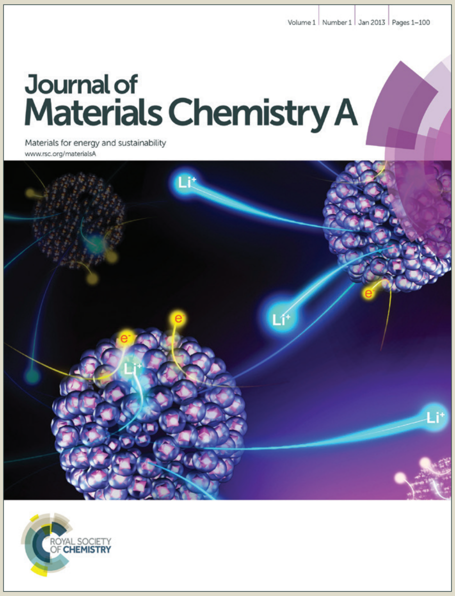
Journal of Materials Chemistry A

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

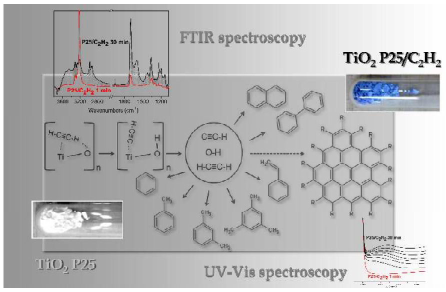
www.rsc.org/materialsA

Acetylene oligomerization at the surface of TiO_2: a step forward in the *in situ* synthesis of nanostructured carbonaceous structures at the surface of photoactive oxides

Sagar Motilal Jain, Jakub Jan Biedrzycki, Valter Maurino, Adriano Zecchina, Lorenzo Mino* and Giuseppe Spoto*

Department of Chemistry and NIS Centre of Excellence, University of Turin, via P. Giuria 7, 10125 Torino, Italy

Table of Contents (TOC) entry.



In situ acetylene oligomerization allows to obtain polycyclic condensed hydrocarbons in close contact with the TiO_2 surface. These products represent intermediate steps to produce photoactive graphene-like layers on TiO_2.

Abstract

The interaction of acetylene with TiO_2 (Evonik P25) was studied as a function of the gas pressure and of the contact time by *in situ* vibrational (infrared and Raman) and electronic (UV-Vis) spectroscopies and by gas chromatography-mass spectrometry analysis (CG-MS) of the reaction products. At low pressure the reaction proceeds through surface adsorption of acetylene and

cyclotrimerization to benzene. At higher pressure ($P > 100$ mbar) the adsorption step is followed by the progressive formation of more complex oligomerization products containing an increasing number of conjugated double bonds. The final products obtained after mild heating at 373 K in acetylene excess absorb in the visible spectral region and confer to the system a strong blue color. These colored species are stable for many days in pure oxygen or air and cannot be extracted by common solvents, appearing strongly anchored to the TiO_2 surface. The formation of saturated $–CH_3$ and $–CH_2$ groups during the oligomerization process and the spectroscopic and GC-MS results show that the colored species consist of polycyclic aromatic hydrocarbons containing a considerable number of condensed rings. Following these results, the controlled oligomerization of acetylene can represent a route for the direct production of graphene-like species tightly anchored to the TiO_2 surface, *i.e.* of composites materials of potential interest in photocatalysis or photovoltaic applications.

Introduction

Efficient conversion of solar energy into electrical power by photovoltaic devices[1] or into fuels by artificial photosynthesis[2, 3] are among the most challenging goals of modern science. The strategies aimed at these purposes include the use of photoactive materials based on semiconductors (see for instance Kubacka *et al.*[4] and references therein). Among them titanium dioxide emerges as one of the most promising candidates because of favourable properties like photo-stability, affordable cost and low toxicity. The main drawback of TiO_2 is represented by the large band gap (3.2 eV for the anatase polymorph)[5] which restrains the absorption of light to the ultraviolet region, *i.e.* to a small fraction only (about 5%) of the whole solar spectrum. Many efforts are so devoted to try to increase significantly the conversion efficiency of TiO_2 by extending the response to the more favourable visible region. These include the doping with metal and non-metal impurities[5-7], the synthesis of oxygen-deficient forms[8] and the coupling of TiO_2 with narrow band gap semiconductors[9]. All these methods aim to reduce the extension of the TiO_2 band gap either by creating inter-band (defective) states or by band bending.

An alternative method is sensitization of TiO_2 by anchoring proper dye molecules (sensitizer) at its surface.[10] In this case the key steps to increase the photo-efficiency are the excitation by visible light of the sensitizer and the subsequent charge transfer from the excited dye to the active solid. Presently Ru-based complexes are the most widely employed dyes for photocatalytic applications[11, 12] as well as for photovoltaic conversion using dye-sensitized solar cells (DSSC),[13] notwithstanding considerable drawbacks represented by their cost and low chemical stability.

In connection with the sensitization route, an interesting observation comes from a paper by Rives-Arnou and Sheppard[14] dating back to 1980 and concerning a Raman study of the interaction of acetylene with the TiO_2 rutile polymorph. It was found that under the laser irradiation acetylene polymerizes on the oxide surface to give adsorbed coloured trans-polyacetylene chains.[14]. In the context sketched above this result can be considered a promising starting point to develop a method to produce *in situ* a dye molecule directly at the surface of a photoactive solid. For this reason, we decided to investigate the reactivity of acetylene on TiO_2 P25, a material prevalently containing the anatase polymorph (85%) and which is often considered a benchmark for photovoltaic and photocatalytic applications.

For the scopes of this paper it is also worth to recall that, whatever is the excitation frequency, limits to the efficiency of solar energy conversion by semiconductor-based systems can also derive from fast charge recombination between the photo-generated electrons and holes. The strategies proposed to enhance charge separation on TiO_2 include the modification of the surface and bulk structure as well as the preparation of nanostructures where a second phase can preferentially trap the electrons or the holes.[15]

In this respect, much interest has been recently attracted by composites of TiO_2 with carbonaceous materials characterized by unusual structural and electronic properties, like carbon nanotubes, fullerenes and graphene nanosheets.[16] In fact these carbon structures combine high affinity for electrons with favourable characteristics like chemical inertness, stability, and tuneable textural and chemical properties.[16-18] The methodologies for preparing TiO_2/carbon composites include the synthesis of the photoactive solid from suitable precursors in presence of the carbon material, solution mixing, hydrothermal and/or solvothermal methods, CVD, etc.[16, 18]

In particular, as far the preparation of metal oxide/graphene composites is concerned, the most widely used technique is the chemical reduction of graphene oxide (GO). Indeed, using solution mixing or hydrothermal methods, semiconductor nanoparticles or their precursors are usually loaded on the graphene oxide sheets which are then reduced to graphene.[17] However, it is expected that significant improvements of the performances could be achieved by more efficient synthetic routes ensuring a better contact between the carbonaceous phase and the semiconductor surface. A closer contact could in fact improve the efficiency of the electron transfer step from the scaffold to graphene and hence the efficiency of the whole photoactive system.[17, 18] In this regard, it is conceivable that *in situ* synthesis of the carbonaceous phase directly at the TiO_2 surface could satisfy the close-contact requisite better than the preparation routes cited above (where one phase is rather deposited onto the other). An example of *in situ* synthesis of graphene/TiO_2 composites is due to Kamegawa *et al.* [19] for a system where TiO_2 anatase is supported on MCM-41 mesoporous silica. The graphene layer was actually obtained by grafting of 2,3-dihydroxynaphthalene at the TiO_2 surface and subsequent carbonization at 1073 K, *i.e.* at a temperature where anatase is known to undergo a phase transformation into the less photoactive rutile polymorph.

In this paper we show that polycyclic condensed hydrocarbons, possibly representing intermediate steps toward the *in situ* synthesis of graphene layers in close contact with the surface, can be obtained on TiO_2 by acetylene oligomerization in very mild conditions (room temperature and sub-atmospheric C_2H_2 pressure) allowing to avoid the anatase to rutile transformation.

The reactivity of the acetylene/TiO_2 system and the possible structure of the products is discussed on the basis of FTIR, Raman and UV-Vis spectroscopic results and gas chromatography–mass spectrometry analysis.

Experimental

TiO_2 used in these experiments was commercial Degussa (Evonik) P25, which is considered a benchmark in the field of photocatalysis owing to its outstanding activity. P25 is prepared by flame hydrolysis of $TiCl_4$ and contains a mixture of about 85% anatase and 15% rutile. The P25 surface area is about 60 m^2/g.[20, 21]

Before acetylene dosage the P25 samples underwent the following consecutive treatments: (i) outgassing at 773 K for 2 hours under high vacuum (residual pressure $< 10^{-4}$ mbar), (ii) oxidation at 623 K with O_2 (15 mbar for 20 minutes, repeated twice) and (iii) cooling down to 293 K in O_2 atmosphere and outgassing of the gas phase at the same temperature. The treatments with O_2 was performed to ensure the full stoichiometry of the resulting TiO_2 phases, designated in the following as activated TiO_2 or, alternatively, activated P25.

All the above treatments were performed in the same cells used for the spectroscopic measurements and also allowing dosage of acetylene from the gas phase. Before usage acetylene was distilled by repeated freeze/thaw cycles to avoid presence of any gaseous impurities. The TiO_2 samples were in form of self-supporting pellets.

The 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.

Raman spectra were recorded by using a Renishaw Raman Microscope spectrometer. An Ar^+ laser emitting at 514 nm was used and the output power was limited to 1% (100% power = 8.2 mW at the sample) in order to avoid sample damage.

Diffuse reflectance UV-Visible spectra were recorded on a Cary 5000 Varian spectrophotometer equipped with a reflectance sphere on thick self-supported pellets.

Gas chromatography–mass spectrometry (GC-MS) were performed with an Agilent gas chromatograph mod 6890 plus equipped with a Varian VA-5MS column (30 meter length, 0.25 mm ID, 0.25 μm phase thickness) and a Agilent mass spectrometer mod 5973 N. Analytical conditions were as follow: injector in pulsed splitless mode (20 PSI) at 573 K; sample volume 1 μL; column oven at 308 K for 6 minutes, first temperature ramp at 10 K min^{-1} till 453 K, second temperature ramp 4 K min^{-1} till 573 K; carrier: He at 1 mL min^{-1} constant flow.

Results and discussion

1) FTIR spectroscopy

As it will be shown in the following, the composition of the surface products formed by the interaction of acetylene with TiO_2 P25 depends on the pressure of the gas phase as well as on the contact time. For this reason, two series of FTIR experiments are illustrated and discussed here: in the first series a collection of transmission spectra was obtained by gradually increasing the acetylene equilibrium pressure from 0.5 up to 10 mbar (low pressure experiment: Figure 1); in the second the spectral sequence was generated by contacting the activated oxide with a single dose of acetylene at an initial pressure of 120 mbar and then collecting spectra at increasing contact time (high pressure experiment: Figure 2). In the high pressure experiment the further effect on the reaction products formed after 30 minutes of contact of increasing the temperature up to 373 K in presence of acetylene gas was also investigated (Figure 2).

a) Low C_2H_2 pressure experiment. The results of a low pressure experiment are reported in Figure 1. The spectrum obtained after the first small dose of C_2H_2 (red curve in Figure 1) shows: (i) a main complex absorption in the ν(≡C-H) stretching region[22, 23] centered at 3225 cm^{-1}, accompanied by an intense shoulder at 3200 cm^{-1} and weaker features at *ca.* 3336, 3248 and 3160 cm^{-1}; (ii) a weak doublet in the ν(C≡C) stretching region[22, 23] with a main component at *ca.* 1950 cm^{-1} and a less intense satellite at *ca.* 1945 cm^{-1}; (iii) a weak and complex absorption in the 1400-1300 cm^{-1} region; (iv) weak features at *ca*. 1690 and 1618 cm^{-1}.

The assignment of the bands in the 3250-3160 cm^{-1} interval to the stretching modes of C_2H_2 molecules perturbed by interaction with the TiO_2 surface is straightforward and supported by the literature concerning the adsorption of acetylene on other oxides[24] and on zeolites.[25, 26] The interaction with the surface of the solid is also responsible for the activation of the ν(C≡C) vibration giving rise to a weak (and possibly complex) absorption at 1954 cm^{-1}, which is redshifted of 20 cm^{-1} compared with the gas phase value, and for the presence of weak absorptions centered at *ca*. 1360 cm^{-1}, close to the frequency of the combination between the symmetric and antisymmetric HCC bending modes ($\delta_{sym} + \delta_{asym}$), measured at 1328 cm^{-1} in gaseous C_2H_2.[27]

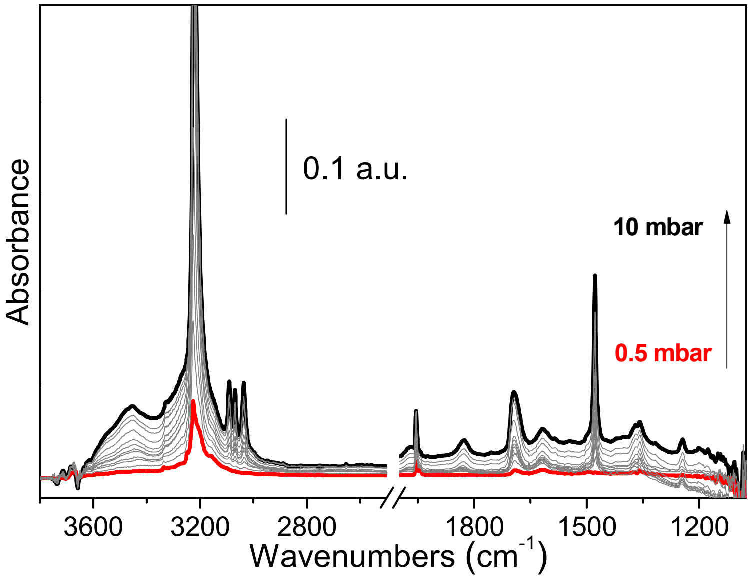


Figure 1. Acetylene/TiO_2 low pressure FTIR experiment: effect of increasing the acetylene pressure. Red curve: after dosage of 0.5 mbar of C_2H_2 on activated TiO_2 P25. Black curve: after dosage of 10 mbar of acetylene. Grey curves: intermediate pressures. All the spectra are background subtracted and therefore negative bands correspond to species which are consumed upon C_2H_2 dosage, while the positive to species which are formed.

The formation of the bands due adsorbed acetylene is apparently accompanied by the erosion of the manifestations due the TiO_2 residual surface OH groups in the 3750-3600 cm^{-1} region[20, 28] and the appearance of a broad and complex absorption in the 3600-3350 cm^{-1} interval (with maxima becoming more evident on increasing the acetylene coverage at *ca.* 3550, 3500 and 3450 cm^{-1}). Although these phenomena certainly suggest the formation of families of OH/C_2H_2 hydrogen bonded surface adducts, this interaction mechanism alone cannot completely explain the complex manifestations of the adsorbed acetylene molecules in Figure 1. Indeed, similar interactions on the strongly acidic OH Brønsted sites of zeolites, expected to perturb the adsorbed C_2H_2 molecules strongly than the weak acidic OH groups of TiO_2, results in a shift of the ν(C-H) mode of only -37 cm^{-1} while the shifts observed here are as large as 60 cm^{-1} and more (up to -127 cm^{-1}). Also the shift of the ν(C≡C) mode actually found here on TiO_2 (*ca.* -20 cm^{-1}) appears too large when compared with that observed on the strongly acidic OH groups of zeolites (-24 cm^{-1}).

On the basis of these considerations, we can infer that adsorption of acetylene on TiO_2 occurs also on OH-free regions of the surface and involve coordinatively unsaturated surface sites or Ti-O acid-base pairs located on different exposed faces, corners or steps.[29]

Concerning the doublet of weak bands at *ca*. 1690 and 1618 cm^{-1} (Figure 1), they are in a region where conjugated double bonds are expected to fall, although they do not find exact correspondence with those of the polyacetylenic species reported by Rives-Arnou and Sheppard[14] on TiO_2 or by some of us in zeolites (where they have carbocationic character).[25]

Going now to the evolution of the spectra upon increasing the acetylene pressure, it can be seen in Figure 1 that the ν(≡CH) component at 3225 cm^{-1} grows preferentially in intensity (while slightly downward shifting to 3220 cm^{-1}) with respect to the satellites at *ca.* 3330, 3250 and 3160 cm^{-1}; this suggests that this band could be associated with acetylene molecules adsorbed on abundant surface sites, like possibly those on extended faces. It is noticeable the contemporary growth of the band of the ν(C≡C) mode at 1950 cm^{-1}.

In parallel the OH bands due to residual hydroxyl groups at 3722, 3690 and 3670 cm^{-1} are completely eroded in favor of the broad and complex band in the 3600-3000 cm^{-1} region due to hydrogen bonded species. Although we cannot exclude a contribution to this phenomenon of acetylene adsorption on the most acidic residual -OH groups, we will see in the following that an hydrogen bonding interaction is also conceivable with the reaction products itself.

Finally, also the 1690 and 1618 cm^{-1} doublet grows in intensity. As it will be clear in the following these bands will become the predominant features in the high pressure spectra.

Besides the features discussed above, increasing the acetylene pressure, we can note a new triplet of absorptions at 3090, 3069 and 3037 cm^{-1}, in the region typical of aromatic C-H stretching vibrations, and of a peak at 1478 cm^{-1}, in the region where aromatic ring deformations modes can be expected. These bands grow in parallel with the acetylene pressure (Figure 1) and readily disappear at the same rate upon outgassing the C_2H_2/TiO_2 system at room temperature (results not shown for brevity), which allows to conclude that they belong to the same surface species. Based on previous literature data[23, 29-31] these bands can be assigned to adsorbed benzene molecules formed by acetylene cyclotrimerisation. Following this assignment the doublet of bands also growing in intensity with the gas pressure at 1970 and 1825 cm^{-1} are attributed to benzene overtones.

On the basis of the above discussion we can therefore conclude that in low pressure conditions (0.5 - 10 mbar) the interaction of acetylene with TiO_2 P25 mainly results in physical adsorption on surface sites and in the formation of oligomerization products prevalently consisting of benzene. As it will be shown in the next paragraphs, by increasing the gas pressure (100 mbar and above) a more complex surface chemistry is prevailing, leading to larger reaction products and revealing an unexpected surface activity of TiO_2 towards acetylene.

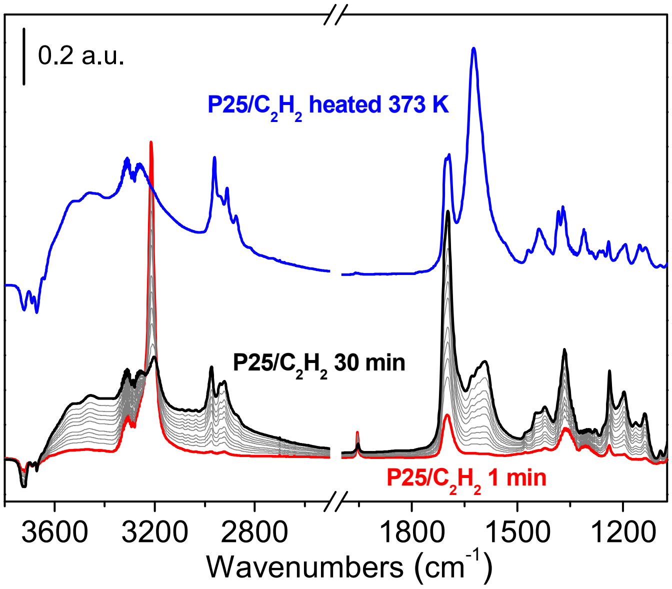


Figure 2. Acetylene/TiO_2 high pressure FTIR experiment: effect of increasing the contact time and the temperature after dosage of 120 mbar of C_2H_2 on activated TiO_2 P25. Red curve: immediately after dosage of 120 mbar of C_2H_2. Black curve: after 30 minutes at the IR beam temperature. Grey curves: intermediate contact times (about 3 minutes for each spectrum). Blue curve: after heating in acetylene atmosphere at 373 K for 30 minutes (the spectrum has been vertically shifted for the sake of clarity). As in Figure 1, all the spectra are background subtracted.

b) High C_2H_2 pressure experiment. The results of a typical high pressure FTIR experiment are reported in Figure 2. The first spectrum (red curve) was obtained immediately after dosage of 120 mbar of acetylene (a pressure chosen to avoid overwhelming of the manifestations of the reaction products by those of the gas phase). The grey spectra were recorded in sequence at interval of about 3 minutes up to a final contact time of *ca*. 30 minutes (black curve). Finally, the blue curve (upward shifted for clarity) shows the effect on the spectrum of the products formed after 30 minutes of contact of further heating the TiO_2/acetylene system at 373 K (in presence of acetylene excess in the gas phase).

In the first spectrum (red curve in Figure 2) the main bands due to the ν(C≡C) and ν(≡CH) modes of adsorbed acetylene can be still recognized respectively at 1954 and 3214 cm^{-1}. The latter is superimposed to the R and P branches of the antisymmetric C-H vibration of the gaseous phase centered at *ca*. 3290 cm^{-1} and 6 cm^{-1} downward shifted with respect to low pressure experiment. It is noteworthy that the formation of these bands at the maximum intensity is not accompanied by the complete erosion of those due to residual OH groups at 3722, 3690 and 3670 cm^{-1}. This observation further confirms that acetylene adsorption occurs also on OH free regions of the TiO_2 surface and involves coordinatively unsaturated surface sites on the extended faces and on steps and defects.

From the red curve of Figure 2 and by comparison with the spectra of Figure 1 it is also evident the vanishing intensity of the bands at 3090, 3069, 3037, 1970, 1825 and 1478 cm^{-1}, due to adsorbed benzene formed by acetylene cyclotrimerization. The formation of this reaction product, which is predominant in low pressure conditions, is hence depressed at higher acetylene pressure in favor of new reaction products which are progressively formed on increasing the contact time.

Among them, the first to be formed immediately after acetylene dosage are responsible for a complex spectrum consisting of at least a triplet of bands at 1698, 1368 (superimposed to R branch of the rotational contour centered at 1328 cm^{-1} of the $\delta_{sym}+\delta_{asym}$ mode of gaseous acetylene[27]) and 1238 cm^{-1} and possibly of weaker features at 1422, 1198, 1138, and 1092 cm^{-1} (red curve in Figure 2). Some of these bands were already present in the low pressure spectra, but with much lower intensity. The complexity of this spectrum is a clear indication that in acetylene excess we immediately observe the formation of reaction products which already have a complex structure involving more than one acetylene molecule.

A complex evolution of the spectrum is then observed on increasing the TiO_2/acetylene contact time at the IR beam temperature (grey and black curves in Figure 2):

(i) the bands due to adsorbed acetylene at 3214 and 1954 cm^{-1} decrease gradually while those of the primary products at 1698, 1368, 1238, 1422, 1198, 1138, and 1092 cm^{-1} grow in intensity in a parallel way. This demonstrates that the adsorbed surface complexes are transformed into products through an activated process;

(ii) new bands associated with conjugated double bonds [14] gradually develop at 1665 (sh), 1630, 1615, and 1590 cm^{-1}. It is noteworthy that the relative intensity of these absorptions changes with the contact time since those at lower frequencies become predominant for longer contact times. This progressive downward shift of the ν(C=C) frequency is an indication that more and more complex oligomerization products containing an increasing number of conjugated double bonds are progressively formed by acetylene insertion. These products are also responsible for the growth of other weak or very weak features at 1478 (very narrow), 1449, 1279 and 1164 cm^{-1};

(iii) the evolution of the spectra in the 2000-1000 cm^{-1} region is accompanied by the growth of a quartet of bands at 2970, 2937, 2920, 2875 (sh) cm^{-1} undoubtedly associated with the stretching vibrations of saturated $-CH_3$ and $-CH_2$ groups;[22]

(iv) the growing of the manifestations discussed in (ii) and (iii) is accompanied by the further progressive erosion of those due to the residual -OH groups of activated TiO_2 in the 3750-3600 cm^{-1} (negative bands in Figure 2) and by the parallel formation of a broad absorption covering the whole 3600-2750 cm^{-1} range. This behavior indicates the occurrence of hydrogen bonding interactions[20] which involve not only the acetylene molecules (as already discussed in the previous parts) but also the reaction products.

Together with the formation of OH groups evidenced by the IR spectra in Figure 2, the hypothesis that the oligomerization reaction is initiated by an heterolytic splitting of the acetylene molecule by reaction with a $Ti^{4+}O^{2-}$ acid/base pair is supported by the observations that it is greatly slowed down when the less Bronsted acidic methyl-acetylene molecule is used instead of acetylene and does not occur at all with dimethyl-acetylene.

It is worth underlining that outgassing the sample at room temperature under high vacuum, while causing the immediate disappearance of the bands due to the adsorbed acetylene, affects very little those related to the reaction products (see Figure S1 in the Supporting Information), as expected for irreversible species chemically adsorbed (anchored) on the surface of the TiO_2 crystals. No significant changes are observed as well if the system is heated up to 373 K in absence of acetylene in the gas phase (see Figure S1 in the Supporting Information).

On the contrary, heating at this temperature in presence of acetylene excess leads to the formation of more complex products containing a higher number of conjugated double bonds. In particular the intensity of the main peak centered at 1694 cm^{-1} is further reduced in favor of the components at 1630, 1615, and 1590 cm^{-1}, which collapse in a strong absorption centered at 1623 cm^{-1} showing an intense shoulder at 1605 cm^{-1} and a weak satellites at 1539 cm^{-1} (see blue curve in Figure 2). The further insertion of acetylene molecules is also confirmed by the complete consumption of the bands due to the adsorbed acetylene at 3214 and 1954 cm^{-1}.

Heating at 373 K in acetylene atmosphere also induces some changes of the absolute and relative intensity of the bands due to the saturated C-H groups: in particular, the couple of bands initially observed at 2970 and 2920 cm^{-1} preferentially grow in intensity and downward shift to 2960 and 2910 cm^{-1} becoming predominant with respect to the doublet at 2937 and 2875 cm^{-1} whose position remain nearly unchanged. The assignment of the of the doublet at 2960 - 2910 cm^{-1} to aliphatic -CH_3 groups is quite straightforward[22], while that of the couple at 2937 and 2875 cm^{-1} is more uncertain. It is in fact compatible with -CH_2 groups (although 2875 cm^{-1} appears as an unusually high frequency for the symmetric methylene vibration) as well as with aromatic -CH_3 methyl groups. However, it is important to stress that the reaction of acetylene with the TiO_2 surface results in the formation of hydrogen rich, saturated species. Since our reactant (C_2H_2) has a ratio C/H=1, the formation of the hydrogen rich -CH_2 and/or -CH_3 moieties requires the parallel production of an highly (or even completely) dehydrogenated counterpart characterized by the presence of a network of conjugated double bonds, as suggested by the IR spectra and further confirmed by the UV-Vis and Raman spectra discussed in the next section.

2) UV-Vis and Raman spectroscopy

The dependence of the UV-Vis spectrum of the TiO_2/C_2H_2 system in the low and high pressure conditions is shown in Figure 3. We can see that in the low pressure conditions (Figure 3a) the UV-Vis spectrum is basically not changed by the dosage of C_2H_2 and only a very weak absorption appears in the visible region of the spectrum. Conversely, in the high pressure conditions (Figure 3b), shortly after acetylene dosage a remarkable absorption in the visible is developed centered at *ca*. 470 nm. On increasing the contact time at room temperature this absorption grows in intensity while progressively shifting to *ca*. 550 nm (black curves in Figure 3b). A further redshift down to the limit of the visible region and increase of the intensity is then observed by heating at 373 K in acetylene atmosphere (blue curve in Figure 3b).

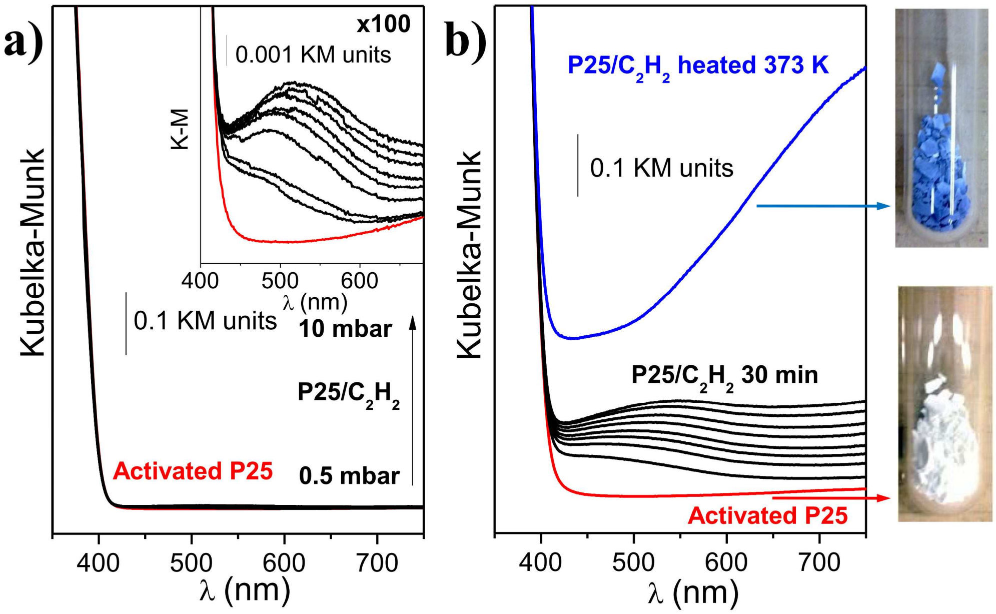


Figure 3. UV-Vis spectra of the acetylene/TiO_2 system. **a)** Effect of increasing the acetylene pressure (0.5-10 mbar range) in the same conditions used for the acetylene/TiO_2 low pressure FTIR experiment (Figure 1). In the inset a magnification (x100) of the very small absorption which appears in the visible region is reported. **b)** Effect of contact time and of thermal treatment at 373 K in the same conditions used for the acetylene/TiO_2 high pressure FTIR experiment (Figure 2). Red curve: spectrum of pure activated TiO_2 P25. Black curves (from the bottom): spectra immediately after dosage of C_2H_2 (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 TiO_2 to the final TiO_2/C_2H_2 system heated in acetylene atmosphere for 30 minutes at 373 K.

As shown in the right part of Figure 3, the evolution of these spectra reflects a change of the sample color which turns from white (activated TiO_2) to blue (after heating at 373 K in acetylene excess). The UV-Vis spectrum is very little affected upon outgassing the TiO_2/C_2H_2 system under high vacuum (results not shown for brevity). This result confirms that we are dealing with irreversible reaction products tightly anchored to the surface of the TiO_2 nanocrystals. Moreover only little changes are observed when exposing the blue samples for some hours to pure O_2 or to air. This observation suggests that the blue color is not basically associated to the presence of Ti^{3+} species which are known to give rise to a similar blue color.[32, 33]

The gradual redshift of the absorption band with the contact time supports the hypothesis already advanced on the basis of the FTIR results of the occurrence of surface reactions leading to acetylene oligomers containing an increasing number of conjugated double bonds. Indeed, in the case of linear polyenes a relation has been established between the number of C=C bonds and the position of the absorption in the electronic spectra, which further depends on the charge of the oligomers (see [14, 25] and references therein).

On the basis of this relationship, the first spectra obtained after acetylene dosage could be compatible with linear oligomers already containing 5-10 conjugated double bonds.[14] However in our case linear polyenes are not probably the most abundant products owing to the absence in the FTIR spectra of the typical bands in the 3100-2990 cm^{-1} associated with the stretching vibrations of olefinic $=CH_2$ and/or =CH- groups.[22] This observation, together with the FTIR evidence given above of the presence of a relevant number of $-CH_3$ and/or $-CH_2$ aliphatic groups, suggests that the final products obtained by reaction of acetylene on the TiO_2 surface can mainly consist in polycyclic aromatics hydrocarbons terminated with methyl and methylene groups (see Figure 5). In these products in fact extended double bonds conjugation (as required by both the FTIR and UV-Vis evidences) is combined with highly dehydrogenated region (as required by the presence of methyl and aliphatic methylenic groups).

This hypothesis seems to be supported by the Raman spectrum reported in Figure 4 of the C_2H_2/TiO_2 system after 30 min of contact, where two main bands are observed at 1590 and 1277 cm^{-1}. The former, which is known as the graphitic (G) band, it is the only feature observed in the first order Raman spectrum of highly ordered, crystalline graphite. The second band (D band) appears in disordered samples of graphite or in amorphous carbon materials containing sp^2 graphitic islands.[34] Interestingly, also the Raman spectra of polycyclic aromatic hydrocarbons (PAHs) are characterized by bands in approximately the same G and D regions.[35]

The two smaller bands, centered at about 1487 and 1150 cm^{-1}, are compatible with the Raman spectra of polyenes adsorbed on TiO_2.[14]

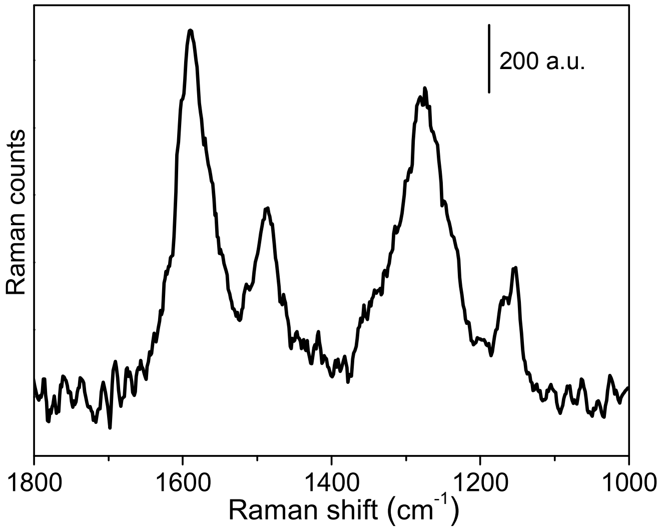


Figure 4. Raman spectra, recorded with a 514 nm laser line, of activated TiO_2 P25 30 minutes after dosage of 120 mbar of C_2H_2 at room temperature.

3) Gas chromatography–mass spectrometry analysis of the products

To achieve deeper insights about the nature of the products formed upon C_2H_2 interaction with TiO_2, we tried to remove them from the oxide surface using different solvents, including dichloromethane, toluene, hexane and acetonitrile. None of these solvents was able to extract all the reaction products since the sample did not recover its white colour after the extraction process. This findings suggest that the organic compounds, especially the heavier fraction, are tightly bound to the surface.

The products extracted with dichloromethane were analysed using gas chromatography–mass spectrometry (GC-MS). The most relevant compounds which were found are benzene, toluene, dimethylbenzene, trimethylbenezene, styrene, diphenylmethane, biphenyl, and naphthalene.

The compound extracted with the highest yield was benzene, which was clearly observed also in the FTIR spectra. Toluene, dimethylbenzene and trimethylbenezene formation is in agreement with the observation of -CH_3 groups in the FTIR spectra. The presence of styrene supports the possibility of the acetylene molecule addition to the aromatic ring which can be the first step to the formation of a second aromatic ring,[36] which is present in biphenyl, diphenylmethane and naphthalene. The observation of these molecules further confirms that the reaction of acetylene on the TiO_2 surface can lead to polyaromatic compounds as already discussed in the previous sections. As suggested by the FTIR, UV-Vis and Raman spectroscopic results, also more complex molecules containing an higher number of aromatic rings are formed, in particular when the temperature and the acetylene pressure are increased (see Figure 5). Indeed, traces of phenanthrene and pyrene have been observed using GC-MS for samples treated at 373 K. Unfortunately, it was not possible to extract the heavier products from the TiO_2 surface, therefore we can only propose a general structure for these polycyclic aromatics hydrocarbons terminated with methyl and methylene groups, which is reported in the right part of Figure 5. A forthcoming more detailed investigation, trying also to dissolve the TiO_2 matrix with HF and using LC-MS with ESI, APCI and APPI ion sources, could provide further insight on the reaction products.

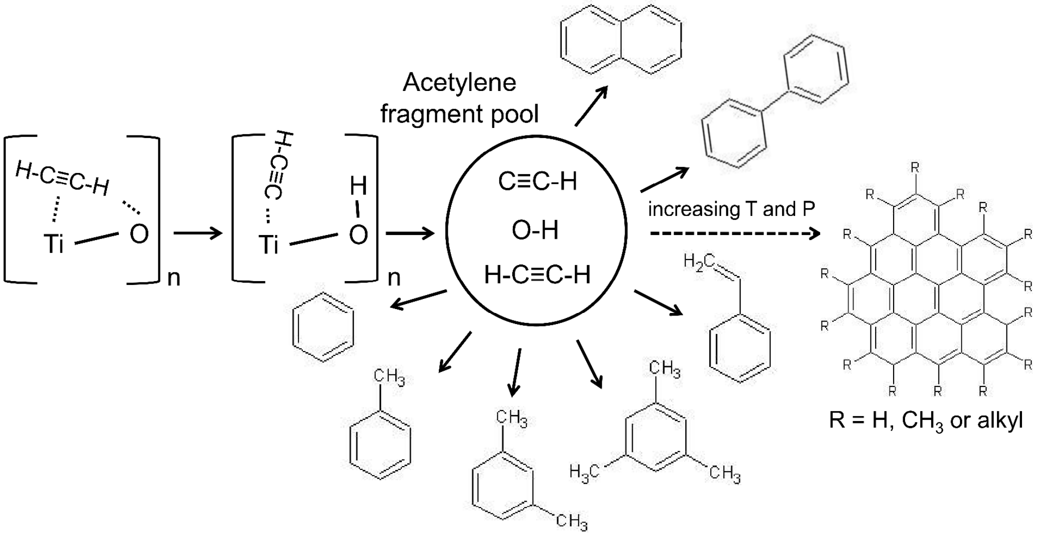


Figure 5. Schematic representation of the reaction of acetylene on TiO_2 P25 showing the first steps of the reaction (adsorption and dissociation of the C_2H_2 at the oxide surface) and the main reaction products highlighted by the spectroscopic results and by the GC-MS analysis.

Conclusions

In this contribution we showed that *in situ* acetylene oligomerization is an effective way to obtain polycyclic condensed hydrocarbons in close contact with the TiO_2 surface. These products can represent intermediate steps toward the *in situ* synthesis of graphene layers on TiO_2 in very mild conditions, allowing to avoid the anatase to rutile transformation.

We investigated the effect of the C_2H_2 pressure, contact time and heating temperature on the composition of the surface products monitoring the reaction by FTIR spectroscopy. In particular, we highlighted that in low pressure conditions ($P < 10$ mbar) at room temperature the main product is adsorbed benzene formed by acetylene cyclotrimerization, as already observed in previous studies.[23, 30, 31] Whereas, if we increase the gas pressure and the temperature, a more complex surface chemistry is prevailing, leading to larger reaction products, containing an increasing number of conjugated double bonds, and revealing an unexpectedly high surface reactivity of TiO_2 towards acetylene. From the fact that the oligomerization process is accompanied by the extensive formation of saturated $–CH_3$ and $–CH_2$ groups (as well as of surface –OH groups) it is inferred that the colored species consist of polycyclic aromatic hydrocarbons containing a considerable number of condensed rings. This hypothesis is confirmed by Raman spectroscopy and by GC-MS analysis, which allowed us to study the smaller reaction products.

The strong absorption in the visible region shown by the TiO_2/C_2H_2 systems heated at 373 K suggests that these compounds could also be useful *in situ* grown sensitizers to improve the visible light activity of the material.

Acknowledgements

Dr. A. Damin is acknowledged for the acquisition of the Raman spectra. This work has been supported by the Italian MIUR through the FIRB Project RBAP115AYN “Oxides at the nanoscale: multifunctionality and applications”.

Author Information. Corresponding authors e-mail addresses: lorenzo.mino@unito.it; giuseppe.spoto@unito.it.

References

1. A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo and H. Pettersson, *Chem. Rev.*, 2010, **110**, 6595.
2. V. Balzani, A. Credi and M. Venturi, *ChemSusChem*, 2008, **1**, 26.
3. G. P. Smestad and A. Steinfeld, *Ind. Eng. Chem. Res.*, 2012, **51**, 11828.
4. A. Kubacka, M. Fernandez-Garcia and G. Colon, *Chem. Rev.*, 2011, **112**, 1555.
5. A. Fujishima, X. T. Zhang and D. A. Tryk, *Surf. Sci. Rep.*, 2008, **63**, 515.
6. X. Chen and S. S. Mao, *Chem. Rev.*, 2007, **107**, 2891.
7. G. Barolo, S. Livraghi, M. Chiesa, M. C. Paganini and E. Giamello, *J. Phys. Chem. C*, 2012, **116**, 20887.
8. I. Justicia, P. Ordejon, G. Canto, J. L. Mozos, J. Fraxedas, G. A. Battiston, R. Gerbasi and A. Figueras, *Adv. Mater.*, 2002, **14**, 1399.
9. H. J. Zhang, G. H. Chen and D. W. Bahnemann, *J. Mater. Chem.*, 2009, **19**, 5089.
10. T. Xu and Q. Qiao, *Energy Environ. Sci.*, 2011, **4**, 2700.
11. H. Osora, W. J. Li, L. Otero and M. A. Fox, *J. Photochem. Photobiol. B-Biol.*, 1998, **43**, 232.
12. A. K. M. Fung, B. K. W. Chiu and M. H. W. Lam, *Water Res.*, 2003, **37**, 1939.
13. G. C. Vougioukalakis, A. I. Philippopoulos, T. Stergiopoulos and P. Falaras, *Coord. Chem. Rev.*, 2011, **255**, 2602.
14. R. Rives-Arnau and N. Sheppard, *J. Chem. Soc., Faraday Trans.*, 1980, **76**, 394.
15. H. He, C. Liu, K. D. Dubois, T. Jin, M. E. Louis and G. Li, *Ind. Eng. Chem. Res.*, 2012, **51**.
16. R. Leary and A. Westwood, *Carbon*, 2011, **49**, 741.
17. Q. Xiang, J. Yu and M. Jaroniec, *Chem. Soc. Rev.*, 2012, **41**, 782.
18. N. Zhang, Y. Zhang and Y.-J. Xu, *Nanoscale*, 2012, **4**, 5792.
19. T. Kamegawa, D. Yamahana and H. Yamashita, *J. Phys. Chem. C*, 2010, **114**, 15049.
20. L. Mino, G. Spoto, S. Bordiga and A. Zecchina, *J. Phys. Chem. C*, 2012, **116**, 17008.
21. L. Mino, G. Spoto, S. Bordiga and A. Zecchina, *J. Phys. Chem. C*, 2013, **117**, 11186.
22. N. B. Colthup, L. H. Daly and S. E. Wiberley, *Introduction to Infrared and Raman spectroscopy*, Academic Press, New York, 1975.
23. Y. Sakata, Z. H. Liu, H. Imamura and S. Tsuchiya, *J. Chem. Soc.-Chem. Commun.*, 1991, 1392.
24. S. Huber and H. Knozinger, *J. Mol. Catal. A-Chem.*, 1999, **141**, 117.
25. S. Bordiga, G. Ricchiardi, G. Spoto, D. Scarano, L. Carnelli, A. Zecchina and C. O. Arean, *J. Chem. Soc.-Faraday Trans.*, 1993, **89**, 1843.
26. E. Broclawik, J. Zalucka, P. Kozyra, M. Mitoraj and J. Datka, *J. Phys. Chem. C*, 2010, **114**, 9808.
27. G. Herzberg, *Molecular spectra and molecular structure II. Infrared and Raman spectra of polyatomic molecules*, D. Van Nostrand Company, Inc., New York, 1947
28. C. Deiana, E. Fois, S. Coluccia and G. Martra, *J. Phys. Chem. C*, 2010, **114**, 21531.
29. A. V. Ivanov, A. E. Koklin, E. B. Uvarova and L. M. Kustov, *Phys. Chem. Chem. Phys.*, 2003, **5**, 4718.
30. K. G. Pierce and M. A. Barteau, *J. Phys. Chem.*, 1994, **98**, 3882.
31. Y. P. Ma, W. Xue, Z. C. Wang, M. F. Ge and S. G. He, *J. Phys. Chem. A*, 2008, **112**, 3731.

32. T. R. Gordon, M. Cargnello, T. Paik, F. Mangolini, R. T. Weber, P. Fornasiero and C. B. Murray, *J. Am. Chem. Soc.*, 2012, **134**, 6751.
33. S. S. Pan, W. Lu, Y. H. Zhao, W. Tong, M. Li, L. M. Jin, J. Y. Choi, F. Qi, S. G. Chen, L. F. Fei and S. F. Yu, *ACS Appl. Mater. Interfaces*, 2013, **5**, 12784.
34. A. C. Ferrari and J. Robertson, *Phys. Rev. B*, 2000, **61**, 14095.
35. F. Negri, C. Castiglioni, M. Tommasini and G. Zerbi, *J. Phys. Chem. A*, 2002, **106**, 3306.
36. H. Richter and J. B. Howard, *Prog. Energy Combust. Sci.*, 2000, **26**, 565.