On the Redox Mechanism Operating along C2H2 Self-Assembly at the Surface of TiO2

(Article begins on next page)

01 May 2024

UNIVERSITÀ DEGLI STUDI DI TORINO

On the redox mechanism operating along C_2H_2 self-assembly at the surface of TiO_2.

Jakub Jan Biedrzycki[a], Stefano Livraghi[*,a], Ingrid Corazzari[a,b], Lorenzo Mino[a], Giuseppe Spoto[a],

Elio Giamello[a].

a) Dipartimento di Chimica, Università di Torino and NIS, Centre for Nanostructured Interfaces and Surface , Via P. Giuria 7, I - 10125 Torino, Italy

b) "G. Scansetti" Interdepartmental Centre for Studies on Asbestos and Other Toxic Particulates, Via P. Giuria 7, I - 10125 Torino, Italy

ABSTRACT: The interaction of acetylene with the TiO_2 surface at room temperature entails a complex set of self-assembly reactions with the formation of products having relatively high molecular weight. In a previous paper by some of us (S. M. Jain et *al*. *J. Mater. Chem. A* **2014**, 2, 12247-12254) the C_2H_2-TiO_2 reaction has been monitored, essentially by Fourier Transform Infrared Spectroscopy (FTIR), at the surface of P25 (a mixture of anatase and rutile, typical benchmark material in the field of photocatalysis) in order to elucidate the nature of the products of this surface reaction. In the present paper the same process was followed, for the first time, using Electron Paramagnetic Resonance (EPR) and monitoring by the Thermogravimetric Analysis (TGA) the weight loss of the material upon heating in order to further investigate the complex mechanism of the surface reaction. This was done using pure anatase and comparing

the EPR results with those concerning both rutile and P25. The self assembly mechanism occurring at the interface is accompanied by the formation of EPR visible Ti^{3+} centres due to electrons injection in the TiO_2 substrate. This finding clarifies that at least one of the reaction channels of this complex process (namely the formation of polycyclic aromatic hydrocarbons) is based on the heterolytic dissociative chemisorption of acetylene followed by a redox interaction between the adsorbate and the solid which allows the creation of the building blocks necessary to assembly polyaromatic molecules.

1. Introduction.

Titanium dioxide is one of the most investigated metal oxides.[1,2] This solid has numerous conventional uses as a white pigment in paintings, paper, and plastics, however, the most stimulating applications of TiO_2 which are currently the object of an intense research activity , are strictly related to its photochemical properties.

Titanium dioxide is an essential component for instance, of systems for the photocatalytic remediation of polluted environments or of devices for water photosplitting [3,4]. The photoinduced charge separation (which is the starting step of the mentioned applications) requires, in the case of bare TiO_2, the use of UV light to overcome the relatively high band gap value of the oxide (around 3 eV).[5] However, visible light can also be harvested in the case of suitably modified TiO_2 based materials[6,7]. In order to induce the photoactivity of titania under visible light, different strategies have been proposed. These range from doping (either with metal[8] or non-metal dopants[9]) to the surface modification obtained by anchoring to the surface dye molecules[10], quantum dots[11] or metal nanoparticles showing surface plasmonic resonance.[12]

Another approach to the surface modification of titania is based on the interaction of organic compounds with the surface of this material. Recently, for instance, D. Mitoraj *et al.* have found that the calcination of TiO_2 in presence of urea led to polycondensation processes with the formation, at the surface, of hetero-aromatic polycyclic compounds[13,14].

Among the organic compounds, whose interaction with the titania surface has been investigated in the past, an important class is represented by alkynes and in particular acetylene.

The removal of acetylene traces in ethylene feed stream via selective hydrogenation is vital for the commercial production of polyethylene since acetylene acts as a poison for the polymerization catalysts. For this reason several studies are focused on C_2H_2 hydrogenation process over metal-loaded and unloaded TiO_2.[15,16]

One of the most interesting reactions involving alkynes on the surface of different oxides, and in particular of TiO_2, involves the self-assembly of the monomers with formation of more complex organic molecules.[17-24] R. Rives-Arnau and N. Sheppard for instance reported the generation of trans-polyacetylene generation by polymerization of acetylene at room temperature on a highly dehydroxylated surface of rutile.[17] Later, K.G. Pierce and M.A. Barteau thoroughly investigated the cyclotrimerization of alkynes to aromatic compounds on reduced TiO_2. This process was observed for a number of alkynes and in all cases it was ascribed to the presence of reduced states like Ti^{2+} in the solid.[19,21,23]

Recently, some of us have reported a FT-IR characterization of the oligomerization processes due to the interaction of acetylene with the surface of P25-TiO_2 (a material produced by pyrolysis of $TiCl_4$ and composed by both anatase and rutile, the main polymorphs of titania) which causes the onset of a remarkable absorption of visible radiation.[24] In that study it has been evidenced the formation, upon simple heating at 373K, of a complex set of products ranging from benzene (derived by acetylene cyclotrimerization) to more complex polyaromatic products. Sensitivity to visible light is not the only possible goal of the C_2H_2-TiO_2 interaction. The large polyaromatic molecules which form at the surface could represent, in fact, a step towards the formation of a graphene layer. The numerous studies aiming to combine titanium dioxide and graphene in order to improve the conduction properties of the TiO_2 matrix witness the interest of the scientific community for such issue.[25,26,27]

In the present work the C_2H_2-TiO_2 interaction has been followed in mild conditions (room temperature) using for the first time Electron Paramagnetic Resonance (EPR) and Thermogravimetric Analysis (TGA) in order to describe the early stages of the interaction and to clarify the details of the reaction mechanisms operating at the surface. A detailed knowledge of the various aspects of this complex process is in fact of vital importance to tailor well defined and more efficient Carbon-TiO_2 composite systems for applications involving the optical and/or the electronic properties of the solid.[28] Our approach, aiming to control the different steps of the

C_2H_2-titania interaction is somehow different from that followed in many cases of simple carbon doping of the same matrix[29].

2. Experimental.

In this work, three different types of TiO_2 were used. The first one was the commercial Aeroxide P25 from Evonik (Essen, Germany), which is considered a benchmark in the fields of photocatalysis and photovoltaics owing to its outstanding activity (here after P25). P25 is prepared by flame pyrolysis of $TiCl_4$ and contains a mixture of about 75 – 85% anatase and 15 – 20% rutile, but also some amorphous part.[30] The P25 surface area is ca. 60 m^2/g.

The second sample was a 100% anatase (hereafter anatase) with a surface area of ca. 70m^2/g obtained via sol-gel synthesis by reaction of a titanium(IV) isopropoxide ($Ti(OC_3H_7)_4$) solution in 2-propanol (molar ratio 1:4) with water (molar ratio between alcohol and water 1:10) performed under constant stirring at room temperature. The gel so obtained was aged overnight at room temperature to ensure the conclusion of the hydrolysis and was subsequently dried at 343 K. Finally the dried material was calcined at 773 K in air (heating rate 10 K/min) for 1 h in order to obtain a well crystallized and fully oxidized material.

The third sample was a commercial micro-rutile (hereafter rutile) from Sigma Aldrich (Saint Louis, MO, USA) containing about 5% of anatase with a surface area of ca. 2 m^2/g.[31]

In some cases (specified in the text with the label "non activated samples") the three above mentioned materials were employed in as-prepared form i.e. without any activation process.

In most of the spectroscopic experiments, the TiO_2 samples were activated following a standard procedure. First, they were outgassed under high vacuum (residual pressure $< 10^{-4}$ mbar) at 673 K for 2 hours in order to remove adsorbed water, surface hydroxyl groups, and other surface impurities. Then, oxidation with 20 mbar of O_2 at the same temperature was performed for 1 h to obtain a fully oxidized, stoichiometric oxide. Next, the samples were cooled down to room temperature in O_2 atmosphere and the gas phase was eventually removed at this temperature by pumping off. Samples prepared by this standard procedure will be indicated in the text as "activated".

All the above treatments were performed in the same cells used for the spectroscopic measurements and allowing dosage of acetylene in the gas phase. Before use, acetylene (C_2H_2)

4

was distilled by repeated freeze/thaw cycles to avoid presence of any gaseous impurities. A typical experiment consisted in a dosage at room temperature of 120 mbar of C_2H_2 on the activated samples.

In the case of the pure anatase, the surface reaction with propyne (C_3H_4) was also tested in order to understand if a modification of the chemical nature of the adsorbed alkyne species can affect the observed processes.

EPR spectra were recorded by a Continuous Wave X-band Brucker EMX spectrometer equipped with cylindrical cavity and operating at a 100 kHz filed modulation. The measurements were carried out at room temperature (RT) and liquid nitrogen temperature (77 K) in cells that can be connected to a conventional high-vacuum apparatus (residual pressure $< 10^{-4}$ mbar). Since no significant EPR signals were observed at RT only spectra recorded at 77K will be reported in the following. The integration and handling of spectra have been carried out by Win-EPR software.

Infrared spectra were recorded on a Bruker IFS 66 FTIR spectrometer equipped with an MCT cryogenic detector; 64 interferograms (recorded at 2 cm^{-1} resolution) were typically averaged for each spectrum. The samples were inspected in the form thin self-supported pellets.

Diffuse reflectance UV-visible spectra (DR-UV-Vis.) were recorded on a Cary 5000 Varian spectrophotometer equipped with a reflectance sphere on thick self-supported pellets.

Thermal gravimetric analysis and evolved volatile analysis (TGA-FTIR) experiments were carried out by an on-line Thermal Gravimetric Analysis coupled with Fourier Transform Infrared instrument from Perkin-Elmer (Waltham, MA, USA) which were used to simultaneously analyse the weight loss of the powders and the nature of the molecules released by the samples upon heating. For the TGA analysis, the ultra-microbalance Pyris 1 from Perkin-Elmer (sensitivity 0.1 µg) was used. The materials were heated under O_2 flow (35 cm^3/min) at a heating rate of 25 K/min in the 298 – 1023 K range. A relatively large amount of sample (ca. 20 mg) was tested in each run to optimize the amount of gases released. Gas phase FTIR analysis of the evolved gas was carried out by a Spectrum 100 (Perkin-Elmer) spectrometer in the 600 cm^{-1} – 4000 cm^{-1} range. Temperature-resolved infrared profiles of each moiety desorbed during the heating ramp were obtained from the intensity of a representative peak of the investigated species and normalized to the amount of sample (mg).

3. Results.

As mentioned in the introduction a detailed FTIR study of the interaction of acetylene with the surface of a commercial TiO_2 sample (P25) has been recently reported which puts into evidence that various reaction products, are generated by surface assisted self-assembly processes.[24]
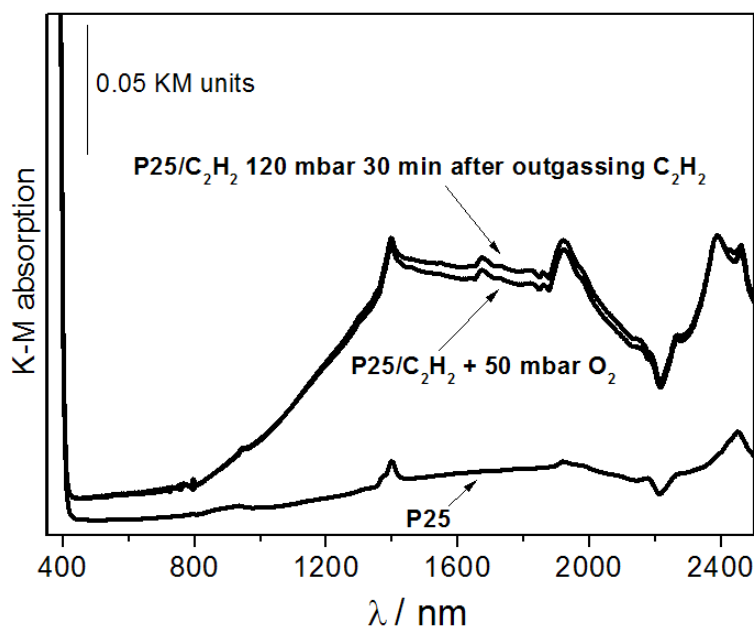

Figure 1: DR-UV-Vis spectra of activated P25 before (a) and after (b) adsorption of C_2H_2 (120 mbar) and successive outgassing of the excess gas phase. The third curve (c) reports the effect of successive O_2 absorption (50mbar).

The process shown in Fig. 1 also modify the optical properties of the activated oxide (activated P25). Upon contacting the surface with 120 mbar of acetylene at room temperature, a slow change of colour from white to light gray is observed which remains unchanged after excess C_2H_2 removal and also after contact with oxygen (curve c). This indicates that upon interaction at room temperature an irreversible modification of the system occurs due to the formation of new stable compounds strongly bound at the TiO_2 surface. These surface compounds are indeed responsible for the complex absorption, ranging from the visible region to the near infra red (NIR) one, that appears beside the typical absorption in the UV region (ca. 400 nm) due to the band gap transition of the oxide (Fig. 1). Similar colour modifications of the solid, upon C_2H_2

6

absorption, have been already reported by other Authors for various substrates such as TiO_2 (rutile) or Al_2O_3. In all these cases the colour change was explained in terms of the formation of self-assembly products of the acetylene molecule.[17,32]

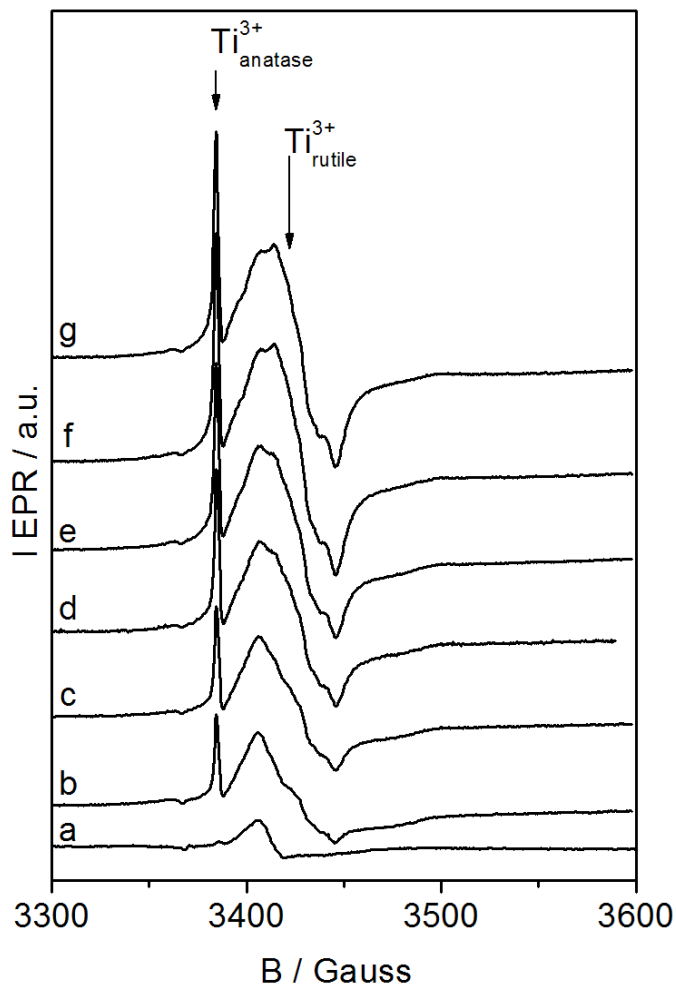### 3.1. Ti^{3+} generation in titania upon interaction with acetylene.

Figure 2: Evolution of EPR spectra of activated TiO_2-P25 contacted with C_2H_2. a) Background; from b) to g) after contact with acetylene for: b) 1.5h, c) 3h, d) 5h, e) 6h, f) 7h, g) 8h. The arrows indicate the EPR features of Ti^{3+} corresponding to the polymorphs constituting P25.

The interaction of acetylene with activated TiO_2 does not only entail a complex surface chemistry (*vide infra*), but involves also the solid with the formation of paramagnetic Ti^{3+} centres as shown by the EPR spectra reported in Fig. 2. The background spectrum of activated P25 (Fig. 2a) presents a weak signal centred at about g= 1.979 due to residual Ti^{3+} centres

7

located in the rutile component which is typical of this material[33] The contact with acetylene causes the appearance of a structured spectrum in the same region (Ti^{3+} resonance, Fig. 2b) which grows with time maintaining the initial profile (Fig. 2c-g). This is based (see below in this Section) on the simultaneous presence of Ti^{3+} centres in both anatase and rutile components of P25.[34-41] Fig 4A monitors the intensity increase of the EPR spectrum during the first 5 hours of contact.

3.2   Comparison of C_2H_2 absorption on different TiO_2 substrates monitored via EPR.

To better discriminate between the contributions of the two polymorphs which compose P25 to the observed EPR signal, the experiment in Fig. 2 was repeated using activated samples of bare anatase and rutile respectively. At variance of P25, in both single phases, no EPR signal is present before C_2H_2 adsorption. After contact with the gas, in both samples an EPR spectrum amenable to Ti^{3+} is given rise. In the case of rutile the EPR spectrum (Fig. 3a) is characterized by a signal having the main **g** components at g_1=1.966 and g_2= 1.948 while in the case of anatase the EPR spectrum is more complex due to the superimposition of two distinct Ti^{3+} signals (Fig. 3b). The first one shows an axial structure characterized by $g_\perp$=1.992, $g_{//}$=1.962 while the second is a broad and featureless signal centred at g=1.93. A previous investigation by some of us[34] has conclusively shown that the former signal (axial) corresponds to Ti^{3+} centres in the regular lattice position of anatase while the second one (broad) is due again to Ti^{3+} which are located at the disordered surface of the nanocrystals. In the case of P25 contacted with C_2H_2, the resulting signal (Fig. 2, Fig. 3c) is due to the superimposition of the signals observed for the pure rutile and anatase phases (Fig. 3a and b respectively). A quantitative comparison of the EPR intensities (calculated by double integration of the spectra) recorded monitoring the acetylene reaction with P25 and with anatase as a function of time is shown in Figure 4 (panels A and B respectively). The figure also reports data obtained using non activated materials (indicated by a square, ■) in order to evaluate the influence of surface hydroxylation on the observed phenomena. Additionally, data obtained adsorbing propyne (i.e. methyl acetylene) are also reported in Fig. 4B. These were performed in order to verify whether the methyl group substitution at one of the carbon atoms, introducing a steric hindrance and reducing the acidity of the alkyne, affects the whole oligomerization process and the formation of Ti reduced centres. The data reported in Fig. 4 are normalized on the specific surface area of each sample.
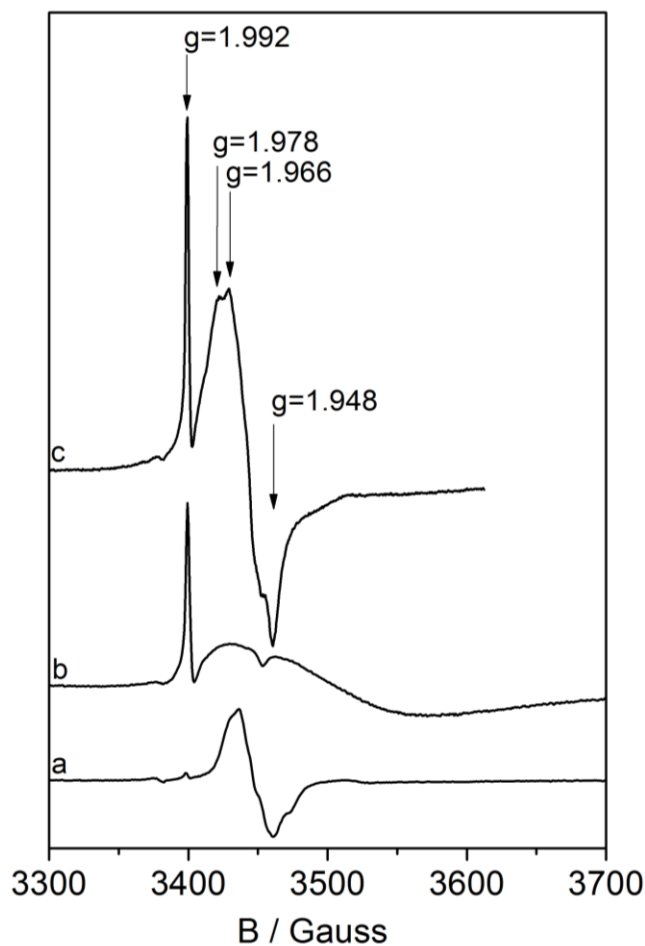
Figure 3: EPR spectra of Ti^{3+} centre generated via C_2H_2 interaction with the surface of TiO_2. a) Rutile b) Anatase and c) P25.

Data reported in Figure 4 and recorded using non activated samples show that for both anatase and P25, the reactivity of the alkynes with this kind of material is quite poor. In both cases in fact no appreciable change of the samples coloration occurs and only a very tiny increment of the Ti^{3+} centre is observed, also after several hours of interaction. Both these evidences indicate that the surface reaction between alkynes and TiO_2 requires a clean, fully activated surface (i.e. a surface containing Ti^{4+} and O^{2-} ions rather than contaminants such as water, carbonates or hydroxyl groups). The activation procedure adopted in this work and described in Section 2, in fact completely removes physisorbed water molecules and the majority of surface hydroxyl groups[42]. The reactivity of the activated samples is much higher and is observed in terms of both

9

the colour and the intensity of the Ti^{3+} EPR signal (Fig. 4). These two parameters, furthermore, grows faster in the case of anatase than in that of P25.

In the case of reaction of propyne with anatase only a slight change of the solid colour is observed and the intensity of the EPR spectra remains constantly lower (about one third) than that observed in the case of acetylene absorption. The presence of a methyl group bound to the acetylenic carbon atom limits therefore the reactivity of the molecule at the surface.
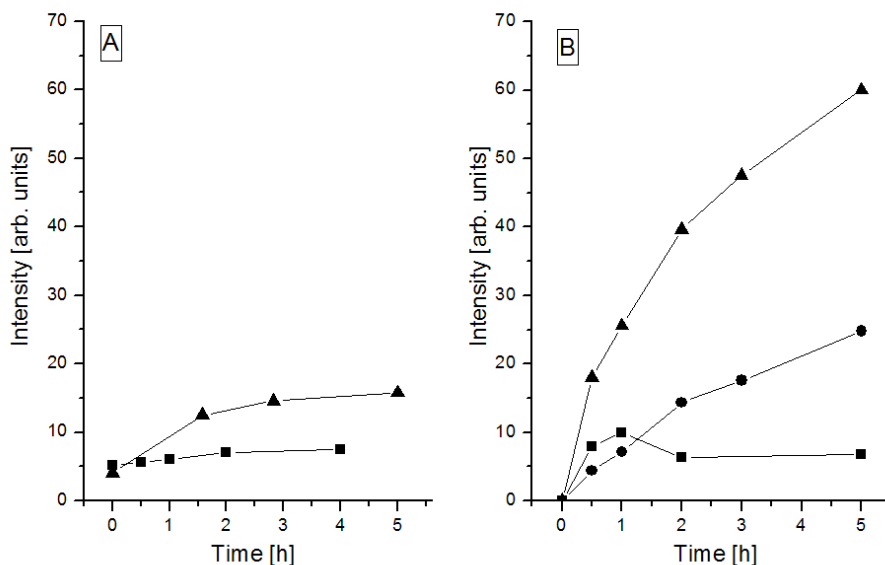

Figure 4: Integrated EPR signals of P25 (Panel A) and anatase (Panel B) TiO_2. Acetylene adsorbed on non activated TiO_2 (squares), acetylene adsorbed on activated TiO_2 (triangles), and propyne adsorbed on activated TiO_2 (circles). The curves were normalized to the surface area of the material

3.3.1 C_2H_2 -Anatase interaction monitored via FTIR

Considering that the most reactive system in quantitative terms seems to be anatase (Fig. 4), the interaction of acetylene with this material was also followed via FTIR spectroscopy (Fig. 6). After the activation process and before the C_2H_2 absorption, the FTIR spectrum is basically composed by a series of quite narrow peaks between 3770-3600 cm^{-1} due to residual isolated surface OH groups. Immediately after the dosage of 120 mbar of gas, a broad absorption between 3800-2800 cm^{-1} grows and simultaneously two new sharp bands appear. The former one at 3214 cm^{-1} is due to the ($\equiv$CH) modes of acetylene (and can be considered as the finger print of this molecule) while the second one at 1695cm^{-1}, is compatible with the formation of C=C double bonds indicating that, after the absorption, C_2H_2 started a saturation processes. A further

evolution of the spectrum is observed increasing the TiO$_2$-acetylene contact time. More in detail the broad band between 3800-2800 cm^{-1} becomes more intense and new signals appear in the 1670-1590cm^{-1} spectral region, associated with the formation of conjugated double bonds[24]. In parallel the vibrational modes in the range 2980-2935cm^{-1} due to saturated C-H (CH$_2$, -CH$_3$) species appears also.
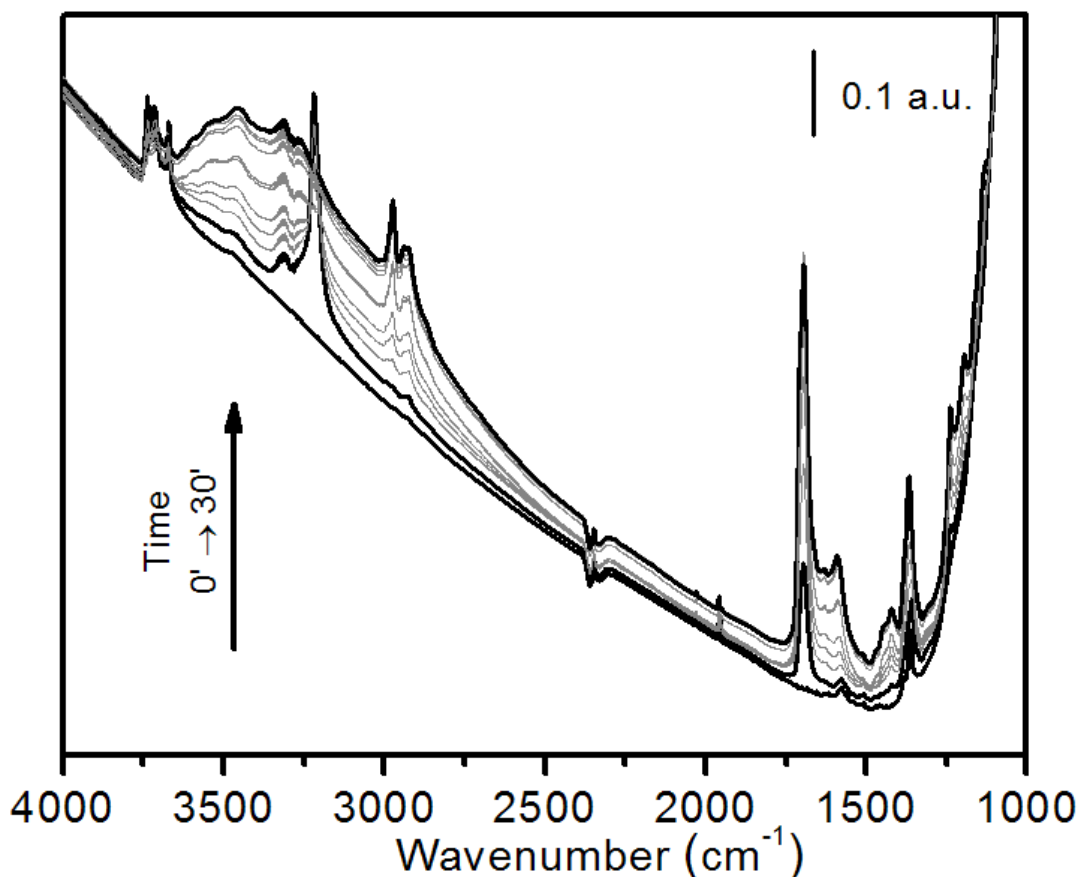

Figure 5: FTIR spectra of the TiO$_2$-acetylene interaction recorded at increasing contact time (range 0-30 min)

The evolution of the above mentioned manifestations is accompanied by the progressive erosion of the band associated to acetylene (3214cm^{-1}) confirming the progressive saturation of the acetylenic carbons.

The broad band in the range 3800-2500 cm^{-1} and centred around 3250 cm^{-1} is usually ascribed to surface OH groups whose vibrational mode is perturbed by the hydrogen bonds. Similarly to what described in the case of P25[24] also in the present case these bands are ascribed to surface OH groups interacting via hydrogen bond with both C$_2$H$_2$ and (since the broad band continuously

increases even with C_2H_2 depletion) with the hydrocarbons resulting from the self-assembly of acetylene. To achieve a convincing mechanism of the observed reactions it is useful to remark that the high intensity of the broad OH band (and its continuous increase) cannot be explained taking into account the few isolated hydroxyl groups initially present at the activated surface. New OH group are thus abundantly formed as the result of the C_2H_2-TiO_2 interaction. For the same purpose it is also worth to note that the starting molecule C_2H_2 has a C/H ratio of 1, while the FTIR spectra unambiguously show the formation of OH groups and also of hydrogen-rich CH_2 and/or CH_3 moieties. This requires the parallel formation of highly (or even completely) dehydrogenated counterparts characterized by the presence of a network of conjugated double bonds, as proposed for the P25[24] and in agreement with data reported in previous works.[17,19,21]

3.3 FTIR-TGA analysis of the products of C_2H_2-TiO_2 interaction.

All the experiments reported above suggest that the production of complex hydrocarbon molecules occurs by prolonged contact between acetylene and titanium dioxide. We have thus investigated, coupling TGA and IR spectroscopy, the demolition of the surface anchored compounds in a flow of oxygen. Since the reactivity was particularly high in the case of anatase we used this polymorph in a series of experiments which are illustrated by Fig. 6. In particular, beside the weight loss upon heating at progressively increasing temperature, the nature of the gas released was continuously monitored by a TG-FTIR analyzer.[43] The recorded thermograms (Fig 6, panel A) were also reported as the first derivative of the weight loss (Panel B) to identify and discriminate more easily the thermal processes. With this experimental approach we have monitored the weight loss of five distinct anatase samples which were respectively: i) non activated, ii) activated, iii) non activated/contacted with C_2H_2, iv) activated/contacted with C_2H_2, v) activated /contacted with propine.

FT-IR analysis indicates, as expected, that the gas evolved during the heating ramp are exclusively H_2O and CO_2. In the right panels of figure 6, the first derivative curves of the thermograms (Panel B) are compared with the FTIR chromatograms relative to H_2O, and CO_2 monitored as a function of the temperature (panels C and D respectively). The thermograms evidence that all the samples lost weight, because of a desorption process, until ca. 750 K. The activated anatase sample shows an overall weight loss corresponding to about 1.0% of the starting weight (Fig.6A curve a) basically due to water desorption (Fig.6C-D curve a). This non

negligible weight loss is due to the fact that during the preparation of the TGA experiment the activated material unavoidably enters in contact with the atmosphere undergoing a rapid rehydration. This phenomenon is roughly the same for all the samples examined. The overall weight loss exhibited by the activated anatase materials after reaction with C_2H_2 and C_3H_4 (panel
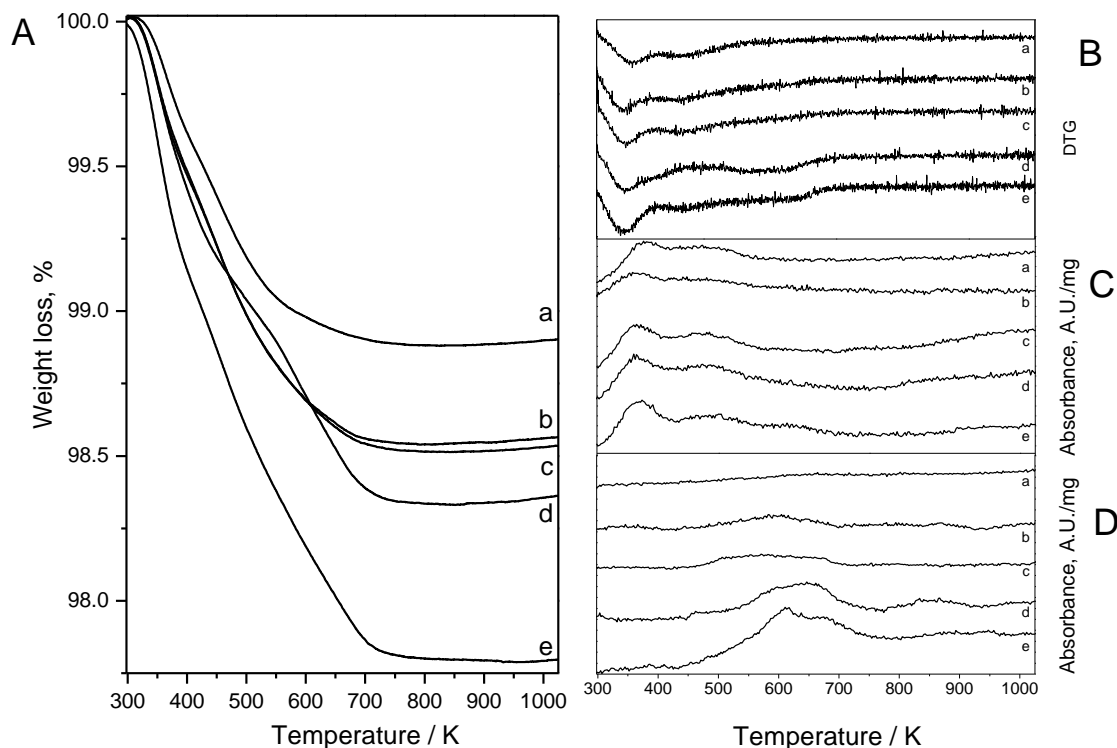

Figure 6: TGA weight loss curves (Panel A) and corresponding derivate thermal gravimetric (DTG) curves (Panel B); FTIR profile of water (3566 cm^{-1}, Panel C) and CO_2 (2359 cm^{-1}, Panel D) for activated anatase (curve a); non activated anatase (b); non activated anatase/C_2H_2 (c); activated anatase /C_3H_4 (d) and activated anatase /C_2H_2 (e)

A, curves d and e respectively) is significantly higher than that observed with the other samples, reaching an overall weight loss of 2.2 % for acetylene and 1.7 % for propyne.

In the temperature range from 500 K to 750 K, the weight loss for activated anatase /C_2H_2 (1.1 %), and for activated anatase /C_3H_4 (0.85 %) is significantly higher than that observed with the other samples analyzed (0.72 % for non activated anatase/C_2H_2, 0.70 % for non activated anatase and 0.55 % for activated anatase). During this additional weight loss from the alkyne-treated activated samples, the FTIR analysis evidenced a rather intense CO_2 profile (Fig. 6, Panel D curves d and e). This result suggests that in this temperature range the combustion of the

adsorbed organic fraction occurs. Furthermore the complexity of the CO_2 desorption profiles indicates that distinct adsorbed species characterized by different molecular weight are present at the surface. This agrees with recent data showing the formation of several different products (in particular aromatic polycyclic hydrocarbons[24]) at the surface of P25. It is worth to note also that the CO_2 profile shows some emission of this molecule in a range of temperature where no further weight loss was observed (from 750 to 1023 K). This result seems to indicate that a fraction of the adsorbed hydrocarbons is initially desorbed and only later the combustion takes place as expected for large organic molecules.

A non-negligible loss of weight was also observed in the case of non-activated/C_2H_2 anatase (Fig.6A curve c), although this material has shown a modest reactivity with the hydrocarbon (see before). This is due to the fact that the non-activated oxide still contains some organic contaminants deriving from the sol-gel synthesis process as confirmed by the TGA curve of the non-activated anatase (Fig. 4A curve b). The two curves (Fig 6A, b and c) are very similar despite the sample corresponding to curve b was never put in contact with acetylene. The key role of the oxide activation process to induce the specific self-assembly reactivity of alkynes on TiO_2 is therefore confirmed by the present results.
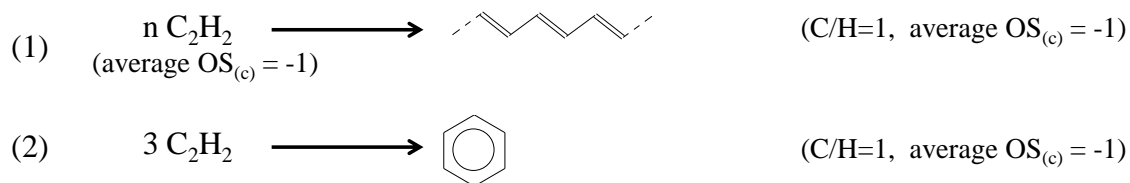
4. Discussion.

The data here reported confirm, adding new crucial information, what was partially known from previous work[14,16,18] and more thoroughly described in a recent paper[24] i.e. the propensity of alkynes (and in particular of acetylene) to undergo complex self-assembling reactions when put in contact with the TiO_2 surface in mild conditions. At variance with reference 24 which was devoted to the reactivity of P25, the well-known solid composed of rutile and anatase crystals connected by solid-solid interfaces, in the present paper we have followed, for the sake of simplicity, the reaction of acetylene with bare anatase. The basic features of the interaction in the case of anatase are not dissimilar from those observed in that of P25 however the pure polymorph seems more reactive than the mixed solid. This can be seen in Fig. 4 (in terms of the EPR spectra intensity) comparing panel A (P25) with panel B (anatase). The capability of forming self-assembled ad-molecules of relevant molecular weight by simple contact at room temperature is confirmed by the TGA experiments in oxygen flow showing at least two distinct

carbon dioxide emissions having maxima at relatively high temperatures (around 600K and 850-900K respectively; Fig. 6, panel D). The basic chemistry of the interaction is jointly described by UV-Vis, FTIR and EPR experiments. The whole reaction in based on various reaction channels, having probably different quantitative importance. From the mentioned set of spectroscopic techniques we basically infer that: i) acetylene is rapidly consumed by the surface reaction (IR, Fig. 4); ii) new surface ad-species show up containing conjugated double bond and/or saturated alkyl groups (IR, UV-Vis, Fig. 1) and causing optical absorption in the visible range; iii) surface OH^- groups are abundantly generated (IR); iv) reduced Ti^{3+} species forms into the solid matrix (EPR).

Points iii) and iv) are critical ones in that they state two fundamental facts. The first one is that, at least for a fraction of the total adsorbed amount, acetylene undergoes a splitting of the C-H bond and loses hydrogen (OH^- formation). The second one is that the surface adsorbates tend to lose electrons which are stabilised in the solid by Ti^{4+} ions ($Ti^{4+} + e- \rightarrow Ti^{3+}$). These two events, which are mutually connected one to each other, are crucial to understand the mechanism of at least one of the main reaction channels operating at the surface, i.e. the formation of polyaromatic hydrocarbons (precursors of extended graphenic-like layers formed at higher temperature) indicated by the growth of FTIR bands corresponding to conjugated double bonds. For this scope it is also necessary to take into account, in parallel, two mutually correlated parameters which are the C/H ratio and the carbon oxidation state (hereafter $OS_{(C)}$) of the reaction products as detailed in the following.

Two processes already described for the C_2H_2/TiO_2 system (and compatible with the optical and vibrational spectra here reported) are the oligomerization to polyacetylene and the cyclotrimerization of acetylene to benzene (reaction 1 and 2):

(1) $n\,C_2H_2$ $\longrightarrow$ (C/H=1, average $OS_{(c)}$ = -1)
        (average $OS_{(c)}$ = -1)

(2) $3\,C_2H_2$ $\longrightarrow$ (C/H=1, average $OS_{(c)}$ = -1)

In these two reactions (see also Scheme 1) both the C/H ratio and the carbon average oxidation state remain unaltered passing from reactants to products. Reactions 1 and 2 represent

therefore a first (non-redox) reaction channel at the surface and are not compatible with the creation of OH groups and of excess electrons.

At variance, the formation of polyaromatic hydrocarbons starting from acetylene involves an increase of the C/H ratio (that is a loss of hydrogen) and an increase of the carbon average OS. Let's consider first the hydrogen loss. This phenomenon must entail a dissociative chemisorption of C_2H_2 which, in principle, could be homolytic or heterolytic. The homolytic dissociation of a C-H bond at the surface of an oxide is relatively infrequent and always occurs by action of O^- ions. These ions are present at the surface in two cases, i) valence induction caused by non stoichiometric defects[44] charge separation caused by irradiation in semiconducting oxide such TiO_2 (O^- actually is a hole localized onto an oxygen ion)[34]. Since the reaction here described takes place in the dark the homolityc splitting of acetylenic C-H is substantially unlikely.

The heterolytic splitting needs the presence of surface $Ti^{4+} – O^{2-}$ pairs capable of polarizing the C-H bond up to the formation of a titanium monoacetylide complex and of an hydroxyl group

(3) $HC \equiv C\text{-}H + Ti^{4+} – O^{2-} \rightarrow$ $HC \equiv C^-$ ---Ti^{4+} + OH^-
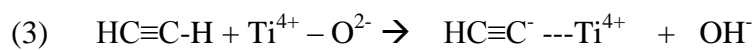
The heterolytic splitting of acetylene is affected by the extent of the surface hydroxylation as it requires free titanium–oxygen pairs. The limited reactivity of a partially hydrated TiO_2 surface (non-activated materials, Fig. 4) agrees therefore with the view indicating reaction (3) as the initial step of the reaction channel leading to polyaromatic molecules. The heterolytic splitting of C-H bonds is a reaction typical of basic oxides such as alkaline earth oxides which are capable of inducing this reaction even reacting with hydrocarbons much less acidic than acetlylene.[45,46] We suggest therefore that activated TiO_2 presents absorption sites basic enough (as proved also by experiments of CO_2 adsorption[47,48]) to split the acetylene C-H bond. The same reaction, by the way, has been observed also in the case of alumina, an oxide, similar to TiO_2 in terms of acid-base properties.[22,32]

The role of the initial C-H dissociative absorption in the whole process is further proved by the experiments of propyne absorption showing a marked reduction of the self-assembling reactivity at the TiO_2 surface. In this compound in fact one of the acetylenic hydrogens is substituted by a less acid methyl group lower having propensity for the heterolytic dissociation.

Let us consider now the formation of paramagnetic Ti^{3+} centres (EPR spectra in Fig. 2 and 3) which were observed in all type of TiO_2 material (anatase, rutile and P25) upon contact with acetylene. The concentration of these centers (EPR intensity) parallels the development of the surface reaction (Fig 4 and Fig. 5) indicating that their formation is a direct consequence of the self-assembling processes that occur on the TiO_2 surface. However, even though these paramagnetic species are, in principle, responsible of a visible light absorption[49] similar to that showed in Fig. 1, the fact that, after oxygen interaction the Ti^{3+} centres disappear and in parallel the optical features are not significantly affected, clearly indicates that the Ti^{3+} concentration is not enough to contribute to such absorption which is dominated by the effect of surface assembled carbon containing species.

Ti^{3+} ions forms at the surface and/or at the bulk of titanium dioxide by trapping of an excess electron ($Ti^{4+} + e^- \rightarrow Ti^{3+}$) in several ways, one of which is the direct electron injection by a chemical species in contact with the surface. This is the case, for instance, of hydrogen atoms which spontaneously ionize creating reduced centers into the solid.[34] In the present case, since a direct electron transfer between the acetylene molecule and the solid is meaningless, the source of the trapped electrons are, reasonably, the acetylide carbanions formed via reaction (3). The instability of adsorbed carbanions towards electron acceptors (and the consequent electron transfer from the formers to the latters) has been documented in the case of alkaline earth oxides. It was shown in that case that carbanions formed by heterolytic splitting of adsorbed hydrocarbons easily transfer an electron on coadsorbed oxygen molecules forming O_2^- superoxide ions and C-centred radicals which initiate a complex oxidative interaction.[45] The situation is not very different in the present case except for the fact that here the solid matrix has a certain propensity to reduction accepting excess electrons:
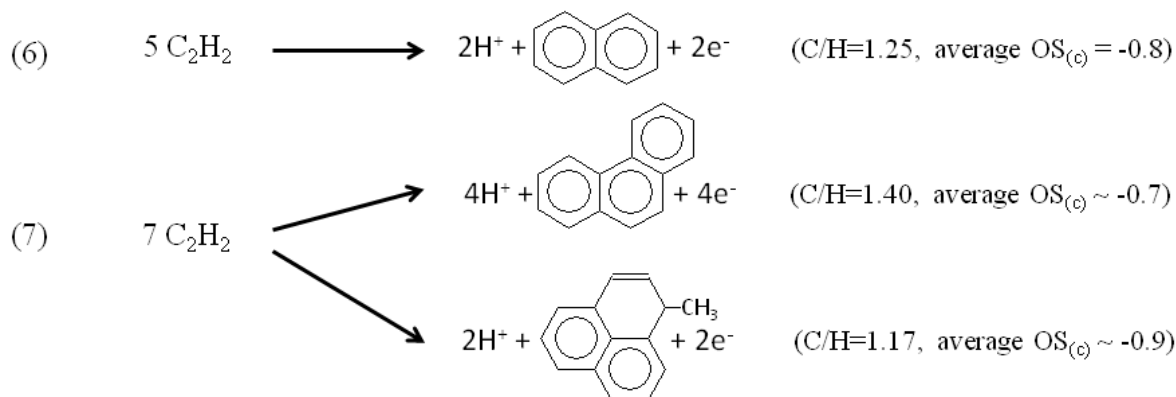
(4) $\quad HC{\equiv}C^-_{(ads)} + Ti^{4+}_{(S)} \quad \rightarrow \quad HC{\equiv}C^{\bullet}_{(ads)} + Ti^{3+}_{(s)}$
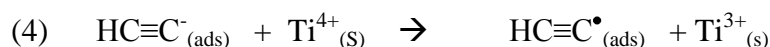
Considering the two reactive steps described by equation (3) and (4) the formation of both surface OH^- and Ti^{3+} is simply accounted for and the building blocks for the formation of polyaromatic hydrocarbons have become available. We propose in fact that these conjugated systems form by a cyclo-oligomerization similar to that leading to benzene (equation 1)

employing both C_2H_2 molecules and $HC\equiv C^{\bullet}$ radicals. In the simplest case (the formation of naphthalene) we can write:

(5) $3\,C_2H_2 + 2\,HC\equiv C^{\bullet} \rightarrow C_{10}H_8$
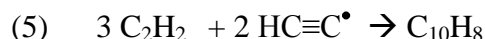
Summarizing the reactions leading to polyaromatic hydrocarbons must be based on a redox mechanism whereby acetylenic carbon $((OS)_C = -1)$ increases its oxidation number along with the transformation into the products. This implies, in parallel, the growth of the C/H ratio of the products themselves. In the reaction channel here described the released electrons are stabilized by the solid which plays the role of oxidant. Other reactions can be envisaged based on the same redox scheme involving the solid, some of which are reactions 6 and 7 which emphasize the formation of H^+ and e^- which are both stabilized by the solid.

(6) $5\,C_2H_2 \longrightarrow 2H^+ + $ [naphthalene] $ + 2e^-$ (C/H=1.25, average $OS_{(c)} = -0.8$)

(7) $7\,C_2H_2$

$4H^+ + $ [phenanthrene] $ + 4e^-$ (C/H=1.40, average $OS_{(c)} \sim -0.7$)

$2H^+ + $ [methyl-acenaphthylene] $ -CH_3 + 2e^-$ (C/H=1.17, average $OS_{(c)} \sim -0.9$)

Very likely, the described mechanism is not the only one operating in this complex interfacial system as suggested by the evidence of other chemical entities such as saturated alkyl groups. The main alternatives to the reduction of the solid are surface redox reactions based on intermolecular electron transfer and proton transfer between adsorbates. This is the most likely way allowing the formation of hydrogen poor molecules such as progressively larger polyaromatic compounds $((OS)_C > -1)$ in parallel with hydrogen rich counterparts having $OS_C < -1$ such as alkene and alkanes or, more probably, molecules containing alkenic or alkyl fragments. The evidence provided by the present study, however, is not sufficient for a thorough description of this further reaction channel with the same accuracy used to detail the above mechanism involving reduction of the solid.

5. Conclusion.

The data here reported show that when acetylene is adsorbed at room temperature on the TiO_2 surface a significant amount of hydrocarbons characterized by a higher molecular weight with respect to the starting molecule are accumulated at the oxide surface. The process occurs in the case of all type of titania (anatase, rutile, P25) and is particularly efficient at the surface of anatase. The self-assembling process needs a fully dehydrated surface (activated solid) since one of the main reaction mechanisms operating at the surface starts with an heterolytic dissociation of the alkyne which needs the presence of a Ti-O pair and ends up with the formation of an adsorbed carbanion and an OH^- group. This is the reason why the presence of surface OH^- (abundantly present at the surface of as-prepared non activated materials) limits the reactivity of the solid. Beside the already described reactions of acetylene polymerization and cyclotrimerization (which do not alter the C/H ratio of the monomer) other complex interaction of redox type occurs at the surface leading to the formation of various aromatic polycyclic compounds having higher C/H ratio and higher C oxidation number with respect to the reactant. We have demonstrated by means of the EPR technique, that Ti^{3+} ions are formed in the solid upon interaction with acetylene thus unravelling one of the main redox reaction channels operating at the surface. This is based on two critical initial steps i.e. the heterolytic splitting of the C-H acetylenic bond and the successive ionisation of the acetylide anion with electron transfer to the solid. Further work is needed in order to unravel the details of the other reaction channels likely occurring at the surface and to better control the self-assembly processes. However acetylene adsorption on TiO_2 can represents a potential way to grow on the TiO_2 surface compounds possessing conjugated double bonds, which in principle can act as an antenna for visible light, similarly to the dyes anchored on TiO_2 in DSSCs.

AUTHOR INFORMATION

Corresponding Author

*Stefano Livraghi, Stefano.livraghi@unito.it

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

ACKNOWLEDGMENT

REFERENCES

(1) Chen, X.; Mao, S. Titanium Dioxide Nanomaterials: Synthesis, Properties, Modifications, and Applications. *Chem. Rev.* **2007**, *107*, 2891-2959.

(2) Diebold, U. The surface Science of Titanium Dioxide. *Surf. Sci. Rep*. **2003**, *48*, 53-229.

(3) Carp, O.; Huisman, C.L.; Reller, A. Photoinduced Reactivity of Titanium Dioxide. *Prog. Solid State Chem.* **2004**, *32*, 33–177.

(4) Fujishima, A.; Rao, T. N.; Tryk, D. A. Titanium Dioxide Photocatalysis. *J. Photochem. Photobiol C: Photochemistry Reviews* **2000**, *1*, 1–21.

(5) Henderson, M. A. A surface Science Perpective on TiO$_2$ Photocatalysis. *Surf. Sci. Rep.* **2011**, *66*, 185-297.

(6) Dozzi, M. V.; Selli, E. Doping TiO$_2$ with p-block Elements: Effects on Photocatalytic Activity. *J. Photochem. Photobiol. C: Photochem. Rev.* **2013**, *14*, 13–28.

(7) Fang, W.; Xing, M.; Zhang, J. A New Approach to Prepare Ti^{3+} Self-doped TiO$_2$ via NaBH$_4$ Reductionand Hydrochloric Acid Treatment. *Appl. Catal. B.* **2014**, *160-161*, 240-246.

(8) Zhu, J.; Deng, Z.; Chen, F.; Zhang, J.; Chen, H.; Anpo, M.; Huang, J.; Zhang, L. Hydrothermal Doping Method for Preparation of Cr^{3+}-TiO$_2$ Photocatalysts with Concentration Gradient Distribution of Cr3+. *Appl. Catal., B* **2006**, *62*, 329-335.

(9) Beranek,; R. Neumann, B.; Sakthivel, S.; Janczarek, M.; Dittrich, T.; Tributsch, H.; Kisch H. Exploring the Electronic Structure of Nitrogen-modified TiO$_2$ Photocatalysts Through Photocurrent and Surface Photovoltage Studies. *Chem. Phys.* **2007**, *339*, 11-19.

(10) O'Regan, B.; Grätzel, M. Molecular Photovoltaic. *Acc. Chem. Res.* **2000**, *33*, 269-277.

(11) Robel, I.; Subramanian, V.; Kuno, M.; Kamat, P. V. Quantum Dot Solar Cells. Harvesting Light Energy with CdSe Nanocrystals Molecularly Linked to Mesoscopic TiO$_2$ Films. *J Am. Chem Soc.* **2006**, *128*, 2385-2393.

(12) Tada, H.; Kiyonaga, T.; Naya, S. Rational Design and Applications of Highly Efficient Reaction Systems Photocatalyzed by Noble Metal Nanoparticle-loaded Titanium(iv) Dioxide. *Chem. Soc. Rev.* **2009**, *38*, 1849-1858.

(13) Kisch, H.; Sakthivel, S.; Janczarek, M.; Mitoraj, D. A Low-Band Gap, Nitrogen-Modified Titania Visible-Light Photocatalyst. *J. Phys. Chem. C* **2007,** *111,* 11445-11449.

(14) Mitoraj, D.; Kisch, H. The Nature of Nitrogen-Modified Titanium Dioxide Photocatalysts Active in Visible Light. *Angew. Chem. Int. Ed.* **2008**, *47*, 9975 –9978.

(15) Anpo, M.; Aikawa, N.; Kodama, S.; Kubokawa, Y. Photocatalytic Hydrogenation of Alkynes and alkenes with Water Over TiO$_2$. Hydrogenation Accompanied by Bond Fission. *J. Phys. Chem.* **1984**, *88*, 2569-2572.

(16) Kim, W. J.; Kang, J. H.; Ahn, I. Y.; Moon, S. H. Deactivation Behavior of a TiO$_2$-added Pd Catalyst in Acetylene Hydrogenation. *J. Catal.* **2004**, *226*, 226–229.

(17) Rives-Arnau, V.; Sheppard, N. Raman Spectroscopic Study of the Polymerization of Acetylene on Titanium Dioxide (Rutile). *J.C.S. Faraday I* **1980**, *76*, 394-402.

(18) Sakata, Y.; Liu, Z.; lmamura, H. Tsuchiya, S. *ln situ* Infrared Spectroscopic Evidence for Cyclotrimerisation of Acetylene to Benzene Over a TiO$_2$ Catalyst. *Chem. Commun.* **1991,** 1392-1393.

(19) Pierce, K.G.; Barteau, M. A. Cyclotrimerization of Alkynes on Reduced TiO$_2$ (001) Surfaces. *J. Phys. Chem.* **1994**, *98*, 3882-3892.

(20) Sherrill, A.B.; Lusvardi, V.S. Barteau, M. A.; Investigation of Cyclooctatetraene on Reduced TiO$_2$(001) as a Possible Intermediate in Alkyne Cyclotrimerization. *Langmuir* **1999**, *15*, 7615-7620.

(21) Sherrill, A.B.; Barteau, M.A. Oligomerization of trimethylsilyl acetylene to form large molecules on reduced surfaces of TiO$_2$(0 0 1). *J. Mol. Catal. A: Chemical* **2002**, *184*, 301–310.

(22) Ivanov, A.V.; Koklin, A.E.; Uvarova, E.B.; Kustov, L.M. A DRIFT Spectroscopic study of Acetylene Adsorbed on Metal Oxides. *Phys. Chem. Chem. Phys.* **2003**, *5*, 4718–4723.

(23) Li, L.; Wang, Y.; Yan, F.; Samuelson, L.A. Photosensitized Solid-state Polymerization of Diacetylenes in Nanoporous TiO$_2$ Structures. J. Kumar, *J. Macromol. Sci. Part A Pure Appl. Chem.* **2010**, *47*, 1161–1166.

(24) Jain, S.M.; Biedrzycki, J.J.; Maurino, V.; Zecchina, A.; Mino, L.; Spoto, G. Acetylene Oligomerization on the Surface of TiO$_2$: a Step Forward in the in situ Synthesis of Nanostructured Carbonaceous Structures on the Surface of Photoactive oxides. *J. Mater. Chem. A* **2014**, *2*, 12247-12254.

(25) Kamat, P.V. Graphene-based Nanoarchitectures. Anchoring Semiconductor and Metal Nanoparticles on a Two-dimensional Carbon Support. *J. Phys. Chem. Lett.* **2010**, *1*, 520–527.

(26) Yang, M-Q.; Zhang, N.; Xu, Y-J. Synthesis of Fullerene-, Carbon Nanotube-, and Graphene-TiO$_2$ Nanocomposite Photocatalysts for Selective Oxidation: A Comparative Study. *ACS Appl. Mater. Interfaces* **2013**, *5*, 1156–1164.

(27) Xing, M.; Xiao L.; Zhang, J. Synergistic Effect on the Visible Lightactivity of Ti^{3+} Doped TiO$_2$ Nanorods/Boron Doped Graphene Composite. *Sci. Rep.* **2014**, *4*, 5493.

(28) Xin, X.; Zhou, X.; Wu, J.; Yao, X.; Liu, Z. Scalable Synthesis of TiO_2/Graphene Nanostructured Composite With High-rate Performance for Lithium Ion Batteries. *ACS Nano* **2012**, *6*, 11035-11043.

(29) Xu, C.; Shaban, Y.A.; Ingler, W.B. Jr.; S.U.M. Khan, Nanotube Enhanced Photoresponse of Carbon Modified (CM)-n-TiO_2 for Efficient Water Splitting. *Sol. Energy Mater. Sol. Cells.* **2007**, *91*, 938–943.

(30) Ohtani, B.; Prieto-Mahaney, O.O.; Li, D.; Abe, R. What is Degussa (Evonic) P25? Crystalline Composition Analysis, Reconstruction from Isolated Pure Particles and Photocatalytic Activity Test. *J. Photochem. Photobiol. A.* **2010**, *216*, 179-182.

(31) Mino, L.; Spoto, G.; Bordiga, S.; Zecchina A. Rutile Surface Properties Beyond the Single Crystal Approach: New Insights from the Experimental Investigation of Different Polycrystalline Samples and Periodic DFT Calculations. *J. Phys. Chem. C.* **2013**, *117*, 11186−11196.

(32) Bhasin, M.M.; Curran, C.; John, G.S. Infrared Study of the Effect of Surface Hydration on the Nature of Acetylenes Adsorbed on 7-Alumina. *J. Phys. Chem.* **1970**, *74*, 3973-3980.

(33) Hasiguti, R. R. The Structure of Defects in Solids. *Ann. Rev. Mater. Sci.* **1972**, *2*, 69-92.

(34) Howe, R. F.; Gratzel, M. EPR Observation of Trapped Electrons in Colloidal TiO_2. *J. Phys. Chem.* **1985**, *89*, 4495-4499.

(35) Macdonald, R.; Howe, R. F.; Zhang, X.; Zhou W. In Situ EPR Studies of Electron Trapping in a Nanocrystalline Rutile. *J. Photochem. Photobiol. A.* 2010, *216*, 238–243

(36) Hurum, D. C.; Agrios, A.G.; Gray, K.A., Rajh, T. M., Thurnauer, C. Explaining the Enhanced Photocatalytic Activity of Degussa P25 Mixed-Phase TiO_2 Using EPR. *J. Phys. Chem. B* **2003**, *107*, 4545-4549.

(37) Livraghi, S.; Chiesa, M.; Paganini, M.C.; Giamello, E. On the Nature of Reduced States in Titanium Dioxide as Monitored by Electron Paramagnetic Resonance. I: The Anatase case. *J. Phys. Chem.* **2011**, 115, 25413-25421.

(38) Livraghi, S.; Rolando, M.; Maurelli, S.; Chiesa, M.; Paganini, M.C.; Giamello, E. Nature of Reduced States in Titanium Dioxide as Monitored by Electron Paramagnetic Resonance. II: Rutile and Brookite Cases. *J. Phys. Chem. C* **2014**, *118*, 22141−22148.

(39) Martyanova, I. N.; Berger, T.; Diwald, O.; Rodrigues, S.; Klabunde, K. J. Enhancement of TiO_2 Visible Light Photoactivity through Accumulation of Defects During Reduction–Oxidation Treatment. *J. Photochem. Photobiol., A* **2010**, *212*, 135–141.

(40) Brant, A. T.; Gilles, N. C.; Yang, S.; Sarker, M. A. R.; Watauki, S.; Nagao, M.; Tanaka, I.; Tryk, D. A.; Manivannan, A.; Halliburton, L. E. Ground State of the Singly Ionized Oxygen Vacancy in Rutile TiO_2. *J. Appl. Phys.* **2013**, 114, 113702.

(41) Yang, S.; Brant, A. T.; Giles, N. C.; Halliburton, L. E. Intrinsic Small Polarons in Rutile TiO_2. *Phys Rev. B* **2013**, *40*, 125201.

(42) Morterra, C. An Infrared Spectroscopic Study of Anatase Properties. *J. Chem. Soc.*, *Faraday Trans. I* **1988**, *84*, 1617-1637.

(43) Giustetto, R. Wahyudi, O. Corazzari, I. Turci, F. Chemical Stability and Dehydration Behavior of a Sepiolite/Indigo Maya Blue Pigment. *Appl. Clay Sci*. **2011**, *52*, 41–50.

(44) Paganini, M.C.; Chiesa, M.; Dolci, F.; Martino, P.; Giamello E. EPR Study of the Surface Basicity of Calcium Oxide. 3. Surface Reactivity and Nonstoichiometry. *J. Phys. Chem. B* **2006**, *110*, 11918-11923.

(45) Garrone, E.; Giamello, E.; Ferraris, M.; Spoto. G. Superoxide Ions Formed Through the Agency of Presorbed Molecules:II. Details on the Mechanism. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 333-337.

(46) Paganini, M.C.; Chiesa, M.; Martino, P.; Giamello, E.; Garrone E.; EPR Study of the Surface Basicity of Calcium Oxide. 1. The Interaction with Alkanes. *J. Phys. Chem. B.* **2003**, *107*, 2575-2580.

(47) Martra, G. Lewis Acid and Base Sites at the Surface of Microcrystalline TiO_2 Anatase: Relationships Between Surface Morphology and Chemical Behavior. *Appl. Catal. A.* **2000**, *200*, 275–285.

(48) Mino, L.; Spoto, G.; Ferrari, A.M. CO_2 capture by TiO_2 anatase surfaces: a combined DFT and FTIR study. *J. Phys. Chem. C.* **2014**, *118*, 25016-2026.

(49) Biedrzycki, J.; Livraghi, S.; Giamello, E.,; Agnoli, S.; Granozzi, G. Fluorine- and Niobium-Doped TiO_2: Chemical and Spectroscopic Properties of Polycrystalline n‑Type-Doped Anatase. *J. Phys. Chem. C* **2014**, *118*, 8462−8473.

T.O.C.
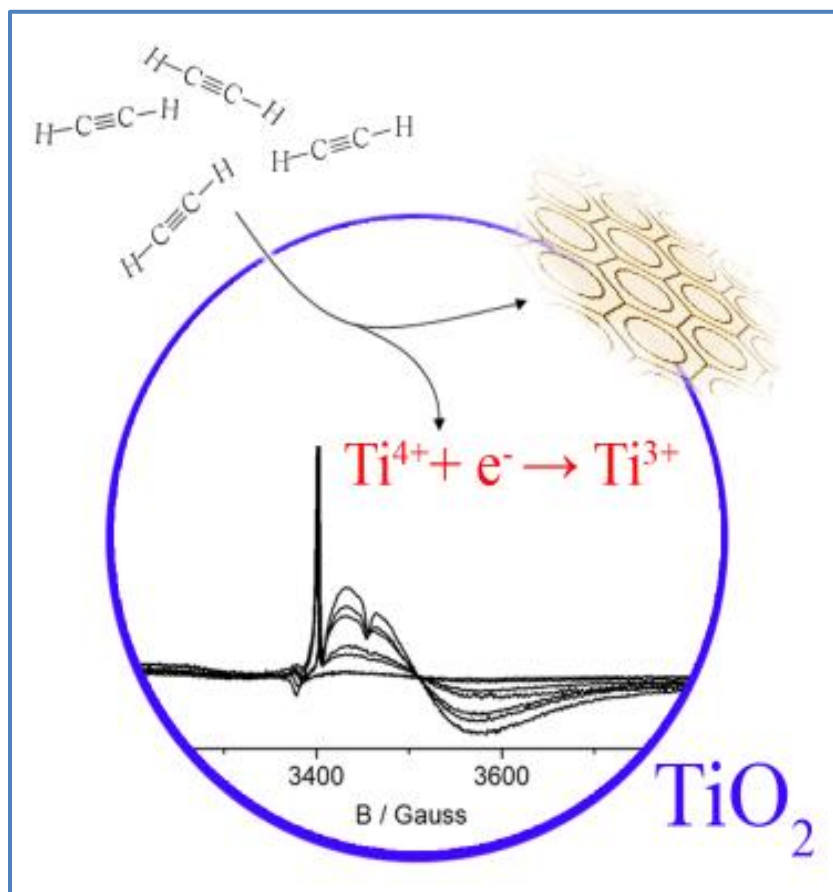
KEYWORDS: TiO_2, Acetylene, self-assembly, EPR, FTIR, TGA, self-assembly, Ti^{3+}