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Photoinduced ethylene polymerization on TiO₂ nanoparticles

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Abstract: Herein we report on the ability of H₂-photoreduced TiO₂ nanoparticles in catalyzing ethylene polymerization without the use of any alkylating agent. Even more, we demonstrate that the same reaction occurs directly on stoichiometric TiO₂ in the presence of ethylene under UV-light irradiation at room temperature, thus without any pre-reduction step. The synergic use of electron paramagnetic resonance and diffuse reflectance UV-Vis-NIR spectroscopy allowed us to identify and correlate different Ti³⁺ EPR signals and UV-Vis-NIR bands; while transmission FT-IR spectroscopy (applied under *in situ* UV-light irradiation) was fundamental to prove ethylene polymerization and to observe ethylene oxidation by-products. The possibility to easily polymerize ethylene in a one-step procedure can be a promising approach to increase the compatibility of TiO₂ as inorganic additive for polyethylene blends.

In the last decades nanostructured materials based on TiO₂ have attracted increasing interest owing to the possible applications in environmental pollution remediation, photovoltaics and photocatalytic hydrogen generation.^[1] With respect to other semiconductors, TiO₂ offers several advantages including low toxicity, chemical and thermal stability, low cost and high resistance to photo-corrosion. Compared to the applications based on the photocatalytic properties, the number of those taking advantage from the surface chemical properties of TiO₂ is rather limited, in agreement with the stability of this oxide. For instance, despite the fact that most of the heterogeneous catalysts for olefins polymerization are based on supported Ti compounds, TiO₂ is inert toward ethylene polymerization. In this context, however, some of us have recently succeeded in transforming TiO₂ into a catalyst for ethylene polymerization, generating surface reduced Ti sites able to convert ethylene to polyethylene without the need of any activator.^[2] These sites were obtained treating TiO₂ at high temperature (773 K) in H₂, resulting in reduced materials characterized by both surface and bulk shallow-trap defect sites in analogy with the so-called “black titania”.^[3] However the hard treatment in H₂ at high temperature is not only expensive in terms of energy and time, but it can also induce an unwanted anatase-rutile conversion and morphological modifications.

The challenge is now to join the potential of photo-activity of TiO₂ with its ability to convert ethylene to polyethylene, operating the whole reaction in mild conditions. Interestingly, reduced species at the surface of oxides can be formed at room

temperature in H₂ atmosphere under UV illumination,^[4] but it has not yet been reported whether or not the reduced Ti species obtained in this way are able to polymerize ethylene. Even more appealing would be the photo-induction of ethylene polymerization on TiO₂ at room temperature without any pre-reduction step, a strategy that could ensure evident advantages on the economy of the whole process.

In this work we address both challenges by using electron paramagnetic resonance (EPR), Diffuse Reflectance (DR) UV-Vis-NIR and transmission FT-IR spectroscopies as fundamental tools to observe the effects of UV-light irradiation on TiO₂ in the presence of H₂ and C₂H₄. The investigated sample was a TiO₂ anatase obtained via sol-gel method, and the UV light irradiation was accomplished using a Newport 500 W Hg(Xe) arc lamp, equipped with a water filter to eliminate the infrared portion of the spectrum (more experimental details are given in Section S1 of the Supporting Information).

Our first goal was to monitor the evolution of the properties of TiO₂ when it is irradiated with UV-light at room temperature in H₂ atmosphere (hereafter H₂-photoreduced sample). According to previous studies, this procedure leads to H₂ splitting and to the consequent formation of surface and sub-surface Ti³⁺ centers.^[4a] The EPR spectrum of the H₂-photoreduced TiO₂ sample (Figure 1A, red) is dominated by a broad absorption feature ($g_x=1.9452$, $g_y=1.918$ and $g_z=1.875$), assigned to Ti³⁺ in a surface disordered environment^[4b] and a second signal characterized by narrow lines and axial structure ($g_{\perp}=1.992$, $g_{\parallel}=1.962$), assigned to regular sub-surface or bulk lattice Ti³⁺ centers.^[5] The presence of these defective Ti³⁺ sites is further confirmed by the DR UV-Vis-NIR spectrum (Figure 1B, red) characterized by a broad absorption in the 400–1700 nm region centered at 800 nm. The UV irradiation in H₂ atmosphere induces also the growth of a broad absorption in the MIR region having a maximum at ca. 2000 cm⁻¹ (Figure 2A and S2, red traces), which is absent in the spectrum of stoichiometric TiO₂ (black) and is ascribed to the presence of free conduction band electrons.^[6] A more detailed discussion of the reduction process is reported in Section S2 of the Supporting Information.

As second step, we tested the reactivity of the H₂-photoreduced sample towards ethylene at room temperature. Both EPR and DR UV-Vis-NIR spectra do not show significant changes at short contact times. A small increase in the overall spectral intensity is observed in both cases only after prolonged contact times (Figure 1, blue). Most probably, ethylene is slowly oxidized in a process involving surface O²⁻ sites, generating further reduced Ti³⁺ sites and oxidation products containing C=O groups (*vide infra*). Simultaneously, in the 2500–2000 nm NIR spectral region (Figure S3) three weak bands appear at 2305, 2355 and 2422 nm, ascribable to the combination of the $\nu(\text{CH}_2)$ and $\delta(\text{CH}_2)$ modes of polyethylene and thus testifying the occurrence of ethylene polymerization reaction.

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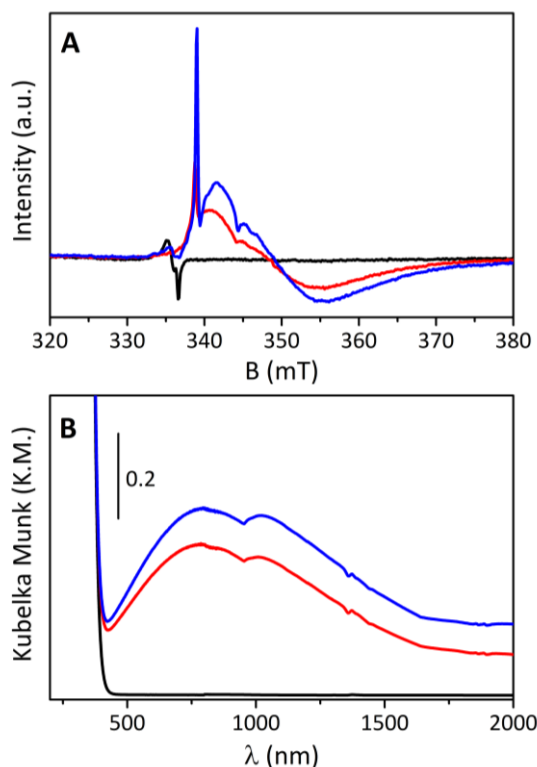


Figure 1. EPR spectra (part A) and DR UV-Vis-NIR spectra (part B) of stoichiometric TiO₂ activated at 773 K (black), the same sample after UV irradiation in the presence of 100 mbar of H₂ (red) and after prolonged contact with 100 mbar of C₂H₄ at room temperature (blue).

It is worth noticing that, as soon as ethylene gas is admitted into the reaction cell (Figure 2A, dark grey spectrum), the broad absorption centered at ~ 2000 cm⁻¹ characteristic of the H₂-photoreduced sample (Figure 2A, red curve) is instantly and completely eroded, suggesting a fast recombination of the free conduction band electrons. In parallel, new IR absorption bands due to adsorbed ethylene (at 3100, 3008 and 1608 cm⁻¹) appear (for details see Section S3). For longer contact times, ethylene polymerization slowly takes place, as testified by the progressive growth of two IR absorption bands at 2922 and 2853 cm⁻¹ respectively assigned to the $\nu_{\text{asym}}(\text{CH}_2)$ and $\nu_{\text{sym}}(\text{CH}_2)$ modes of polyethylene (Figure 2B, spectra from grey to blue). The position, evolution and intensity ratio of the CH₂ bands, along with the absence of absorption bands due to CH₃ moieties (expected at 2965 and 2872 cm⁻¹ for $\nu(\text{CH}_3)$ and at 1379 cm⁻¹ for $\delta(\text{CH}_3)$)^[7] are indicative of the formation of high-density polyethylene (HDPE) having a negligible amount of branches. Along with the spectroscopic features of polyethylene, extremely weak signals appear in the 1650–1350 cm⁻¹ spectral region at 1626, 1570 and 1343 cm⁻¹. These bands are attributed to products of ethylene oxidation, such as formaldehyde, acetaldehyde, formate, methylformate or acetate, which remain adsorbed on the surface of TiO₂.^[9] The observation of these products testifies that ethylene is further reducing TiO₂ in the present experimental conditions (low pressures). It is worth recalling here that the stoichiometric TiO₂ sample does not polymerize ethylene at room temperature

(see Section S3), so confirming that the reduction is a necessary step to develop reactivity.

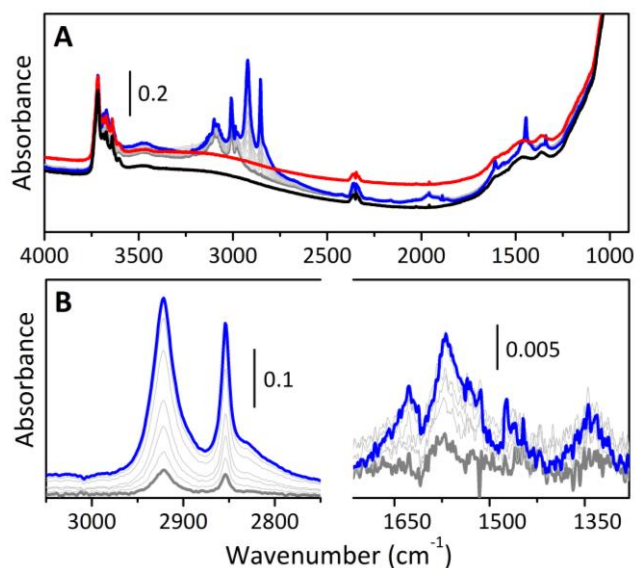


Figure 2. FT-IR spectra of stoichiometric TiO₂ activated at 773 K (black), after UV irradiation in H₂ (red) and contacted with 100 mbar of C₂H₄ at room temperature up to 7 hours (grey to blue). Part A shows the whole 4000–1000 cm⁻¹ spectral region. Magnifications of the 3050–2750 and 1715–1300 cm⁻¹ spectral regions are shown in part B, in which the initial spectrum in C₂H₄ is subtracted from all curves.

The second challenge was to accomplish ethylene polymerization on stoichiometric TiO₂, exploiting the potential of ethylene itself to act as reducing agent under UV light irradiation. The feasibility of this route is demonstrated by both EPR and DR UV-Vis-NIR spectroscopies. The EPR spectrum (Figure 3A) of the stoichiometric anatase sample (black) is only slightly affected by the presence of ethylene (grey), while remarkable changes occur after 15 minutes of UV irradiation at room temperature (purple), resulting in the characteristic spectrum of Ti³⁺ species in anatase. Interestingly, in this case the ratio between the narrow line species and the broad absorption feature is inverted with respect to the H₂-photoreduced sample (Figure 1A). This observation indicates the formation of a larger fraction of surface Ti³⁺ species with respect to bulk ones. The DR UV-Vis-NIR spectra (Figure 3B, same color code) confirm the EPR results. Indeed, for C₂H₄-photoreduced TiO₂ a broad and apparently featureless absorption band appears in the 500–2000 nm region, indicating the formation of Ti³⁺ species. This spectrum, however, is different from that of the H₂-photoreduced sample (Figure 1B), characterized by a more defined band centered at 800 nm. Combining the EPR and UV-Vis-NIR data we propose that the band centered at 800 nm in the UV-Vis-NIR spectrum can be associated to the narrow EPR lines and axial structure ($g_{\perp}=1.992$, $g_{\parallel}=1.962$) assigned to regular sub-surface or bulk lattice Ti³⁺ centers. On the contrary, the broad absorption extending in the NIR region beyond 2000 nm can be linked to the EPR broad absorption feature ($g_x=1.9452$, $g_y=1.918$ and $g_z=1.875$) and assigned to Ti³⁺ in a surface disordered environment.

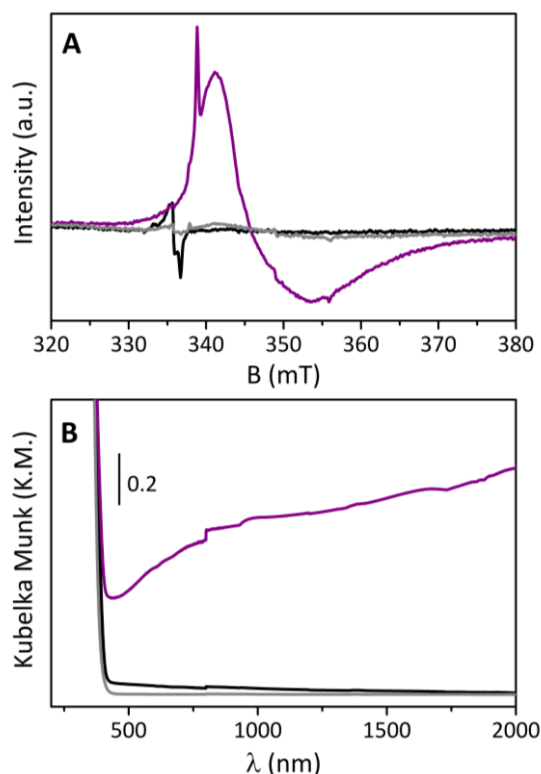
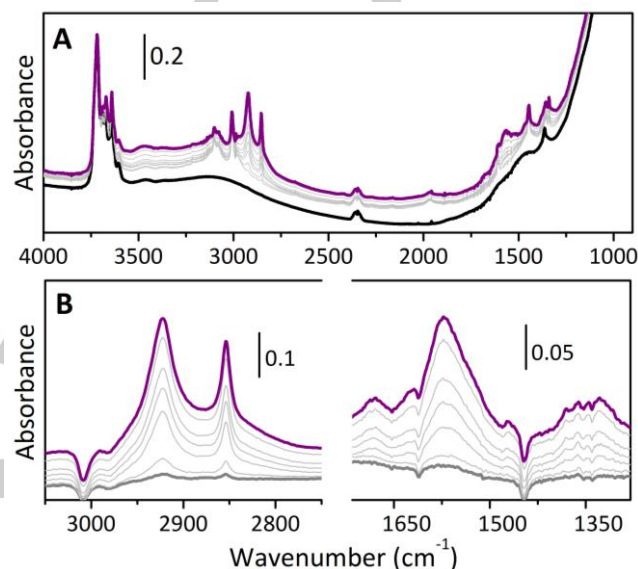


Figure 3. EPR spectra (part A) and DR UV-Vis-NIR spectra (part B) of the stoichiometric TiO_2 activated at 773 K (black) in contact with 100 mbar of ethylene (grey) and UV irradiation in ethylene (purple).

Summarizing, EPR and UV-Vis-NIR spectroscopies revealed that under UV irradiation ethylene reduces preferentially the TiO_2 surface with respect to atomic H^\bullet , which can diffuse in the solid,^[9] generating subsurface and bulk Ti^{3+} centers. However, they did not show if ethylene polymerization occurred. Indeed, the extension of the broad absorption to the NIR region hinders the observation of the $\nu(\text{CH}_2)$ and $\delta(\text{CH}_2)$ combination modes of polyethylene. To clarify this point we performed a time-resolved FT-IR experiment where a TiO_2 stoichiometric sample was continuously irradiated with the UV source in the presence of ethylene at room temperature. The experiment required the adoption of an *ad hoc* experimental set-up,^[10] comprising an aspherical fiber bundle focusing assembly on the UV source and a large core liquid light guide which focused the radiation emitted by the lamp directly on the sample inside the FT-IR spectrophotometer (passing through the KBr windows of the IR cell). This set-up allowed us to observe the simultaneous occurrence of the TiO_2 reduction/ethylene oxidation and ethylene polymerization reactions (Figure 4).

The FT-IR spectrum of stoichiometric TiO_2 in contact with ethylene (dark grey curve in Figure 4) is dominated by the IR absorption bands of adsorbed ethylene (as discussed in section S3). At increasing irradiation time (from grey to purple) the whole spectra profile increases in absorbance, proving the occurrence of TiO_2 reduction. This broad absorption has a maximum at ca. 2000 cm^{-1} and it is due to the excitation of electrons in the conduction band. Simultaneously, IR absorption bands grow at

2922 and 2853 cm^{-1} , testifying the formation of polyethylene at the surface of the TiO_2 sample. New signals appear also in the 1700 – 1300 cm^{-1} spectral region (main components at 1680 , 1618 and 1572 with a shoulder at 1532 cm^{-1} , along with a group of weaker bands in the 1380 – 1320 cm^{-1} region), which are attributed to products of ethylene oxidation (i.e. formaldehyde, acetaldehyde, formate, methylformate or acetate).^[8] These latter bands are considerably more intense with respect to those observed for the reaction of ethylene with H_2 -photoreduced TiO_2 (see Figure 2B). These data unequivocally demonstrate that concomitant TiO_2 reduction and ethylene polymerization occur under UV irradiation



of TiO_2 in the presence of ethylene.

Figure 4. FT-IR spectra of stoichiometric TiO_2 activated at 773 K (black), upon ethylene admission to the IR cell (grey) and after 1 hour of *in situ* UV irradiation (from grey to purple). Part A shows the whole 4000 – 1000 cm^{-1} spectral region. Magnifications of the 3050 – 2750 and 1715 – 1300 cm^{-1} spectral regions are shown in part B, in which the initial spectrum in C_2H_4 before starting the UV irradiation is subtracted from all the spectra.

In conclusion, with respect to our previous work in which TiO_2 is reduced at high temperatures to promote ethylene polymerization,^[2] we proposed here a much easier and quicker way to perform the same reaction. We demonstrated that ethylene polymerization occurs on TiO_2 nanoparticles reduced by UV-light in H_2 atmosphere at room temperature and without the use of any alkylating agents. We went much further in this evidence, showing that ethylene polymerization takes place directly on TiO_2 under direct UV light irradiation, leading to a successful one-step production of a TiO_2 /polyethylene composite. Ethylene resulted more selective in the formation of Ti^{3+} surface species with respect to H_2 under the same experimental conditions. We have also been able to identify and correlate the different Ti^{3+} EPR signals with the UV-Vis-NIR bands. The spectroscopic results discussed in this work highlight the crucial role of Ti^{3+} species in promoting ethylene polymerization, contributing to the debate present in the olefin oligomerization/polymerization literature.

Photoinduced ethylene polymerization on TiO_2 cannot compete with the existing highly efficient ethylene polymerization

processes, based on fragile catalyst supports which continuously fragment during ethylene polymerization, exposing new active sites. However, it might have a potential interest for producing TiO₂/polyethylene composites to be used as additives in polyethylene blends, thus solving the problem of compatibility between the inorganic material and the polymer in a smart, simple and economic way.

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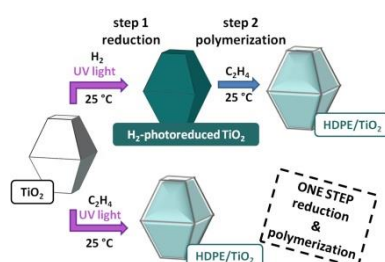
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Keywords: Ti³⁺, H₂-photoreduced TiO₂, EPR spectroscopy, FT-IR spectroscopy, UV-Vis-NIR spectroscopy, HDPE.

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COMMUNICATION

One-step is better: UV light irradiation of TiO_2 nanoparticles leads to the successful one-step production of a TiO_2 /polyethylene composite without the use of any alkylating agent or pre-reduction step.



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