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Mechanism of cyclo-oligomerisation of C₂H₂ on anatase TiO₂ (101) and (001) surfaces and their reduction: Electron Paramagnetic Resonance and Density Functional Theory study

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Abstract

De-hydroxylated, hydroxylated and hydrated anatase TiO₂ samples have been exposed to acetylene at RT. The interaction leads to formation of polycyclic aromatic hydrocarbons (PAH) and is accompanied by the appearance of Ti³⁺ ions, as shown by Electron Paramagnetic Resonance spectra. Fully or partly de-hydroxylated samples show the higher reactivity whereas the hydrated samples are chemically inert. The experimental results point towards a crucial role of the more reactive (001) facets of anatase nanoparticles. Density functional theory calculations show that acetylene physisorbs on the anatase (101) surface without activation of the C-H bond. The reduced (101) surface (O vacancies) leads to acetylene activation but not to dissociative adsorption. On the contrary, the de-hydroxylated (001) anatase surface is very active and leads to the spontaneous splitting of the C-H bond with formation of a Ti-C₂H and an OH groups. This is followed by subsequent additions of C₂H₂ molecules with formation of PAH. During the dissociation of C₂H₂ radical species do not form and electrons are not transferred to the surface because direct Ti-C covalent bond forms on the surface. However, the ring closure in the formation of the aromatic compounds leaves behind H atoms that donate their valence electrons to the oxide. This results in the appearance of EPR active Ti³⁺ centers.

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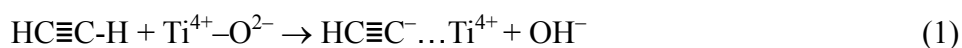
1. Introduction

One of the most relevant mechanism of catalysts deactivation is the formation of large aromatic hydrocarbon molecules, carbonaceous species or carbon coke on the surface of the catalyst, a process that blocks the active sites and kills the corresponding activity.^[1,2] This is classified as a poisoning effect of chemical type as it derives from chemical reactions occurring on the surface of the catalyst. Other deactivation mechanisms are fouling, i.e. physical deposition of species from the fluid phase, thermally induced loss of surface area, sintering, etc.^[1]

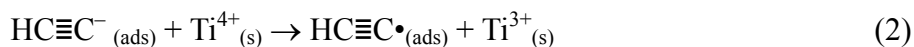
Formation of carbonaceous species is of key importance in every catalytic reaction, but is particularly relevant when the catalyst is in contact with carbon-derived molecules like in the production of biofuels from cellulosic biomass.^[3,4,5] A key step in bio-oil upgrading is the ketonization of carboxylic acids,^[5,6,7] which occurs on oxides like TiO₂ and ZrO₂ often activated by the presence of supported metal particles. This detrimental phenomenon of catalyst deactivation can be minimized by using catalysts that do not promote the formation of large aromatic carbon species, for instance by blocking the active sites or facets that can promote these undesired processes.

In this work we consider the C₂H₂-TiO₂ reaction, a relatively simple process that has been investigated recently in some detail and that provides an excellent example of how the surface of an oxide catalyst can be modified in order to avoid or to promote a given process. It was found that the heterolytic dissociative chemisorption of acetylene on TiO₂ gives rise to a redox interaction between the adsorbate and the acid-basic sites of the oxide surface, resulting in the formation of polyaromatic molecules with an increase of C/H ratio.^[8] Since both the C/H ratio and the degree of polymerization of acetylene tend to grow with time and temperature increase, the surface process can also be seen under a different point of view, alternative to that of surface deactivation. It is in fact evident that the limit of a progressive cyclo-polymerisation and dehydrogenation of acetylene is a sort of extended graphene-like layer. This consideration adds a further reason of interest to the described system in that the preparation of graphene-oxide nanocomposites have been pursued by various research groups in the recent past.^[9,10]

In a recent paper devoted to unravel the mechanism of the whole C₂H₂-TiO₂ interaction, Biedrzycki et al. suggested that this heterolytic splitting requires a pair of Ti⁴⁺-O²⁻ ions which enables the polarization of the C-H bond, followed by the formation of a titanium monoacetylide complex and an hydroxyl group.^[11] The corresponding initial C-H dissociative adsorption can be written as:



Based on the observation of an increase in the EPR signal, it has been suggested that after the acetylide carbanions is formed *via* Eq 1, one electron is transferred to an electron accepting site on the oxide surface with consequent reduction of the oxide (formation of Ti^{3+} ions):



(here "ads" and "s" indicate adsorbed and surface species, respectively). Based on reactions (1) and (2), the formation of OH^- groups and Ti^{3+} ions is regarded as the initial step to generate polyaromatic hydrocarbons. For example, naphthalene could be obtained by reaction of 3 C_2H_2 molecules and 2 $\text{HC}\equiv\text{C}\cdot$ radicals:



There are at least three aspects that still need to be clarified about these reactions and their consequences. The first one is the role of surface hydroxylation on the efficiency of the process. Oxide surfaces can split water and be covered by OH groups that can lead to a substantial change in the surface reactivity. The second question to be answered is the nature of the active sites and, most important, of the active facets of the anatase nanoparticles that promote the reaction. Finally, the detailed mechanism that leads to an electron transfer and to the reduction of the oxide surface still needs to be clarified.

For this reason we have performed additional experiments that have been complemented by a detailed theoretical analysis of the process. Three different anatase samples with various level of hydroxylation have been prepared and have been exposed to acetylene at room temperature (RT). The progression of the self- assembling reaction on variously hydroxylated materials has been followed by EPR monitoring the intensity of the Ti^{3+} signal as a function of time, this spectroscopic parameter being actually proportional to the degree of advancement of the process.^[11]

To the best of our knowledge the bonding and dissociative adsorption of acetylene on titania have not been addressed computationally before. Therefore, we performed DFT calculations in the attempt to better understand the mechanism of acetylene activation, the reaction of polymerization from adsorbed C_2H_2 molecules to C_{10}H_8 and the formation of Ti^{3+} centers in the oxide. We investigated in particular the reactivity of the quantitatively dominant (101) facet and that of the minority (001) one considering fully dehydroxylated surfaces only as the experimental results (*vide infra*) show unambiguously that the reaction does not take place on hydrated anatase nanoparticles. In the following of the paper it will be provided evidence that only the less abundant (001) surfaces are able to promote the acetylene self assembly reactions with the formation of large carbon units

occurring in parallel with an electron transfer from the adsorbate to the oxide surface in the course of the reaction.

In this study we only considered thermodynamic aspects of the reaction, without computing the energy barriers for the various reaction steps. However, it is known experimentally that the reaction occurs already at RT, and therefore the corresponding energy barriers must be relatively small.

The paper is organized as follows. In Section 2 we report the details of the experimental and theoretical approaches used. Section 3 is dedicated to the results and is divided in sub-sections. Section 3.1 reports the EPR spectra and their evolution as function of time and level of hydroxylation of the anatase samples. In § 3.2 we report the DFT results on the interaction of acetylene with the dominant (101) surface of anatase TiO₂. In § 3.3 the reactivity of the (001) facet is discussed based on DFT calculations. Summary and conclusions are reported in Section 4.

2. Experimental and theoretical methods

2.1 Experimental details

The anatase TiO₂ sample was obtained via sol-gel synthesis as described in a previous paper.^[12] In the present work three samples of the same batch were submitted to different activation treatments of the surface in order to evaluate the role of the surface hydroxylation in the acetylene/TiO₂ reaction. All the treatments were performed in the same cells used for the spectroscopic measurements and allowing dosage of acetylene from the gas phase. Before use, acetylene 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 C₂H₂ on the samples.

Sample 1. Fully de-hydroxylated anatase. First, the material was outgassed under high vacuum at 673 K for 2 hours in order to remove adsorbed water, surface hydroxyl groups, and other surface impurities (if any). Then oxidation with 20 mbar of O₂ at the same temperature was performed for 1 h to obtain a fully oxidized, stoichiometric oxide. Next, the sample was cooled down to room temperature in O₂ atmosphere and the gas phase was eventually removed at this temperature by pumping off. Samples prepared by this procedure will be indicated in the text as “activated”.

Sample 2. “Hydroxylated” anatase. The material was first activated (as described for sample 1) and then contacted with water vapor ($P_{\text{H}_2\text{O}} = 30\text{mbar}$) at RT for 1.5 hours. The material was then outgassed at 423K for 30 minutes in order to remove physisorbed water leaving unaffected the OH⁻ groups due to water dissociation.^[13] In the final step the hydroxylated material was reoxidized in O₂ at 423K for 1h in order to recover the fully oxidation state weakly modified by the previous

treatment in vacuo at 423K.

Sample 3. Hydrated anatase. Same as sample 2 but outgassed, after the first activation, at room temperature (RT) rather than at 423K. In this conditions some physisorbed water is still present beside the OH groups.^[13]

Continuous Wave EPR spectra (CW-EPR) were recorded by a X-band Bruker EMX spectrometer equipped with cylindrical cavity and operating at a 100 kHz field modulation. The measurements were carried out at liquid nitrogen temperature (77 K) in cells that can be connected to a conventional high-vacuum apparatus (residual pressure $< 10^{-4}$ mbar).

2.2 Computational Details

Density functional theory (DFT) calculations were performed using the VASP 5.3 code^[14] and the projector augmented wave (PAW) approach.^[15,16] The exchange and correlation energy was computed by means of the generalized gradient approximation (GGA) using the functional proposed by Perdew-Burke-Ernzerhof (PBE).^[17] In order to partly correct for the self-interaction error, the GGA+U approach was employed.^[18,19] This leads to a better estimate of the band gap and a reduced propensity to delocalize the electron density which is typical of standard GGA approaches.^[20,21] In this study, we set the Hubbard parameters to $U-J = 3$ for Ti, which assures a reasonable compromise between the structural and electronic properties of TiO_2 ^[22,23,24] and the energetics of surface reactions.^[25] Van der Waals (vdW) interactions between the adsorbed species and titania have been included using the pair-wise force field implemented by Grimme (DFT-D2).^[26] However, we replaced the C_6 parameters and van der Waals radii R_0 of Ti ions by those of Ar since the size of the Ar atom is closer to that of the Ti^{4+} cation.^[27] This approach is referred to as PBE-D2' in the following.

We set the kinetic energy cut-off for the plane-wave expansion to 400 eV and a Γ -centered k-point sampling was employed. The slab dimensions of anatase (101) and (001) surfaces are 11.54 Å x 10.48 Å x 16.61 Å ($\text{Ti}_{60}\text{O}_{120}$) and 11.54 Å x 11.54 Å x 15.48 Å ($\text{Ti}_{63}\text{O}_{126}$), respectively. To avoid the interaction between the replica of the slab, at least 14 Å of empty space above the adsorbate was included. Relaxation of the ionic coordinates was carried out with a threshold of 10^{-2} eV/Å; the electronic loop was performed within a tolerance of 10^{-5} eV. Atomic charges have been obtained on the basis of the Bader partition method.^[28]

3. Results and Discussion

3.1 Acetylene reaction from EPR spectra

As shown in previous work 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 with respect to the monomer.^[8] In short, this gas-solid interaction leads to the formation of benzene (cyclotrimerization) and of PAH (polycyclic aromatic hydrocarbons) at the surface and of Ti^{3+} ions in the solid that are formed by electron injection from the surface reactants.^[11]

The appearance of the Ti^{3+} signal can thus be adopted as an indirect evidence of the occurrence of the acetylene self-assembly processes.

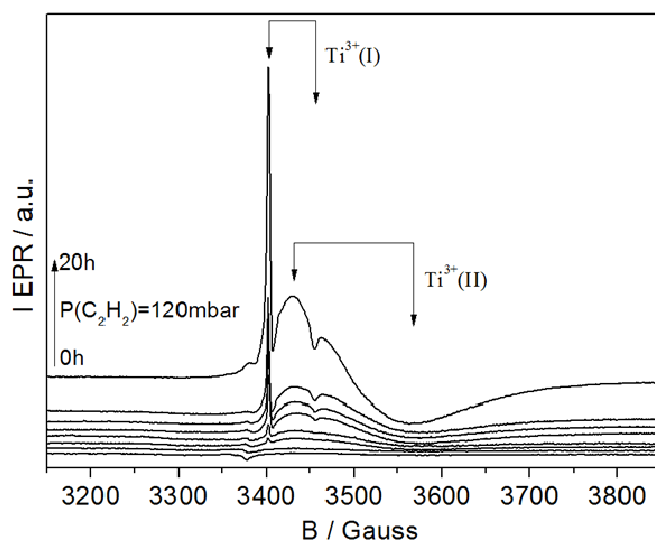


Figure 1 - Evolution with time (0-20 h) of the EPR spectra observed after contact of activated anatase with C_2H_2 . Since the integrated intensity depends on the square of the linewidth, the $\text{Ti}^{3+}(\text{II})$ species is much more abundant than $\text{Ti}^{3+}(\text{I})$.

Figure 1 shows the evolution of the EPR spectra recorded in the case of the activated anatase sample contacted with acetylene at RT. The EPR spectrum is due to the superimposition of two distinct Ti^{3+} signals. The first one (labeled as $\text{Ti}^{3+}(\text{I})$ in Fig. 1) is narrow and shows an axial structure characterized by $g_{\perp}=1.992$, $g_{\parallel}=1.962$ while the second (labeled as $\text{Ti}^{3+}(\text{II})$ in Fig. 1) is a broad and featureless signal centered at $g=1.93$. The first species is predominant in electron rich TiO_2 systems obtained via mild reduction pathways such as the electron injection occurring upon contact with atomic hydrogen or Na vapors.^[29] The second signal ($\text{Ti}^{3+}(\text{II})$) is instead predominant in heavily reduced TiO_2 systems, obtained for example via thermal annealing in vacuum at high temperature and is due to the presence of Ti^{3+} in the disordered environment at the surface of the nanocrystals.^[30] Its large linewidth reflects the complex situation occurring on the defective reduced surface. The intensity of both signals growth with time and the corresponding spectrum reaches a maximum after about 20 hours (upper signal in Fig. 1). The features of the various spectra

in Fig. 1 are the same except for the intensity indicating that we are in presence of an activated phenomenon with a relatively low rate of reaction. Interestingly, the solid propagates a minor fraction of the electrons released during the surface interaction towards the bulk (where they are trapped by regular Ti^{4+} lattice ions) while the large majority of the electrons remains close to the surface ($\text{Ti}^{3+}(\text{II})$) somehow in contact with the organic oligomeric aggregates.

The comparison of the EPR spectra obtained in the case of C_2H_2 contact for 20 h with the three samples obtained following the three different activation procedures described in the Experimental Section is reported in Fig. 2.

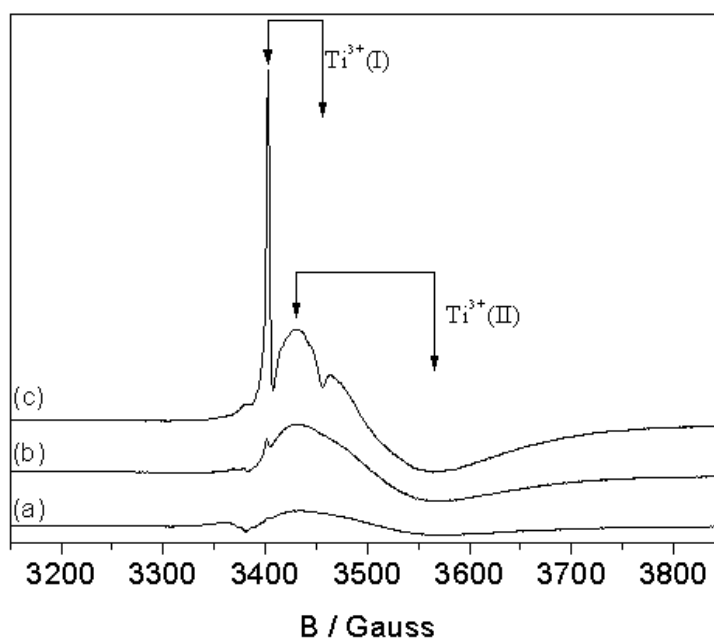


Figure 2 - EPR spectra of Ti^{3+} centres generated via C_2H_2 interaction (120 mbar for 20 h at RT) with the surface of TiO_2 . (a) Hydrated, (b) hydroxylated, and (c) activated, fully dehydroxylated surfaces, respectively.

This figure clearly indicates that the reactivity of the activated surface (Fig. 2c) is much larger than that shown by both the hydrated sample (evacuation at RT, 2a) and that outgassed at 423K (hydroxylated sample, 2b). This means that the presence of free Ti^{4+} and O^{2-} ions at the surface is essential to entail acetylene self-assembly. Furthermore, comparison between the spectra of the two partially hydrated materials (Fig. 2 a and b) suggests additional considerations.

The process of hydration-dehydration of the anatase surface was carefully followed in the past by infra-red spectroscopy (on polycrystalline materials) and, later, investigated by theoretical calculations. ^[31,32] IR spectroscopy clearly indicates that molecularly adsorbed water is totally removed by outgassing between RT and 423K while higher temperatures are needed to get rid of the

surface hydroxyl groups (i.e. of dissociatively adsorbed water). The hydrated sample therefore contains, beside surface OH⁻ groups, molecular water ubiquitously physisorbed at the surface which is absent in the hydroxylated material (423K). Furthermore, recent theoretical calculations^[31] and photoelectron spectroscopy studies on single crystals^[33] converge in indicating that, among the most commonly exposed facets of anatase, the (001) surface is the only one capable of dissociating water.^[33] It is reasonable therefore to describe the hydroxylated material as containing OH⁻ groups mainly at the (001) facet, while, in the same sample, the (101) surface should be essentially water free. The high reactivity of the fully dehydroxylated (activated) material, Fig. 2c, thus suggests the essential role of the (001) surface in the process of C₂H₂ polymerization. The hydroxylated sample, Fig. 2b, whose (101) surfaces (reasonably more abundant) are OH⁻ free, is in fact much less active than the activated one. The reactivity is further hampered if also molecular water, Fig. 2a, covers the surface.

In summary, the results indicate that the reaction of C₂H₂ polymerization at the anatase surface is slow and activated. The reaction involves electron injection in the solid, the electrons being distributed between bulk and surface Ti⁴⁺ ions with a prevalence of the second type (Fig.1). The comparison of samples with different degree of hydration points to the essential role of the (001) surface in entailing the complex reactivity between acetylene and the anatase surface while the (101) facet does not contribute (or, at least, contributes to a minor extent) to the process. This is consistent with experimental results^[34,35,36] and theoretical evidence^[32] suggesting that in anatase nanoparticles the minority (001) surface is photo-catalytically more reactive than the dominant (101) surface and that this surface plays a key role in the reactivity of anatase powders. With this in mind we have tackled the computational study of the interaction of C₂H₂ with these two TiO₂ surfaces.

3.2 DFT calculations on C₂H₂ on anatase (101) surface

The (101) is the most stable surface of anatase, and therefore it is logical to start the investigation of the reaction between acetylene and TiO₂ from this surface. The adsorption energy is calculated on the basis of the following equation:

$$\Delta E = E(\text{C}_2\text{H}_2/\text{TiO}_2) - E(\text{TiO}_2) - E(\text{C}_2\text{H}_2)_{(\text{g})} \quad (4)$$

Various adsorption sites have been considered, and both molecular, Fig. 3(a), and dissociative, Fig. 3(b), adsorptions have been studied. It turns out that on the (101) surface of stoichiometric anatase molecular adsorption with a $\Delta E = -0.53$ eV is preferred compared to dissociative adsorption. This latter process, with $\Delta E = +0.06$ eV, see Table 1, is in fact endothermic. In the undissociated state the molecule remains linear, and undistorted, Fig. 3(a). The interaction is largely due to dispersion forces and the state is typical of physisorbed species. More interesting is the dissociative adsorption, Fig. 3(b), despite the fact that it is thermodynamically unfavorable. Here the molecule has been split

into a CCH^- and an H^+ fragments adsorbed on top of surface Ti^{4+} and O^{2-} ions, respectively, Fig. 3(b). Both singlet and triplet electronic configurations have been considered in order to see if the bond breaking mechanism follows an homolytic dissociation, with formation of two radicals, or an heterolytic dissociation, with formation of ionic species. The singlet turns out to be preferred and the adsorbed species can be formally described as $\text{C}_2\text{H}^- + \text{H}^+$, Fig. 3(b). Notice however that the use of the notation CCH^- and H^+ has mainly the scope to indicate that two fragments in singlet ground state are produced by the reaction with the surface. In fact, one could see the process as the result of the homolytic splitting of the HCC-H bond, with formation of H^\bullet and $^\bullet\text{CCH}$ radicals. The H^\bullet atom binds to a surface O^{2-} ion with formation of a proton, H^+ , plus one electron that reduces a surface Ti^{4+} ion to Ti^{3+} ; the $\text{Ti}^{3+}_{(s)}$ $3d^1$ ion combines with the $^\bullet\text{CCH}$ radical to form a σ bond and a stable Ti-CCH surface complex, Fig. 3(b). In the end, the two processes are fully equivalent and what is important is that according to the calculations no stable radical species are formed as a consequence of the C-H bond dissociation.

These results show that the regular (101) surface of anatase is rather inert towards acetylene and that activation of the molecule does not occur on the non-defective surface where only physisorption occurs, in line with the experimental data. Furthermore, no change in the concentration of Ti^{3+} centers and in the intensity of the corresponding EPR signal is expected.

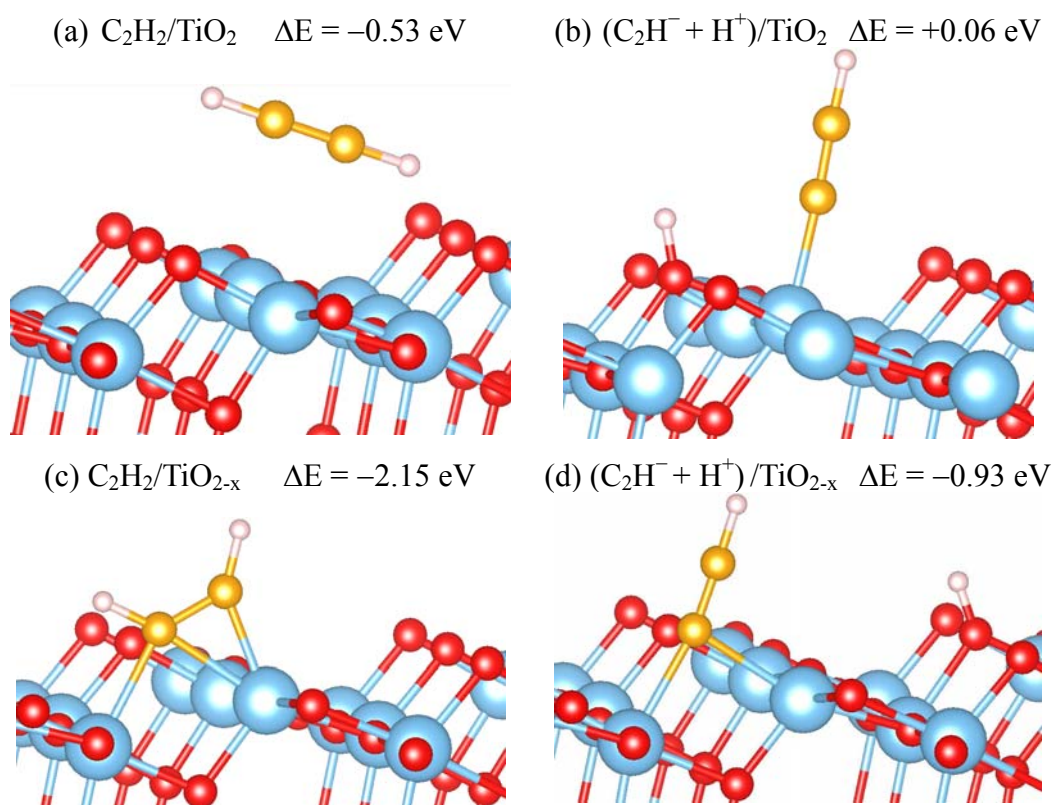


Figure 3 - Optimized structures of acetylene interacting with anatase. (a) molecular adsorption (physisorption) and (b) dissociative adsorption on the stoichiometric TiO_2 (101) surface ($\text{Ti}_{60}\text{O}_{120}$ atoms in the supercell). (c) molecular adsorption and (d) dissociative adsorption on the reduced TiO_{2-x} (101) surface ($\text{Ti}_{60}\text{O}_{119}$ atoms in the supercell).

Next, we have considered the interaction of acetylene on a reduced anatase (101) surface, Fig. 3(c) and 3(d). To this end we have considered a (101) surface where an O atom has been removed, forming in this way an oxygen vacancy either on surface (Vo1) or subsurface (Vo4) sites (for the nomenclature refer to ref. 37). Not surprisingly, the presence of the defect results in an enhanced reactivity. In a first configuration the C_2H_2 molecule is adsorbed with the C-C bond parallel to the surface and the π electrons pointing towards the cavity left by the missing oxygen, Fig. 3(c). The binding energy becomes large, $\Delta E = -2.15$ eV, Table 1, and the molecule is considerably distorted with pronounced loss of linearity. The ground state is singlet. The reason is that the two extra electrons associated to the O vacancy in TiO_2 combine with the two electrons of one of the broken π bonds of acetylene which therefore loses triple bond character. The hybridization of C atoms changes from sp to sp^2 and the CCH angle changes substantially, Fig. 3(c). The two C atoms of the C_2H_2 molecule form direct covalent bonds with the Ti^{3+} ions of the vacancy. Notice that the systems can also be seen as a negatively charged $\text{C}_2\text{H}_2^{2-}$ molecule interacting with two Ti^{4+} sites. Despite this notable activation, the C-H bonds remain intact.

In a second approach we considered a dissociated acetylene molecule, with one of the C atoms taking the place of the missing oxygen on the surface, and one H atom going to a surface O_{2c} ion to form an OH group, Fig. 3(d). This dissociative adsorption is exothermic, $\Delta E = -0.93$ eV (Table 1), but is more than 1 eV higher in energy than the molecular state described above, Fig. 3(c). The lowest configuration for the dissociative adsorption of Fig. 3(d) is a triplet state, but the two excess electrons are localized on two subsurface Ti^{3+} ions which are not involved in the bonding with the hydrocarbon fragments, Fig. 4(a). The fragments that form upon dissociation can be safely described as CCH^- and H^+ where the C-end of CCH^- replaces the missing oxygen.

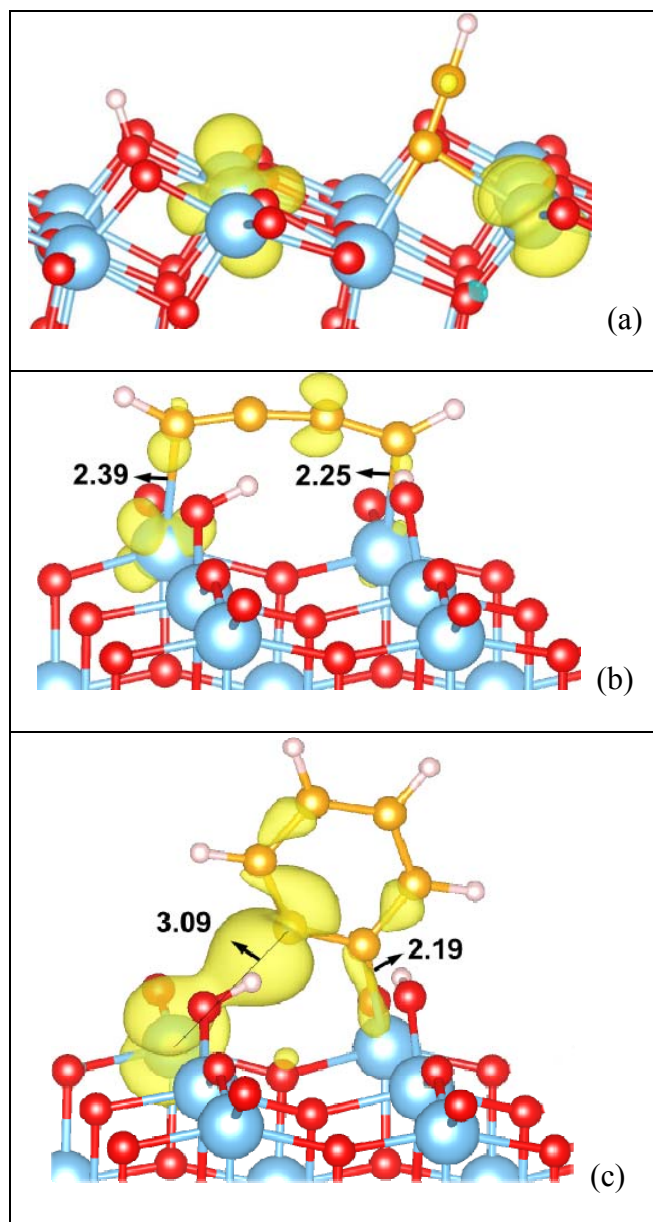


Figure 4 - Spin density ($0.005 \text{ e}/\text{\AA}^3$) in triplet configurations for hydrocarbon fragments bound to the anatase surface. (a) Dissociative adsorption of C_2H_2 on an O vacancy ($\text{Vo}1$) of the (101) surface: two unpaired electrons due to the vacancy formation are localized on lattice Ti^{3+} ions. (b) C_4H_2 unit adsorbed on stoichiometric (001) surface: the triplet excited state corresponds to breaking a Ti-C σ bond with formation of a Ti^{3+} ion and a $\text{C}_4\text{H}_2^\bullet$ radical. (c) C_6H_4 unit adsorbed on stoichiometric (001) surface: the triplet excited state corresponds to breaking a Ti-C σ bond with formation of a Ti^{3+} ion and a $\text{C}_6\text{H}_4^\bullet$ radical.

We also considered a reduced surface where O has been removed from the deeper layers of the oxide surface (see $\text{Vo}4$ in Table 1). This leads to an electron rich system but without morphological irregularities in the top layer. The results show that the system behaves as the stoichiometric surface

and that dissociative adsorption is highly endothermic, Table 1. Therefore, the calculations indicate that only if the O vacancies are present in the surface layer they can have an effect on the adsorption of acetylene.

These results indicate that the (101) surface is rather unreactive towards acetylene and that molecular activation (but not dissociation) is only possible in correspondence of point defects like surface O vacancies. In the following step we have considered the (001) anatase surface. Anatase nanoparticles most frequently expose (101) surfaces, together with a smaller amount of (001) facets.

Table 1 Energies (in eV) and spin population in the unit cell ($N_\alpha - N_\beta$, in μ_B) of acetylene molecules interacting with the stoichiometric and reduced anatase (101) and the stoichiometric (001) surfaces (PBE+U-D2' results).

Surface	System	Surface species	Fig.	ΔE^a (eV)	ΔE_{LH}^a (eV)	Spin (μ_B)
101	Stoichiometric	C_2H_2/TiO_2	3(a)	-0.53	0.0	0
		$(C_2H^- + H^+)/TiO_2$	3(b)	0.06	-	0
101	Reduced (Vo1)	C_2H_2/TiO_{2-x}	3(c)	-2.15	-	0
	Reduced (Vo1)	$(C_2H^- + H^+)/TiO_{2-x}$	3(d)	-0.93	-	2
	Reduced (Vo4)	$(C_2H^- + H^+)/TiO_{2-x}$	-	+0.42	-	2
001	Stoichiometric	$(C_2H^- + H^+)/TiO_2$	5(a)	-2.03	-1.50	0
			-	-0.06	-	2
		$(C_4H_2^{2-} + 2H^+)/TiO_2$	5(b)	-2.26	-1.73	0
			4(b)	-1.26	-	2
		$(C_6H_4^{2-} + 2H^+)/TiO_2$	5(c)	-3.91	-3.38	0
			4(c)	-2.65	-	2
		$(C_{10}H_8 + 2H^+)/TiO_2$	6(b)	-7.52	-6.46	0
		$C_{10}H_{8(g)} + (2H^+/TiO_2)$	7(b)	-5.98	-4.92	0

(a) ΔE is the reaction energy computed with respect to gas-phase acetylene; ΔE_{LH} is the reaction energy computed with respect to an adsorbed acetylene molecule (see text).

3.3 DFT calculations of cyclotrimerization of C_2H_2 on anatase (001) surface

The higher reactivity of the (001) surface is shown by the fact that the simple adsorption of

acetylene near a $\text{Ti}^{4+}\text{-O}^{2-}$ pair results in spontaneous molecular dissociation, Fig. 5(a). Starting the geometry optimization with the molecule parallel to the surface, one observes the formation of an acetylide carbanion bound to a Ti^{4+} ion and an hydroxyl group, Fig. 5(a). The adsorption energy with respect to acetylene in gas-phase is $\Delta E = -2.03$ eV, which means that the chemisorbed state of acetylene on the (001) surface is 1.50 eV more stable than physisorbed acetylene on the (101) surface. Also in this case we notice that the system can be described as the result of the formation of two H^\bullet and $\bullet\text{CCH}$ radicals, with H^\bullet that donates one electron to the surface with formation of H^+ bound to a surface O^{2-} ion (surface hydroxyl OH^-) and a $\text{Ti}^{3+}_{(s)}$ center. This latter species binds the $\bullet\text{CCH}$ radical to form a Ti-CCH closed shell surface complex which, in analogy to Section 3.2 can also formally be described as a surface $\text{Ti}^{4+}\text{-C}_2\text{H}^-$ complex. It is interesting to analyze what happens when one forces the system to be in a triplet state. First of all this is 2 eV higher in energy, Table 1; furthermore, the spin density (not shown) appears within the TiO_2 phase, indicating that the lowest singlet-triplet excitation involves O and Ti atoms of the support and is not connected to any local excitation of the Ti-CCH fragment. This is a sign of the fact that a strong Ti-C surface bond is formed and is consistent with the high singlet-triplet excitation energy.

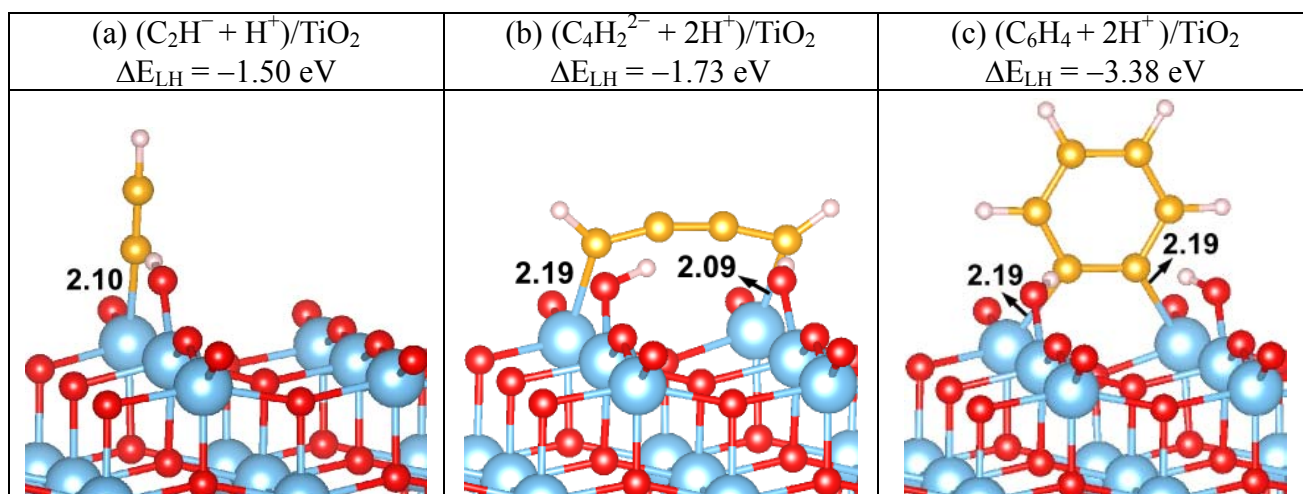
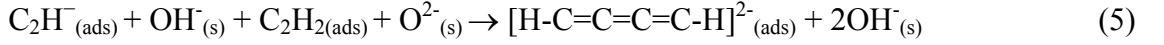


Figure 5 - Cyclotrimerization of C_2H_2 to $\text{C}_6\text{H}_4 + 2\text{OH}$ on the stoichiometric anatase TiO_2 (001) surface ($\text{Ti}_{63}\text{O}_{126}$ atoms in the supercell). The energies reported refer to a Langmuir-Hinshelwood reaction mechanism (see text).

Given the relatively low binding of acetylene on the (101) surface, -0.53 eV, it can be assumed that the molecule will easily diffuse on this surface and reach other facets on titania nanoparticles like the (001) one where the reaction can take place, following a Langmuir-Hinshelwood (LH) mechanism. Of course, we have no evidence that the reaction follows a LH mechanism and not an Eley-Rideal one. Assuming that the reaction follows a LH mechanism, we simply include the cost

to detach the molecule from the surface in the energetic of the reaction. Under the assumption of a LH mechanism, other acetylene molecules can also diffuse and react with the C_2H^- fragment:

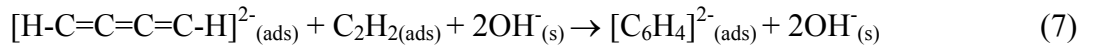


This results in the dimerization of acetylene with formation of a $[C_4H_2]^{2-}$ dianion plus another hydroxyl group, and another Ti^{3+} ion, Fig. 5(b). This second step is therefore strictly similar to the first one, apart from the final coupling of the two negative fragments. The $H-C=C=C-C-H$ unit can be better described as a $H-C^{\bullet}=C=C^{\bullet}-C-H$ biradical species interacting with two surface $Ti^{3+}_{(s)}$ ions. In fact, the hydrocarbon chain is linked to the surface via formation of two $Ti-C$ σ bonds, Fig. 5(b). The reaction with the second acetylene, eq. 5, leads to an energy gain of -1.73 eV computed with respect to a $C_2H_{2(ads)}$ molecule adsorbed on the most stable (101) face (LH mechanism):

$$\Delta E_{LH} = E[(C_4H_2^{2-} + 2OH^-)/TiO_2(001)] - E[C_2H_2/TiO_2(101)] - E[(C_2H^- + OH^-)/TiO_2(001)] \quad (6)$$

This means that, from a thermodynamic point of view, the dimerization and formation of a carbon chain is very favourable. The calculation of the triplet state for the $C_4H_2^{2-}$ surface complex leads to an excited state which is 1.0 eV higher than the singlet ground state, Table 1. In the triplet configuration one electron remains localized on a Ti^{3+} ion while the second is delocalized over the $H-C=C=C-C-H$ fragment, Fig. 4(b). This reinforces the fact that a direct covalent bond is formed between Ti 3d and C 2sp orbitals. The triplet configuration corresponds to the homolytic breaking of one of these bonds, Fig. 4(b). In fact, the $Ti-C$ distances, 2.09 and 2.19 Å in the singlet configuration, become 2.25 and 2.39 Å in the triplet one, Fig. 4(b).

In the next step we assume that another $C_2H_{2(ads)}$ molecule, always diffusing from the (101) surface, reaches the $C_4H_2^{2-}$ unit, Fig. 5(b), and reacts with it to form a six-membered C_6H_4 ring, Fig. 5(c):



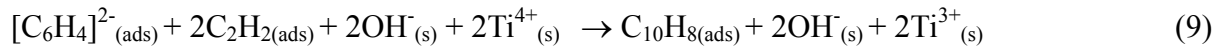
The reaction energy, defined as:

$$\Delta E_{LH} = E[(C_6H_4^{2-} + 2OH^-)/TiO_2(001)] - E[C_2H_2/TiO_2(101)] - E[(C_4H_2^{2-} + 2OH^-)/TiO_2(001)] \quad (8)$$

is very large and negative, -3.38 eV. The C_6H_4 fragment has two C atoms with radical character directly pointing towards two surface Ti^{3+} ions and is bound to the surface via two $Ti-C$ σ bonds, Fig. 5(c). This third step differs from the two previous ones in that it is a simple addition of a C_2H_2 molecule to the $C_4H_2^{2-}$ dianion. The entire structure has a therefore a singlet ground state and no

unpaired electrons are generated in the course of the reaction. The lowest triplet corresponding to the C_6H_4 fragment, Table 1, is about 1.3 eV higher and results in the breaking of one of the two Ti-C bonds, in full analogy with the C_4H_2 unit described above, so that the cyclic C_6H_4 unit remains anchored to the surface via a single C atom, Fig. 4(c). Also in this case one Ti-C bond becomes much longer than the other one as a consequence of the singlet-triplet excitation (3.09 Å versus 2.19 Å), Fig. 4(c).

At this point the polymerization has started and one can assume that it proceeds in the same way by incorporation of additional acetylene molecules. The process has not been investigated in each single step. Rather, we considered the global reaction of two C_2H_2 molecules with the six-membered C_6H_4 species of Fig. 5(c) to form a polycyclic aromatic hydrocarbon, $C_{10}H_8$. Notice that in this step the hydrocarbon cycle is closed and there are no longer unsaturated C atoms that can efficiently bind to the surface. In the calculations of the reaction energetics, we have considered the acetylene molecules coming from the (101) surface, $C_2H_{2(ads)}$ and we have assumed that the $C_{10}H_8$ unit remains adsorbed either on the (101) or on the (001) surfaces, $C_{10}H_{8(ads)}$:



The entire process leaves behind an hydroxylated surface (two hydroxyl groups on the unit cell used), a partially reduced solid (two $Ti_{(s)}^{3+}$ ions) and an adsorbed naphthalene molecule, Fig. 6(a) and 6(b).

To compute the energy of reaction (9) we have estimated the adsorption mode of naphthalene on anatase. Naphthalene binds to the (101) surface with an energy of 0.64 eV, Table 2; the bonding is dominated by dispersion forces. On the (001) surface two orientations of the molecule have been considered, and in the most stable one the molecule is bound by 1.54 eV, Table 2 and Fig. 6(b).

Table 2 Adsorption energies of one $C_{10}H_8$ molecule physisorbed on stoichiometric anatase (101) and (001) surfaces (PBE+U-D2' level).

	ΔE (eV)
$C_{10}H_8/TiO_2$ (101)	-0.64
$C_{10}H_8/TiO_2$ (001) (1)	-1.54
$C_{10}H_8/TiO_2$ (001) (2)	-1.29

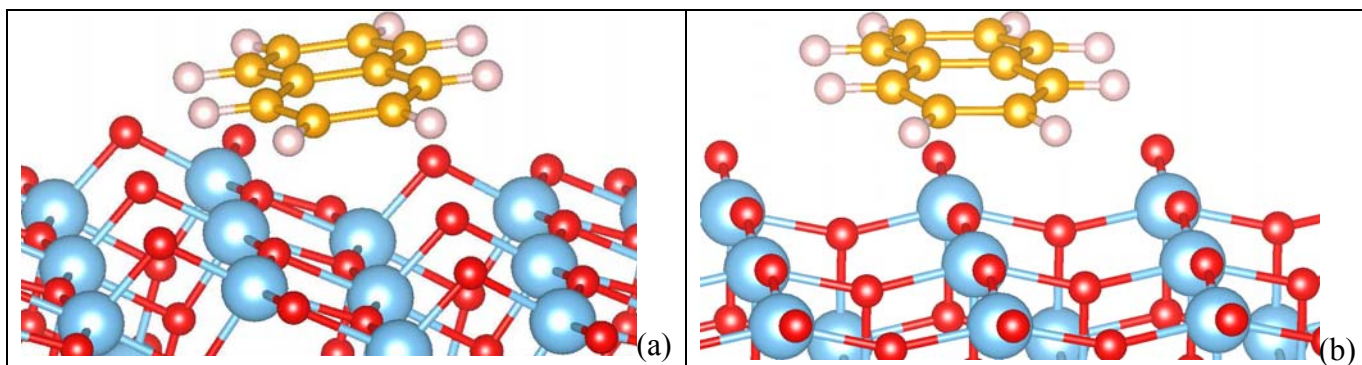


Figure 6 – Naphthalene adsorbed on (a) the (101) and (b) the (001) anatase surfaces

The overall energy gain for the process described in eq. (9) is defined as:

$$\Delta E_{LH} = E(C_{10}H_8 + 2OH^-/TiO_2(001)) - 2E[C_2H_2/TiO_2(101)] - E[(C_6H_4^{2-} + 2OH^-)/TiO_2(001)] \quad (10)$$

and is of -6.46 eV assuming that the C_8H_{10} molecule remains adsorbed on the (001) facet (most stable adsorption mode).

Reaction (9) is the key step to understand the appearance of the signal associated to the Ti^{3+} centers in the EPR experiments, see Fig. 1 and Fig. 2. In fact, the final result of the reaction is that a new C-C bond replaces two single Ti-C surface bonds. Two electrons are released in the process and are transferred to the oxide surface which becomes reduced. The situation can be seen in a different but equivalent way. The formation of the polycyclic aromatic hydrocarbon leaves behind two H atoms per $C_{10}H_8$ molecule formed. The addition of an H atom to the surface of titania is well known to result in the formation of a surface hydroxyl and an electron trapped in a Ti^{3+} polaronic center.^[38] Fig. 7 shows the spin density plot deriving from the addition of a single H atom to the anatase surface as described by the present DFT+U approach. As expected, this results in an OH group and a Ti^{3+} center with localized spin density on the Ti 3d states.^[39] Various solutions exist for this defect center,^[23] due to the mobility of the trapped electron in states just below the conduction band, an aspect which is not relevant for the present discussion. In a similar way, excess electrons are generated also by the addition of two H atoms to the supercells used in the present calculations, as shown in Fig. 7. Of course, OH groups form also in the initial steps of the reaction, when the C-H bond of acetylene is broken.

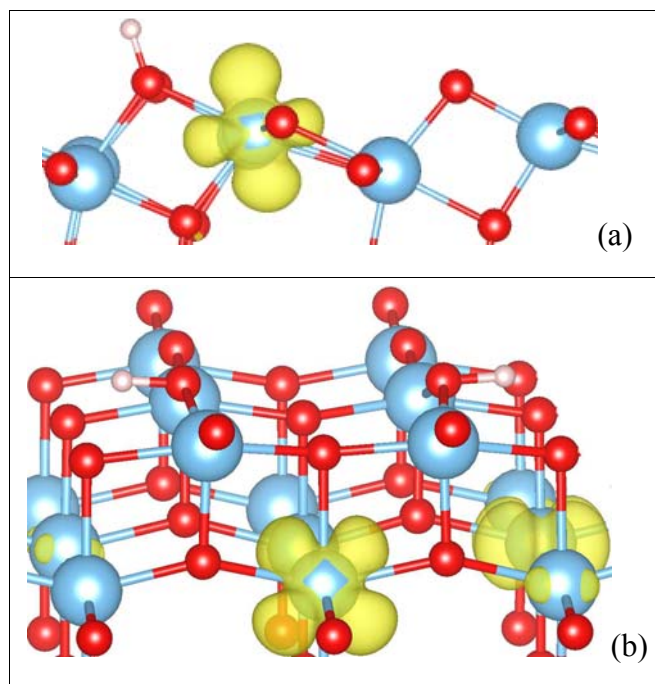


Figure 7 - Spin density (in yellow) of H atoms adsorbed on an O site of the anatase (101) surface. (a) single H atom: the excess electron is trapped on a Ti_{5c} ion; (b) two H atoms: the excess electrons are localized on a pair of Ti_{6c} ions. Other solutions exist at similar energies.

4. Summary and conclusions

We have studied by EPR spectroscopy the reaction of acetylene adsorbed on anatase powder samples to form polycyclic aromatic hydrocarbons. It has been shown previously that the reaction of acetylene polymerization is accompanied by a corresponding growth of the signal associated to paramagnetic Ti³⁺ centers, which allows one to follow the reaction by EPR spectroscopy.^[11] Three different anatase samples have been prepared with various levels of hydroxylation: fully dehydroxylated, partly hydroxylated, and hydrated anatase. The results clearly show that the fully dehydroxylated sample is by far the more active in acetylene activation and cyclo-oligomerisation while the hydrated materials are substantially inactive.

The reaction has been studied by DFT calculations. These show unambiguously that the (101) facets of de-hydroxylated anatase are inactive in promoting the C-H bond activation. The reduced surface, where O vacancies are present, is more active but does not promote acetylene cyclotrimerization. Things are completely different when one considers the more reactive (001) surface. Figure 8 reports the reaction coordinate diagram for the cyclo-polymerization of acetylene to naphthalene described above.

The first step consists in the adsorption of C₂H₂ arriving from the gas-phase. The molecule physisorbs on the most abundant and more stable anatase (101) surface with an adsorption energy of -0.53 eV. However, no dissociation is possible, and, as we mentioned above, even the reaction

with surface defects would lead to stable surface complexes but not to C-H bond breaking. The molecules can diffuse on the (101) surface of titania nanoparticles until they react with the less abundant but more active (001) facets (or, alternatively, the molecules can directly bound to this surface from the gas-phase). Here spontaneous dissociation occurs, with C-H bond breaking. With respect to physisorbed acetylene on the (101) surface there is an energy gain of 1.50 eV. Assuming a Langmuir-Hinshelwood mechanism, a second C_2H_2 molecule can reach the dissociated species and react with the C_2H^- fragment to form a stable four-membered $C_4H_2^{2-}$ chain with an energy gain of 1.73 eV, Fig. 8. The addition of another C_2H_2 molecule leads to a six-membered C_6H_4 ring with two C atoms anchored to two surface Ti ions via Ti-C σ bonds. The process is accompanied by an energy gain of 3.38 eV. Finally, as two additional C_2H_2 molecules react with the C_6H_4 intermediate, a naphthalene $C_{10}H_8$ molecule forms and remains bound to the surface by dispersion forces. As a consequence of the entire process, two H atoms remain adsorbed on the surface with formation of Ti^{3+} centers. The last reaction leads to an energy gain of 6.46 eV, Fig. 8.

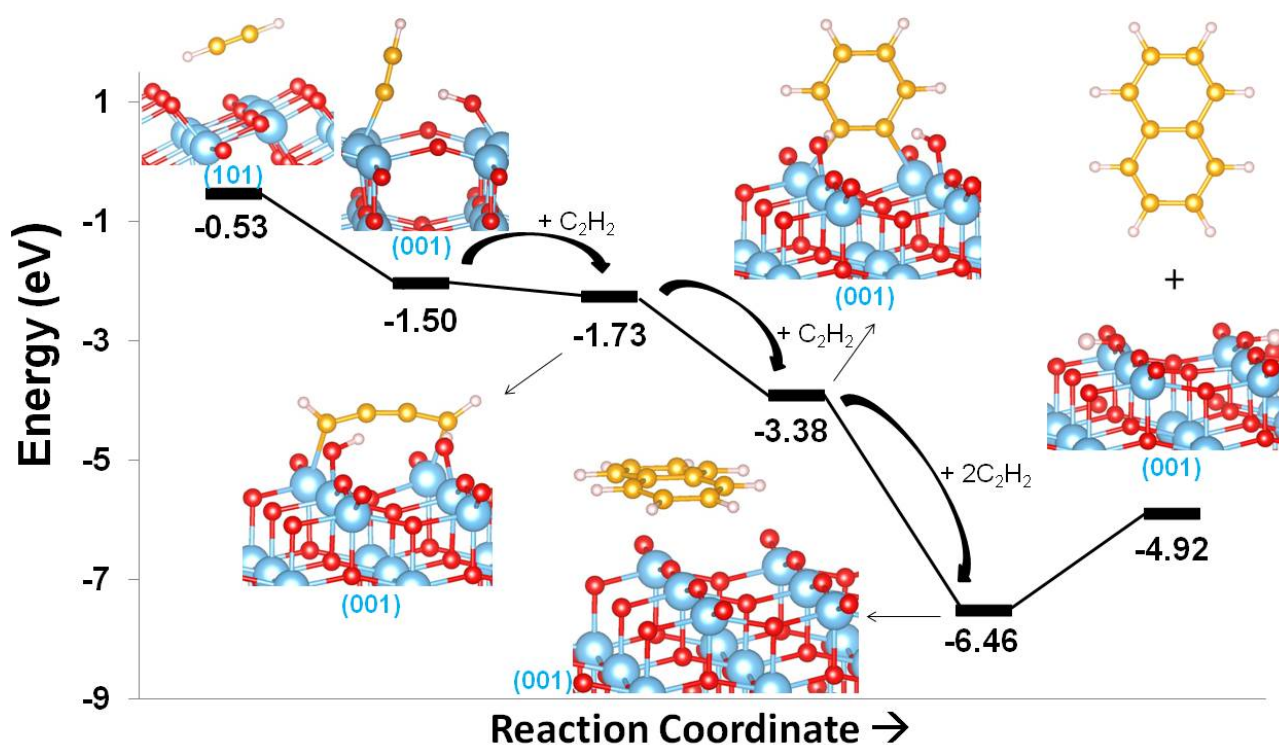
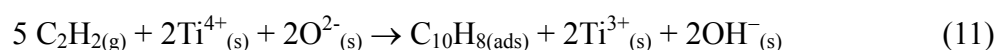


Figure 8 - Reaction profile for the cyclo-polymerization of C_2H_2 to $C_{10}H_8$ on stoichiometric (001) anatase surface. The reported energies refer to a Langmuir-Hinshelwood mechanism (see Table 1).

The overall reaction can be summarized as follows:



and explains the reduction of the surface by formation of the polycyclic aromatic molecules.

The final desorption of naphthalene from the surface costs 1.54 eV, which is a considerable amount of energy and suggests that the most active (001) facet of the titania nanoparticles can become covered by polycyclic aromatic carbon species in the course of the reaction. This could lead to a progressive deactivation of the oxide catalyst if the (001) facets become completely covered by these carbonaceous species.

The results from the EPR experiments and from the DFT calculations provide some indication on how possibly avoid deactivation of catalysts based on anatase nanoparticles. In fact, we have shown that in the presence of fully hydroxylated or hydrated surfaces there is no tendency to form polycyclic aromatic compounds. Of course, it is possible that also other processes of particular importance for a given catalytic process are hindered in this way. However, according to a different point of view and as already mentioned in the Introduction, the described process can be seen as a preliminary step to prepare TiO₂ materials containing large polycyclic hydrocarbons or even graphene fragments. The evolution of the system towards the *in-situ* generation of carbon-TiO₂ nanocomposites is currently under investigation in our laboratories.

Acknowledgments

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