P} << \text{3HP} < \text{2HPP}$.^[69a,69c]

Nevertheless, the quantum confinement shifts the band gap in the opposite direction with respect to what is desirable to exploit a large fraction of the solar spectrum. Several routes have been exploited to overcome this drawback, such as: (i) the adsorption of selected dyes which HOMO-LUMO levels properly matching that of the - $\text{Ti} < \text{C} > \text{O} < \text{C} > \text{Ti} < \text{C} > \text{O} < \text{C} > \text{Ti}$ -semiconductor conduction band;^[69d,70] (ii) the reduction of a fraction of Ti^{4+} atoms of the chain to Ti^{3+} via reaction with NaN_3 ;^[32n] or (iii) the encapsulation of small Ag nanoparticles (NPs) inside the ETS-10 channels.^[67] By exploiting the cation exchange properties of the material,^[8d,71] Ag^+ -ETS-10 has been obtained following a two-step process: first the protonic form (H-ETS-10) has been obtained from the Engelard $\text{Na}^+ < \text{C} > \text{K}^+$ -ETS-10 by exchanging Na^+ and K^+ cations with NH_4^+ and

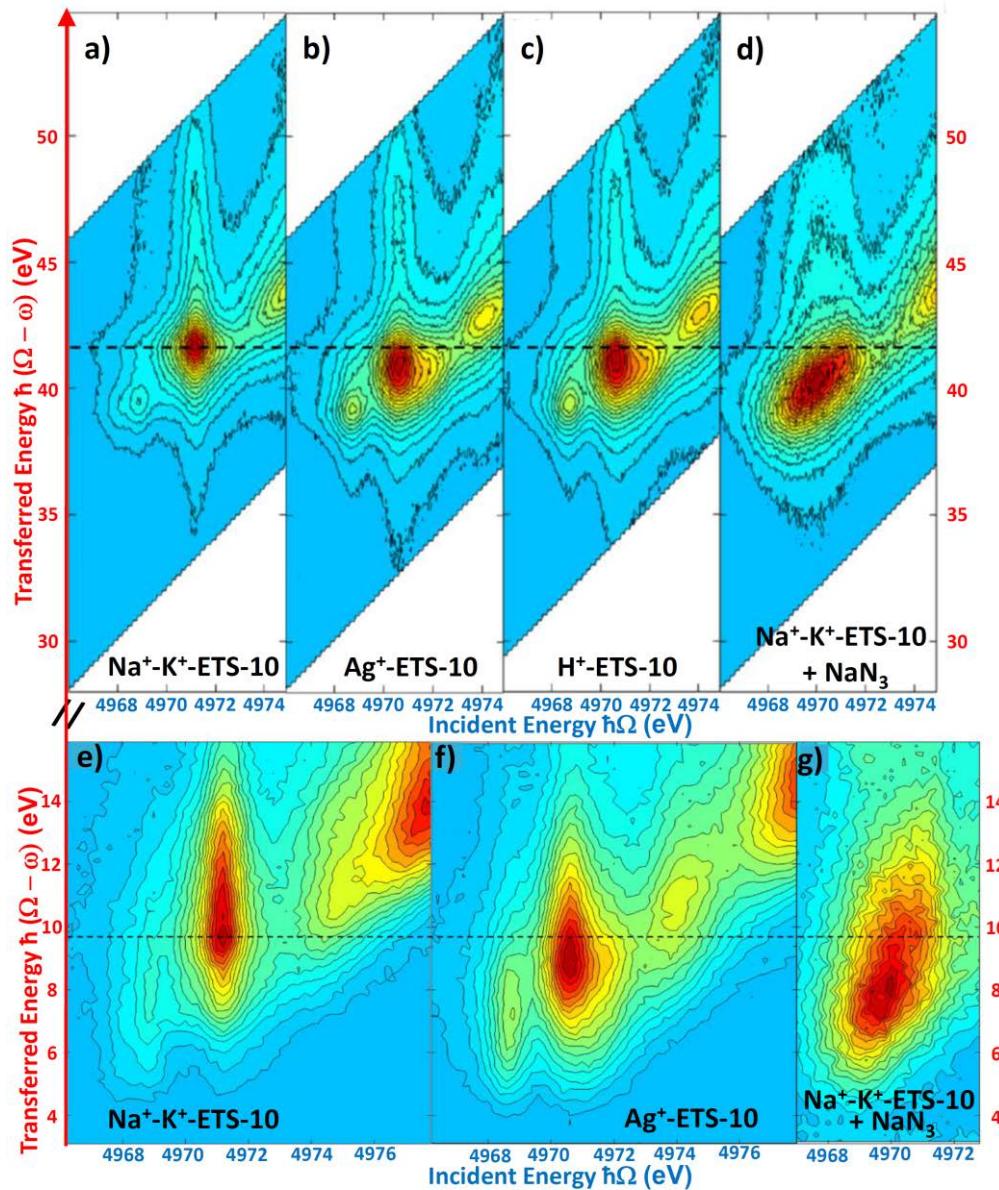
successive calcination. The obtained H⁺-ETS-10 was then impregnated with an aqueous solution of AgNO₃, resulting in Ag⁺-ETS-10.^[67] Through chemical (interaction with H₂ at increasing temperatures) and photochemical (exposure to UV-light) reactions, the Ag⁺ ions were reduced to Ag⁰, thus forming Ag nanoparticles (NPs), which size can be tuned by reverse treatments (i.e. exposure to O₂ or to visible light).^[67]

The induced modification of the electronic structure of ETS-10 by the described methods has been monitored by optical spectroscopy (Figure⁴b), high resolution fluorescence detected (HRFD) Ti K-edge XANES (Figure⁴c), by resonant core to core XES (Figure⁵a-d) and by resonant valence to core XES and (Figure⁵e-g). From these datasets, we observe that the valence band of ETS-10 varies remarkably when Ag NPs are present within the microporous channels. The same holds when interaction with NaN₃ induces reduction of a significant fraction of Ti⁴⁺ to Ti³⁺ species within ETS-10. More insights have been obtained by coupling the experimental data with DFT calculations.^[68]

The HRFD XANES spectra reported in Figure⁴c testifies that the interaction with NaN₃ causes a red shift of the edge of about 1.8 eV (evaluated at $\mu_x=0.3$, compare black and red curves), reflecting the effective reduction from Ti⁴⁺ to Ti³⁺ of a significant fraction of Ti atoms. This implies a change in the formal electronic structure of Ti from d⁰ to d¹, resulting in the promotion of an electron per reduced Ti atom in the conduction band of the <C->Ti-O<C->Ti<C->O<C->Ti- quantum wire, which is mainly given by a linear combination of Ti(3d) atomic orbitals.^[32n] This effect modifies the pre-edge features, red shifting the first one at 4970.6 eV with a significant broadening (probably due to the presence of multiple, unresolved components). An even more drastic broadening occurs in the 4975–4982 eV range, where a broad absorption overshadows any defined structure.

Summarizing, standard UV-Vis spectroscopy and advanced synchrotron radiation-based techniques have been used to testify the modification of the band gap of the <C->Ti<C->O<C->Ti<C->O<C->Ti- semiconductor chains in ETS-10 material subjected to the treatments aimed to activate photon absorption in the visible range for photocatalytic applications.

Figure⁵ RIXS maps of modified ETS-10 materials. (a-d) Experimental resonant core to core-XES maps ($3p/d \rightarrow 1s$) of $\text{Na}^+ < \text{C} > \text{K}^+$ -ETS-10, Ag^+ -ETS-10, H^+ -ETS-10 and $\text{Na}^+ < \text{C} > \text{K}^+$ -ETS-10 after interaction with sodium azide (NaN_3) reducing agent, respectively. (e-g) Resonant valence to core-XES maps of $\text{Na}^+ < \text{C} > \text{K}^+$ -ETS-10, Ag^+ -ETS-10, and $\text{Na}^+ < \text{C} > \text{K}^+$ -ETS-10 after interaction with NaN_3 . The incoming and the emitted photon of energies are represented by $\hbar\Omega$ and $\hbar\omega$, so that $\hbar(\Omega < M > \omega)$ represents the energy transfer of the two-photon process. Data collected at ESRF ID26 in collaboration with P. Glatzel and E. Gallo, reproduced with permission from Ref.^[68]



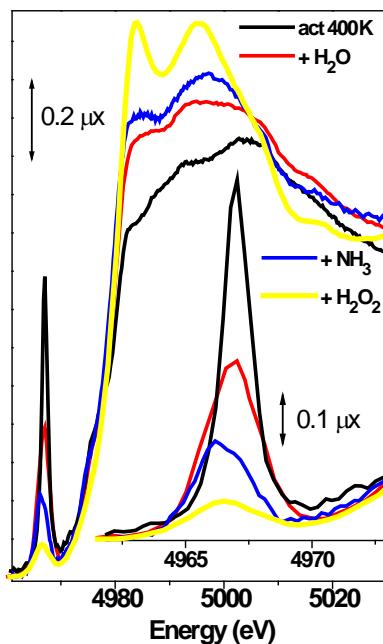
3.2. TS-1

Among Ti based catalysts, the microporous titanium silicalite-1 (TS-1) is certainly a cutting-edge material, revolutionizing the field of liquid-phase oxidation catalysis, in particular concerning epoxidation and ammoximation reactions.^[9a] In fact, TS-1 is extremely active and selective (both

values are higher than 90% at industrial conditions) in these processes and, since hydrogen peroxide (H_2O_2) is the oxidizing agent, the use of hazardous chemicals (e.g. chlorohydrin) associated to previous technologies is avoided and water is the only major reaction byproduct.^[9b]

Beside the obvious technological interest, TS-1 has stimulated academic research since its discovery due to its unique structural and spectroscopic properties. The most important feature of TS-1 is probably its ideally single-site nature: a fraction of the silicon atoms in the MFI zeolitic framework is isomorphously substituted by titanium ones, retaining the tetrahedral coordination and leading to an expansion of the crystallographic cell due to the longer $\text{Ti}-\text{C}-\text{O}$ bond distance ($\sim 1.8 \text{\AA}$)^[9d,72] with respect to the $\text{Si}-\text{C}-\text{O}$ one ($\sim 1.6 \text{\AA}$).^[73] Due to the strain induced to the framework by such expansion, the amount of Ti atoms that can be incorporated is quite limited (below 3 wt% of TiO_2 in the best materials).^[74] The difficulty in Ti incorporation often leads to the synthesis of poor quality samples containing, beside the perfect tetrahedral Ti sites, additional species ranging from extended extra-framework TiO_2 phases to low-nuclearity Ti sites, whose exact structure and properties are still object of debate.^[75]

The “academic history” of TS-1 under the experimental profile can be ideally divided in three decades since it has been discovered in the ‘80s:^[9a] (i) the assessment of the coordination geometry of perfect tetrahedral Ti;^[9d,32h,32r,72,76] (ii) the fundamental understanding of the spectroscopic properties of perfect sites, also in interaction with molecules;^[32i-l,77] and (iii) the characterization of defective Ti sites and their correlation with catalytic properties.^[75a,75c,75d,78] Our research group have actively taken part to all these steps, contributing in the elucidation of the multi-faceted nature of TS-1. Hereafter, some milestones of this path are commented.



Figure⁶ Effect of interaction with adsorbates having increasing interaction strength with Ti^{4+} sites of TS-1: H_2O (red), NH_3 (blue), and H_2O_2 (yellow). For comparison, also the spectrum of the TS-1 dehydrated at 400°K has been reported (black). Unpublished figure reporting spectra previously published in refs.^[77d,77e]

Figure⁷ RIXS maps of TS-1 catalyst exposed to different chemical environments. Parts (a--e): experimental resonant core to core-XES maps ($3\text{p}/\text{d} \rightarrow 1\text{s}$) of TS-1 activated at 400°C , after interaction with H_2O from the vapor phase, with H_2O from the liquid phase, with NH_3 from the vapor phase and with a $\text{H}_2\text{O}/\text{H}_2\text{O}_2$ liquid solution, respectively. Parts (f--i): resonant valence to core-XES maps of TS-1 activated at 400°C , after interaction with H_2O from the vapor phase, with H_2O from the liquid phase, and with NH_3 from the vapor phase, respectively. The incoming and the emitted photon energies are represented by $\hbar\Omega$ and $\hbar\omega$, so that $\hbar(\Omega < \text{M} > \omega)$ represents the energy transfer of the two-photons process. Data collected at ESRF ID26 in collaboration with P. Glatzel and E. Gallo, reproduced with permission from Ref.^[68]

Figure⁸ Relationship between the composition (i.e. fractions of perfect Ti, non-perfect Ti and anatase) of TS-1 catalysts with increasing defectivity (from A to C) and their catalytic activity (quantified as turnover number, TON, at 30^min of reaction) in HPPO process. The red diamonds highlight the perfect Ti vs TON relationship, whose almost linear trend is showed by the red dashed line. Previously unpublished figure reporting data from ref.^[75d]

Figure⁹ a) Location and relative stability of the 24 T sites as substituted by Ti. b) TS-1-NH₃ phase diagrams computed for sites T9 and T10. Previously unpublished figure reporting data from ref.^[32w]

Figure¹⁰ a) Valence to core XES spectra obtained from DFT calculations performed with various functionals (II-VIII) using clusters where Ti substitutes Al (red curves) and P (black curve) clusters; experimental valence to core XES spectrum of activated Ti-C-ALPO-5 (scattered curve). b) Black and red curves, as in part a) for the B3LYP functional; the blue curve represents the best fit to the experimental spectrum (scattered curve) obtained with linear combination of the two pure models (90 and 10% of the black and red curves). c) Representation of the calculated most important orbitals of cluster with Ti in P position, responsible for the valence to core -XES signal using the B3LYP functional. Reproduced with permission from Ref.^[32t] copyright ACS 2014.

In 1994 Bordiga *et al.* rigorously demonstrated the tetrahedral coordination of perfect Ti sites on the basis of XAS data:^[9d,72] previously published papers , in fact, could not fully exclude the presence of fractions of higher coordinated Ti centers.^[79] Bordiga and co-workers ruled out all the previous uncertainness by performing XAS on carefully synthesized samples, totally dehydrated at high temperature (“activated”) in order to eliminate all the ancillary ligands coordinated to Ti sites. As a countercheck, the activated samples were contacted with small basic molecules (i.e. NH₃) in order to simulate the status of the bare materials before the high temperature activation procedure. The XANES spectrum of the activated TS-1 exhibited a sharp pre-edge feature at 4968.9^{eV} (black spectrum in Figure⁶). This band is significantly less intense in the sample still hosting the template in the pores^[9e,80] or after interaction with adsorbates (remaining spectra in Figure⁶).^[9d,72,77a] The band is due to the 1^s→3pd electronic transition involving Ti⁴⁺ atoms in tetrahedral coordination.^[9d,72,76a,81] Conversely, the same electronic transition for Ti⁴⁺ species in TiO₂ (anatase or rutile)^[82] or in ETS-10 titanosilicate,^[66,81b,83] see Figure⁴c, where Ti⁴⁺ species are in octahedral environment, is characterized by a very low intensity due to the small pd hybridisation which occurs in octahedral symmetry. Indeed, the transitions A_{1g}→T_{2g} are symmetrically forbidden in the case of perfect octahedral coordination of Ti⁴⁺, while the transition A₁→T₂ is allowed in the case of tetrahedral coordination of Ti⁴⁺, as in the case of [TiO₄] units hosted in the dehydrated MFI framework.

Upon the dosage of ligands of increasing basic strength this signal was progressively suppressed, testifying the recovery of a more centrosymmetric coordination symmetry on Ti (Figure⁶). The EXAFS analysis fully confirmed the XANES outcomes, providing a

coordination number for the first ligands sphere of 4.4 ± 0.6 atoms, which expanded to 5.5 ± 0.6 upon re-adsorption of ligands.^[9d,72] These results have been later confirmed by more accurate XAS measurements collected in the same chemical conditions.^[77a,77b]

Figure⁷ reports the RIXS study (analogous to that reported in Figure⁵ for ETS-10) of the TS-1 catalyst in different chemical environments: activated at 400°C (parts a,f), after interaction with H_2O from the vapor phase (parts b,g), with H_2O from the liquid phase (parts c,h), with NH_3 from the vapor phase (parts d,i) and with a $\text{H}_2\text{O}/\text{H}_2\text{O}_2$ liquid solution (part e). Resonant core to core (r-ctc) and resonant valence to core (r-vtc) and XES maps are reported in Figure⁷ a--e and Figure⁷ f--i, respectively. These experimental data have been the basis of the XES studies by Gallo et al.^[32r,32s,68] While XANES spectra provide information on the unoccupied DOS,^[27,84] the RIXS spectra reported in Figure⁷ provide information on the occupied DOS^[25d,29b] that contribute in filling the 1^{s} core-hole created in Ti^{4+} upon absorption of an X-ray of sufficient energy. For the activated TS-1, three valence bands at $\hbar(\Omega < M - \omega) = 8.4^{\text{eV}}$ (strong), 10.0^{eV} (medium) and 11.5^{eV} (weak) contribute to the RIXS peak obtained exciting in the $\hbar\Omega = 4969 < M - \omega < 4971^{\text{eV}}$ region (Figure⁷ f). The interaction with adsorbates implies a significant blue shift of the transferred energy $\hbar(\Omega < M - \omega)$ in the vtc-XES (Figure⁷ g--i). The peak broadening observed in the XANES spectra upon molecular adsorption (Figure⁶) is reflected in the RIXS maps by a widening of the $\hbar\Omega$ region contributing to the r-ctc peak (Figure⁷ a--e).

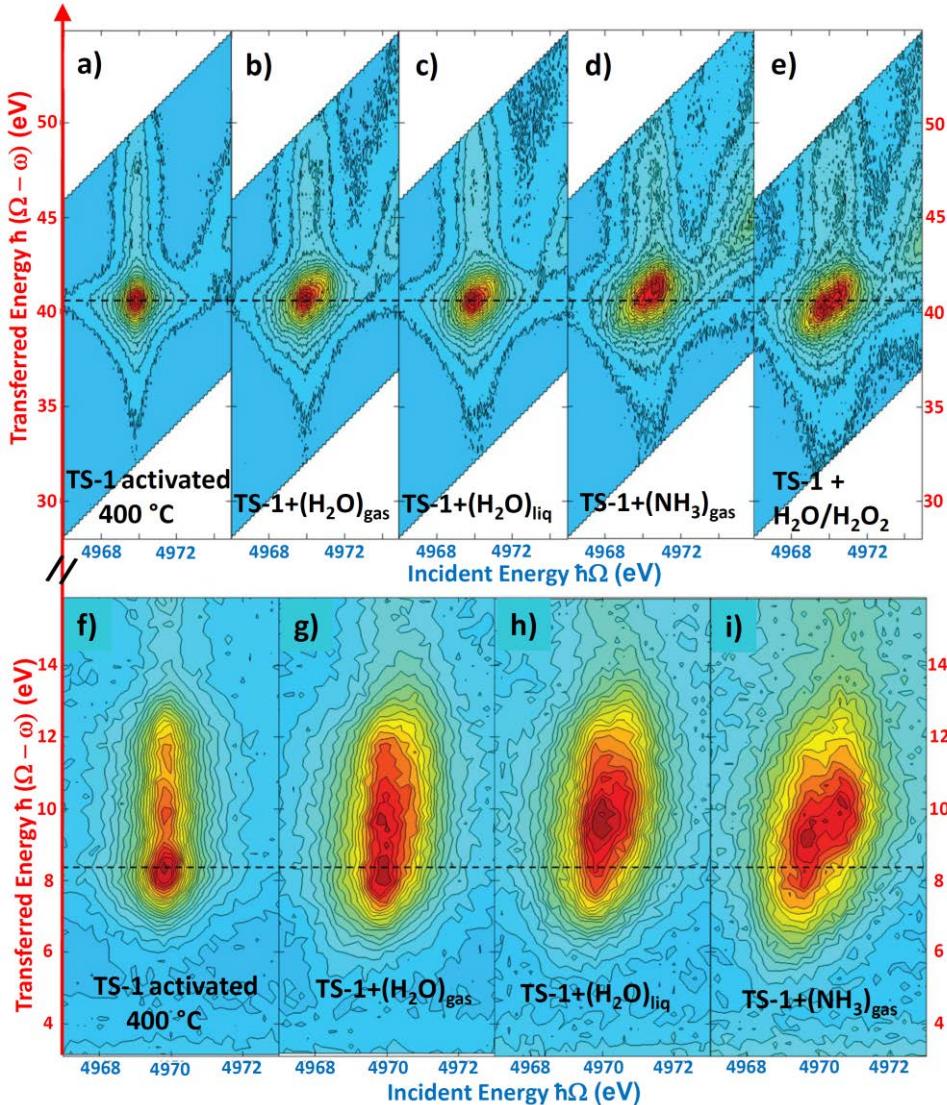


Figure 7 RIXS maps of TS-1 catalyst exposed to different chemical environments. Parts (a--e): experimental resonant core to core-XES maps ($3p/d \rightarrow 1s$) of TS-1 activated at 400°C , after interaction with H_2O from the vapor phase, with H_2O from the liquid phase, with NH_3 from the vapor phase and with a $\text{H}_2\text{O}/\text{H}_2\text{O}_2$ liquid solution, respectively. Parts (f--i): resonant valence to core-XES maps of TS-1 activated at 400°C , after interaction with H_2O from the vapor phase, with H_2O from the liquid phase, and with NH_3 from the vapor phase, respectively. The incoming and the emitted photon energies are represented by $\hbar\Omega$ and $\hbar\omega$, so that $\hbar(\Omega < M > \omega)$ represents the energy transfer of the two-photons process. Data collected at ESRF ID26 in collaboration with P. Glatzel and E. Gallo, reproduced with permission from Ref.^[68]

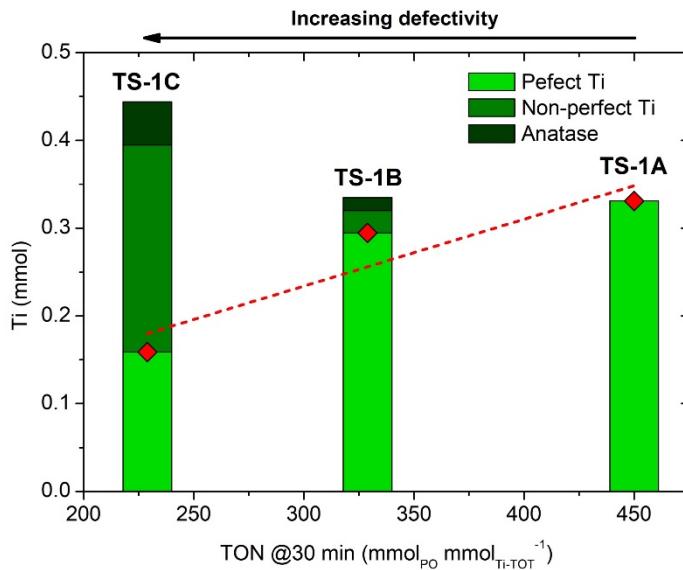
At the beginning of 2000s, our group contributed to elucidate the nature of the vibrational features typical of perfect Ti sites, as such or in interaction with H_2O_2 . Ricchiardi *et al.*^[32h] ascribed the characteristic IR and Raman features at $960^{\text{cm}^{-1}}$ and $1125^{\text{cm}^{-1}}$ to

antisymmetric and symmetric Si<C->O<C->Ti stretching modes, also inferring the physical origin of the strong resonance enhancement of the latter band, observed in the Raman spectra collected with UV excitation.^[32h,32m,85] Few years later, Bordiga *et al.* took again advantage of the resonance Raman to clarify the nature of the active sites formed upon interaction of perfect Ti with H₂O₂ molecules, identified as Ti-peroxo species on the basis of a comparison with reference compounds.^[86] In the same period, the first computational works on TS-1 relying on *ab initio* methods have been performed as well. Due to the size (288 atoms per unit cell) and complexity (at least 12 possible Ti sites per unit cell) of the real system, TS-1 has been originally modeled through cluster approaches, by using embed strategies relying on lower level calculations (molecular mechanics) to describe the zeolite framework or by choosing simplified model systems (e.g. Ti chabazite).^[32c,32g-j,87] Even though these studies have properly described the structural and vibrational features of the perfect Ti sites, the limitations ascribed to these simplified models have not allowed them to be fully validated, e.g. on the basis of adsorption energetics.

Recently, our investigation on TS-1 catalysts continued, aiming to elucidate the role of non-perfect Ti sites in the overall reactivity (with particular regard to the hydrogen peroxide to propylene oxide process, HPPO). The complexity of this task can be easily perceived referring to the recent literature on this topic:^[75a,75c,75d,78] several types of non-perfect Ti sites have been identified from their spectroscopic fingerprints, however without giving a definitive proof on their structures. Furthermore, there is not a general agreement on the effect (incremental or detrimental) of non-perfect species on catalytic performances.

In our last work, non-perfect species have been proposed as inactive toward H₂O₂ conversion, whereas their effect on selectivity cannot be fully clarified.^[75d] In order to give a rigorous demonstration, a wide spectroscopic characterization (including UV-Vis, FTIR, Raman and XANES spectroscopies) has been performed over a set of TS-1 with increasing defectivity, also quantifying the species belonging to the main Ti families. In detail, some peculiar signals of perfect Ti (the IR band at 960^{cm}⁻¹,^[9a,32h] semi-quantitatively confirmed by Ti K-edge XANES pre-edge feature as well)^[75d,84c] and bulk titania (the anatase Raman peak at 144^{cm}⁻¹)^[88] have been exploited to quantify these phases, also by taking advantage of a set of materials synthesized ad hoc for the sake of calibration. Being known the total amount of Ti from elemental analysis, the fraction

of non-perfect Ti (i.e. different from perfect and anatase species) has been obtained by difference. These data have been compared with the catalytic activity exhibited by the materials in HPPO reaction, showing a closely straight relationship between the concentration of perfect Ti in the sample and the catalyst activity (expressed as turnover number for the propene oxide formation at 30^{min} of reaction). A summary of the results is given in Figure⁸.



Figure⁸ Relationship between the composition (i.e. fractions of perfect Ti, non-perfect Ti and anatase) of TS-1 catalysts with increasing defectivity (from A to C) and their catalytic activity (quantified as turnover number, TON, at 30^{min} of reaction) in HPPO process. The red diamonds highlight the perfect Ti vs TON relationship, whose almost linear trend is showed by the red dashed line. Previously unpublished figure reporting data from ref.^[75d]

No correlation was instead found among the amounts of non-perfect Ti/anatase, suggesting these species do not have a direct impact on the catalyst activity.

Beside the experimental work, we focused our research activities on the improvement of the existing models and methods for the computational description of TS-1. First, methodological aspects concerning the modeling of adsorption in Ti-zeolites have been dealt with: the previous literature, regardless the models and methods adopted, usually reported interaction energies among Ti and small molecules (like NH₃ and H₂O) about 50% lower than experimental values.^[32d,32j,32l] A preliminary study has been performed to address this issue, exploiting a Ti-chabazite as simplified model system.^[32v] With respect to the past, dispersive forces have been included according to two different strategies: (i) through the Grimme D2 scheme,^[89] and (ii) through a cluster-periodic

ONIOM scheme, exploiting post Hartree-Fock methods (complete basis set MP2 and CCSD(T)) in the description of the model region. This work demonstrated that dispersive forces fill the gap between simulated and experimental interaction energies, independently from the way they are introduced in the calculation. Thus, Grimme D2 scheme has been showed to be the most suitable strategy, since it can be directly applied to a periodic model at a negligible computational cost.

Exploiting the methodological insights from the latter work, the problem to properly represent TS-1 has been pursued.^[32w] The natural way to simulate TS-1 is a periodic approach, taking advantage of the crystalline structure of the MFI framework. A relevant point is then to determine the number of the possible symmetry independent substitutional sites for Ti: in previous literature works, the *Pnma* space group has been considered for MFI, thereby requiring a screening over 12 tetrahedral (T) sites.^[32p,32q,32u] However, since single substitution are considered (resulting in a Si/Ti=95), the system should be more appropriately treated under the lower symmetry *P2₁n* group, in agreement with the experimental diffraction data on low Ti-loading materials,^[74a] but doubling the number of possible substitutional positions.^[90] Another critical point in the description of the MFI framework is its superior flexibility, generating a complex potential energy surface (PES) to be explored during geometry relaxation, having as a major risk to stick in local minima rather than in the desired absolute minimum. In order to reduce the impact of this drawback, the PES has been explored starting the geometry optimizations from different structural guesses, thus allowing different minima regions to be accessed. Choosing the most stable minimum for each T site, a safer energy ranking for substitution has been obtained (see Figure⁹<figr9>).

From this energetic screening, the occupancy of each T site has been estimated through the Boltzmann distribution: it resulted that only seven T sites accounts for more of the 99% of the ones substituted by Ti, with a strong preference toward sites T10 (33%), T9 (31%) and T15 (18%). Since their expected abundance, the last three have been exploited in the simulation of NH₃ adsorption, in order to validate the model. Depending on the sites, a slight heterogeneity in the computed ΔH values for adsorption has been estimated (ranging between <M->65 and <M->85^{kJ^{M->1}}), however compatibly with the experimental observations.^[77a,77b] Interestingly, a site-dependent behavior of the adsorption ΔG has been observed in the case of a second adsorbed NH₃ molecule (see Figure⁹<xfigr9>b). Single adsorption is in fact strongly favored at site T10 in

the T - p range of usual experimental conditions. Instead, site T9 favors double adsorption, where the TS-1 adduct with a single NH_3 molecule is stable only in a narrow range of T - p . Other sites (e.g. T15) shows intermediate behaviors, where the presence of single or double adducts is conditioned by T - p . These results support, for the first time, the findings from Gallo et al. concerning RIXS analysis of TS-1 (see Figure 7),^[32s] which exhibited a preferential 5-fold coordination of Ti upon NH_3 adsorption, as small variations of T and/or p (eventually induced by the measurement itself) can lead to a change in the coordination sphere of Ti.

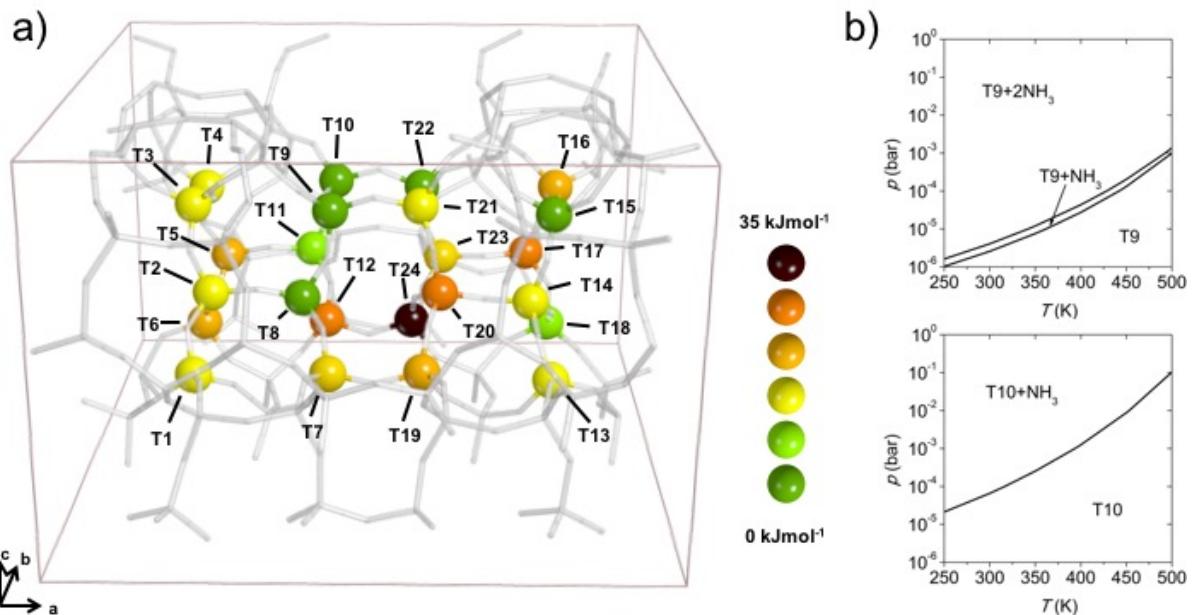


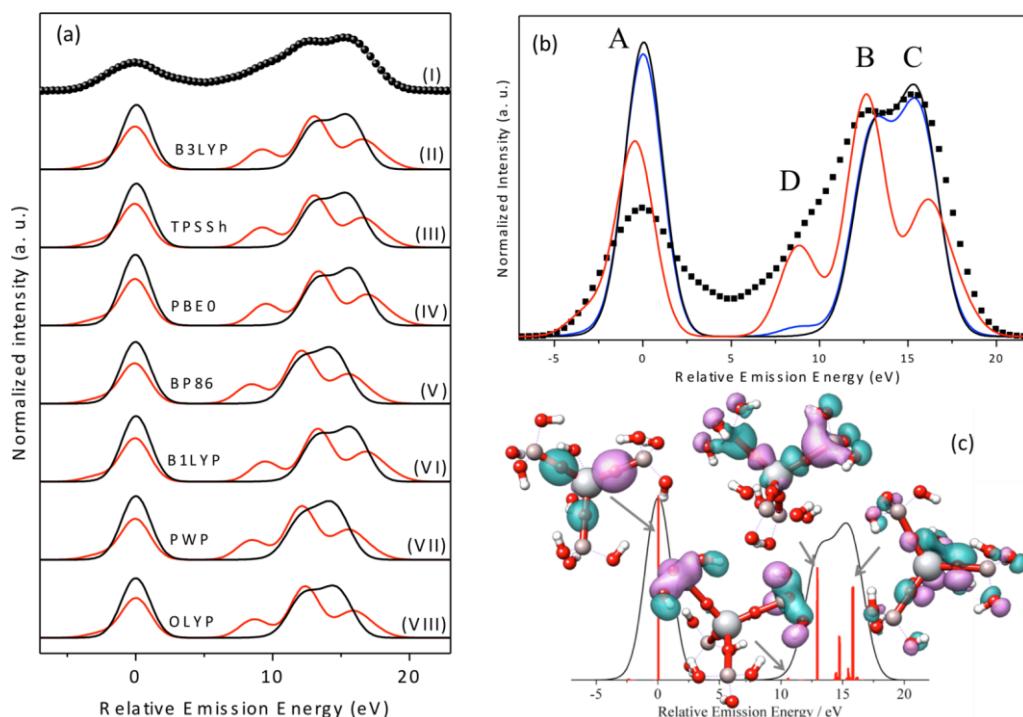
Figure 9 a) Location and relative stability of the 24 T sites as substituted by Ti. b) TS-1-NH₃ phase diagrams computed for sites T9 and T10. Previously unpublished figure reporting data from ref.^[32w]

3.3. Ti-C->AlPO

Starting from the pioneering works from the Flanigen group^[91] concerning the synthesis of heteroatom-containing aluminophosphate molecular sieves, it was evident that many topological structures typical of zeolitic materials can be achieved with strictly alternating Al and P tetrahedral framework sites, resulting in the development of a variety of AlPO and SAPO structures doped with transition metal^[16c,92] or Si ions,^[16c,93] respectively.

This short, last, section is devoted to show the ability of valence to core XES spectroscopy to discriminate ligands (even in the second shell) characterized by similar Z numbers. This

peculiarity represents an important advantage of XES spectroscopy^[28,29,30b,32r,68,94] with respect to the other X-ray based techniques such as XRD, EXAFS and XANES. Gallo et^{al.}^[32t] used valence to core XES spectroscopy, supported by DFT calculations, to prove that then insertion of Ti atoms in the AlPO-5 framework mainly occurs at the P position with a smaller fraction substituting Al (10%), see Figure¹⁰<figr10>.



Figure¹⁰ a) Valence to core XES spectra obtained from DFT calculations performed with various functionals (II–VIII) using clusters where Ti substitutes Al (red curves) and P (black curve) clusters; experimental valence to core XES spectrum of activated Ti-<C->AlPO-5 (scattered curve). b) Black and red curves, as in part a) for the B3LYP functional; the blue curve represents the best fit to the experimental spectrum (scattered curve) obtained with linear combination of the two pure models (90 and 10% of the black and red curves). c) Representation of the calculated most important orbitals of cluster with Ti in P position, responsible for the valence to core -XES signal using the B3LYP functional. Reproduced with permission from Ref.,^[32t] copyright ACS 2014.

4. Summary and Outlook

This review shows how cutting-edge synchrotron radiation spectroscopies such as extended X-ray absorption spectroscopy (EXAFS) X-ray absorption near edge structure (XANES), high

resolution fluorescence detected (HRFD) XANES, emission spectroscopy (XES) and resonant inelastic X-ray scattering (RIXS) have significantly contributed to the structural and electronic characterization of Ti-based catalysts and photocatalysts representing an important additional value with respect to standard laboratories spectroscopies (UV-Vis, IR, Raman, EPR, NMR etc.). Selected examples are representative of the authors research activity in the last two decades and cover both TiO_2 nanomaterials and microporous titanosilicates (ETS-10, TS-1 and $\text{Ti} < \text{C} > \text{AlPO-5}$). Parallel computational studies, which facilitated the interpretation and rationalization of experimental findings, have been also discussed.

In the next future, we foresee that a new class of Ti-based catalyst and photocatalyst will emerge: Ti-metal-organic frameworks (MOFs).^[95] Indeed chemical and photo reactivities of MOFs can be optimized by exploiting their outstanding structural tunability (linkers, cornerstones and their possible functionalization)^[96] combined with the possibility of semiconductors or metal nanoparticles loading inside their cavities. The first exciting examples are already present in the recent literature, such as: NH_2 -functionalized Ti-MIL-125;^[97] the photovoltaic cell realized by the Garcia group^[98] using $\text{NH}_2\text{-UiO-66(Zr/Ti)}$ MOF where the standard UiO-66(Zr) ^[99] has been functionalized acting on both the linker and the inorganic cornerstone; the Ti-NTU-9 which displayed strong absorption in the visible region at 1.72 eV;^[100] MOF-901^[101] and MOF-902,^[102] both active in the photocatalyzed polymerization of methyl methacrylate; .

Acknowledgements

Several colleagues have been involved in the results here reviewed, among them: S. Bordiga, M. Chiesa, A.M. Ferrari, E. Giamello, G. Martra, G. Spoto, A. Zecchina (University of Turin) for the studies on TiO_2 ; G. Agostini, S. Bordiga, P. Calza, F. Llabres i Xamena, E. Pelizzetti, C. Prestipino, A. Zecchina, (University of Turin) and E. Gallo and P. Glatzel (ESRF, Grenoble) for the studies on ETS-10; G. Belussi, A. Carati, M.G. Clerici, G. Leofanti, G. L. Marra, M. Padovan, G. Petrini, M. Ricci, G. Spanò, (EniChem), E. Gallo and P. Glatzel (ESRF, Grenoble), and S. Bordiga, F. Bonino, A. Damin, A. Zecchina, (University of Turin) for the studies on TS-1; G. Berlier (University of Turin), E. Gallo, P. Glatzel, O. Mathon and S. Pasquarelli (ESRF, Grenoble) and A. Piovano (ILL, Grenoble) for the studies on TiAlPO. All reported affiliations refer to the time period when the collaboration occurred. The authors thank Evonik Resource Efficiency for the lively support to our recent research on TS-1 and for having provided the samples related to Figure 8. CL acknowledges the Mega-grant of the Russian Federation Government to support scientific research at the Southern Federal University, No. 14.Y26.31.0001.

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