

AperTO - Archivio Istituzionale Open Access dell'Università di Torino

Photodegradation of organic pollutants on TiO₂ P25 surfaces investigated by transmission FTIR spectroscopy under in situ UV-Vis irradiation

This is the author's manuscript

Original Citation:

Availability:

This version is available <http://hdl.handle.net/2318/1622854> since 2017-01-23T10:12:21Z

Published version:

DOI:10.1515/zpch-2015-0733

Terms of use:

Open Access

Anyone can freely access the full text of works made available as "Open Access". Works made available under a Creative Commons license can be used according to the terms and conditions of said license. Use of all other works requires consent of the right holder (author or publisher) if not exempted from copyright protection by the applicable law.

(Article begins on next page)

This is the author's final version of the contribution published as:

Mino, Lorenzo; Negri, Chiara; Zecchina, Adriano; Spoto, Giuseppe.
Photodegradation of organic pollutants on TiO₂ P25 surfaces investigated by
transmission FTIR spectroscopy under in situ UV-Vis irradiation.
ZEITSCHRIFT FÜR PHYSIKALISCHE CHEMIE. 230 (9) pp: 1441-1451.
DOI: 10.1515/zpch-2015-0733

The publisher's version is available at:

<https://www.degruyter.com/view/j/zpch.2016.230.issue-9/zpch-2015-0733/zpch-2015-0733.pdf>

When citing, please refer to the published version.

Link to this full text:

<http://hdl.handle.net/>

Photodegradation of organic pollutants on TiO₂ P25 surfaces investigated by transmission FTIR spectroscopy under *in situ* UV-Vis irradiation

Lorenzo Mino*^{1,2}, Adriano Zecchina¹ and Giuseppe Spoto¹

¹Department of Chemistry and NIS Centre, University of Torino, via Giuria 7, Turin, Italy

²INRIM, National Institute of Metrological Research, Strada delle Cacce 91, Turin, Italy

Received; accepted

Abstract:

A new transmission FTIR set-up has been developed to investigate photocatalytic reactions under *in situ* UV-Vis illumination and in controlled atmosphere. This system was employed to study the evolution of the surface species during the photodegradation of phenol and oxalic acid on TiO₂ P25. As far as phenol is concerned, dosage from the gas phase on the activated oxide surface resulted in dissociative adsorption for coverages below the monolayer and in physisorption beyond this limit. Experiments under UV irradiation showed no relevant photocatalytic activity in absence of O₂, the only spectroscopic consequence being the increase of a monotonic IR absorption, covering nearly the whole MIR range, related to UV-generated free conduction electrons. Only the contemporary addition of O₂ and H₂O to the TiO₂/phenol system allowed us to observe an efficient photodegradation reaction and to highlight the IR manifestations of some of the photodegradation products which are formed. In particular, oxalic acid appeared to be the main intermediate product adsorbed at the oxide surface during phenol photodegradation. For this reason the photoreactivity of pure oxalic acid on TiO₂ under UV irradiation was also investigated.

*Correspondence author (e-mail: lorenzo.mino@unito.it)

Keywords: TiO₂ P25, photocatalysis, phenol, oxalic acid, *in situ* IR spectroscopy

Introduction

Titanium dioxide has been widely studied for its widespread application in photocatalysis and in dye-sensitized solar cells [1]. Concerning water remediation, several investigations have been performed focusing the attention on reactions in aqueous suspensions containing the TiO₂ photocatalyst and the organic substrate which has to be mineralized. Usually, the standard procedure to investigate the reaction intermediates relies on chromatographic separation techniques of the species present in solution and their analysis by coupled mass spectrometry (HPLC/GC-MS). It is however a matter of the facts that the most interesting reactions initiating the degradative cycle can be thought to occur at the catalyst surface and one could therefore expect that, to better understand the reaction mechanism, it would be crucial to directly investigate the surface species present during the photodegradation.

In this respect, infrared spectroscopy is particularly appealing owing to its ability to identify specific functional groups and its sensitivity to adsorbed surface species. Indeed, total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) has already been employed to follow the evolution of the surface intermediates during the photodegradation of organic substrates [2-4]. However, the ATR acquisition mode shows some issues in terms of sensitivity, spectral quality and full control of the sample conditions with respect to transmission FTIR spectroscopy. Therefore we decided to develop a different set-up to irradiate *in situ* the sample with an intense UV-Vis beam while acquiring transmission FTIR spectra in controlled atmosphere. This approach was adopted to study the photodegradation of phenol and oxalic acid adsorbed from the gas phase on the surface of TiO₂ P25. The phenol reaction has been already studied by FTIR transmission spectroscopy using *ex situ* UV irradiation [5]: our *in situ* set-up allows to follow the time evolution of the photodegradation reaction in a more detailed way and helps the identification of the intermediates. Our approach could also be useful to investigate

the influence of well-defined coverages of adsorbates (e.g. water and oxygen) on the photodegradation kinetics.

Materials and methods

The photocatalyst used in this work is Degussa (Evonik) TiO₂ P25, which is widely used for its high photocatalytic activity. The fumed TiO₂ nanoparticles of P25 are obtained by flame pyrolysis of TiCl₄. The synthesis leads to a mixture of *ca.* 80% anatase and 20% rutile with a specific surface area (BET) of 60 m²/g [6]. As it has been established by FTIR spectroscopy of adsorbed CO and HRTEM, this material consists of particles having a complex polyhedral shape, mainly exposing (101) anatase surfaces [7-9].

For transmission IR spectroscopy measurement a slurry of TiO₂ and water with a typical concentration of 450 g/l was prepared and deposited on Si wafers. This approach was adopted since the self-supported pellets which are usually employed for transmission IR measurements are too thick (20-50 μm) to be completely penetrated by the UV-Vis radiation which is strongly absorbed and/or scattered by the TiO₂ nanoparticles.

The infrared spectra were recorded on a Bruker IFS 28 FTIR spectrometer at 2 cm⁻¹ resolution using a MCT cryogenic detector; 64 interferograms were typically averaged for each spectrum.

All the measurements were performed at the IR beam temperature in transmission mode. For this aim, the sample was inserted in a cell with KBr windows and connected to a conventional vacuum line (residual pressure of 5·10⁻⁴ mbar), allowing the adsorption-desorption experiments to be carried out *in situ* and in controlled atmosphere.

Before the IR measurements, the TiO₂ samples were outgassed at 773 K for 2 hours. Subsequently, 25 mbar of O₂ were sent twice, maintaining constant the temperature for 20 minutes in order to burn accurately all the eventual hydrocarbons present at the surface and in the cell and to restore the full stoichiometry of the oxide. Then, the samples were cooled down to 373 K in O₂ atmosphere and further cooled down to room temperature under outgassing. At the end of the procedure, the sample, which will be named activated P25 in the following, was white in color, as expected for stoichiometric (fully oxidized) TiO₂.

The *in situ* photodegradation experiments were performed using a Newport 500 W Hg (Xe) arc lamp as source of UV-Vis radiation. The use of a water filter and a liquid light guide allowed to completely cut out the heating effects of the IR emission of the lamp. The radiation emitted by the UV-Vis lamp was transferred to the sample by means of a large core (3 mm) Newport liquid light guide.

Results and discussion

The IR spectrum of the phenol/TiO₂ system

Figure 1 shows the FTIR spectra of increasing doses of phenol from the gas phase on a highly dehydroxylated TiO₂ P25 sample. On the basis of previous literature results [5, 10], we can assign the main bands in the spectrum at lower phenol coverages (grey curves in Figure 1) as follows:

- the peak growing at 3618 cm⁻¹ is due to the stretching mode of the free OH groups, while the broad band in the 3600-3200 cm⁻¹ range is ascribed to hydrogen bonding;
- the bands at 3064, 3032 and 3016 cm⁻¹ are related to the aromatic C-H bond stretching;
- the peaks at 1591, 1491 and 1481 cm⁻¹ are due to the ν(C=C) modes of the aromatic ring;
- a doublet due to the ν(C-O) mode (slightly coupled with ring vibrations) can be found at 1290 and 1274 cm⁻¹;
- the bands due to the β(CH) in-plane bending modes are observed at 1163 and 1151 cm⁻¹.

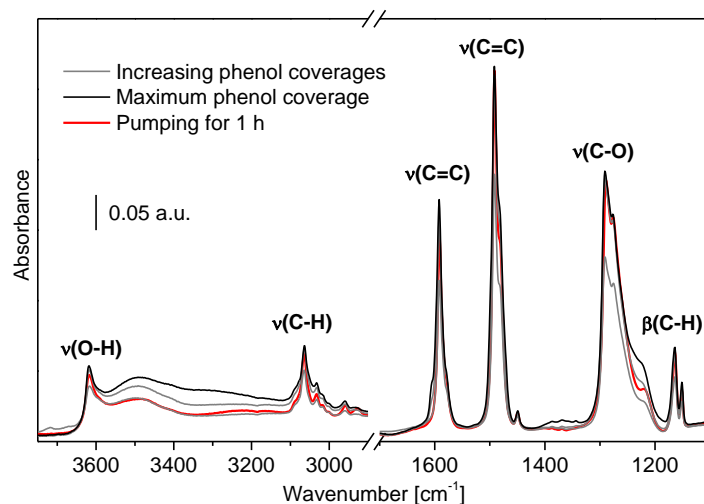


Figure 1. FTIR spectra of phenol adsorbed via vapour phase at progressively increasing coverages (grey and black curves) on TiO₂ P25 previously outgassed at 773 K and subsequent outgassing for 1 hour at beam temperature (red curve). The spectrum of the activated material has been subtracted from all spectra.

When the coverage is increased, additional manifestations, typical of the solid phase, appear at 1606, 1370 and 1221 cm⁻¹. Of particular interest is the peak at 1370 cm⁻¹, which is due to the combination of the $\delta(\text{O-H})$ and a ring mode and is therefore typical of non-dissociated (not deprotonated) phenol molecules: its absence in the spectra at lower coverages suggests that the activated TiO₂ surface readily dissociates the slightly acidic phenol molecule on acid/base Ti-O centres to form OH groups and adsorbed Ti-phenolates. This hypothesis is further confirmed by the growth of the broad absorption in the 3600-3200 cm⁻¹ range, which can be attributed to the formation of the new families of hydroxyls. In this respect it is also noticeable that when a large amount of phenol is dosed (black curve in Figure 1) the peak at 1370 cm⁻¹ is clearly visible, suggesting that a surface multilayer of undissociated phenol is formed. Upon outgassing at room temperature (red curve in Figure 1), this phenol excess can be easily removed, while the dissociated monolayer is irreversibly adsorbed.

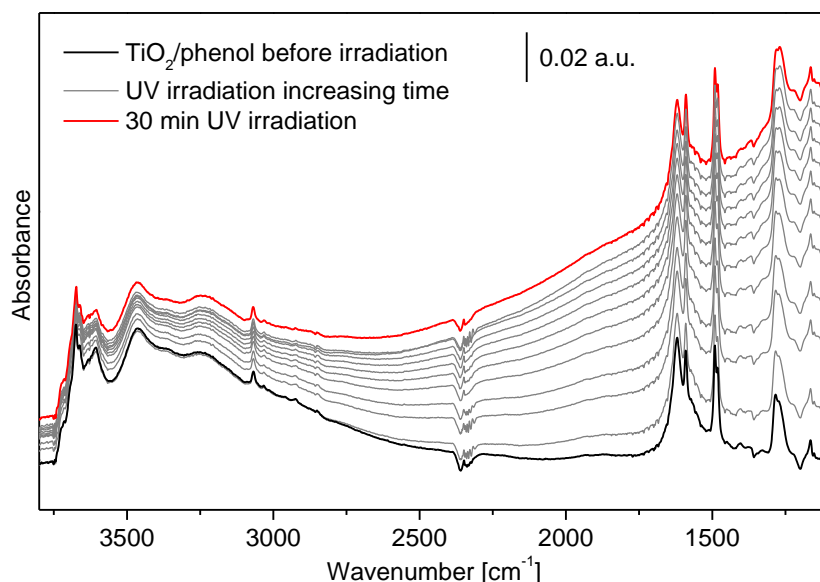


Figure 2. FTIR spectra at increasing irradiation time (up to 30 min, red curve) of activated TiO₂ P25 with a low coverage of adsorbed phenol. The black curve refers to the TiO₂/phenol system before starting UV irradiation. The spectrum of the activated material has been subtracted from all spectra.

Figure 2 illustrates the effect of the UV irradiation of the photocatalyst in presence of a low coverage of adsorbed phenol in vacuum. As can be seen, after 30 minutes of UV irradiation (red curve in figure 2) the phenol bands do not decrease in intensity, i.e. no relevant photocatalytic activity is observed, but we can notice a continuous increase of the absorbance, which starts at *ca.* 4000 cm^{-1} and increases exponentially toward 1000 cm^{-1} (where the spectral cutoff, due to bulk Ti–O vibrations, appears). This spectral feature, which is reversible when the UV lamp is switched off, has been ascribed to the absorption of IR radiation by the UV-generated free conduction band electrons [11].

Effect of water on pre-adsorbed phenol

The absence of photocatalytic activity for the TiO_2 /phenol system in vacuum (Figure 2) can be related to the lack of reactive species ($\text{H}_2\text{O} \rightarrow \text{OH}\cdot$) and of trapping electron species (O_2), which are essential ingredients for the photocatalytic reactions [12, 13]. In order to confirm this hypothesis, we tried initially to dose H_2O on pre-adsorbed phenol. In Figure 3 the amount of molecular water can be monitored by the intensity of the bending mode initially centered at 1620 cm^{-1} and then progressively shifting till 1635 cm^{-1} owing to hydrogen bond interactions among the water molecules in the surface multilayer. In parallel a broad absorption related to the $\nu(\text{OH})$ mode grows in the 3600–2900 cm^{-1} range. Also the phenol vibrational modes are perturbed by the presence of water and the most intense $\nu(\text{C}=\text{C})$ mode is now shifted at the highest water coverage (black spectrum in Figure 3) to 1484 cm^{-1} with a shoulder at 1493 cm^{-1} , while the $\nu(\text{C}-\text{O})$ doublet becomes broad and centered at 1265 cm^{-1} . Finally, the appearance of a weak band at *ca.* 1370 cm^{-1} , ascribed to a mode with $\delta(\text{O}-\text{H})$ bending character, shows that some phenate species are converted back to molecular phenol.

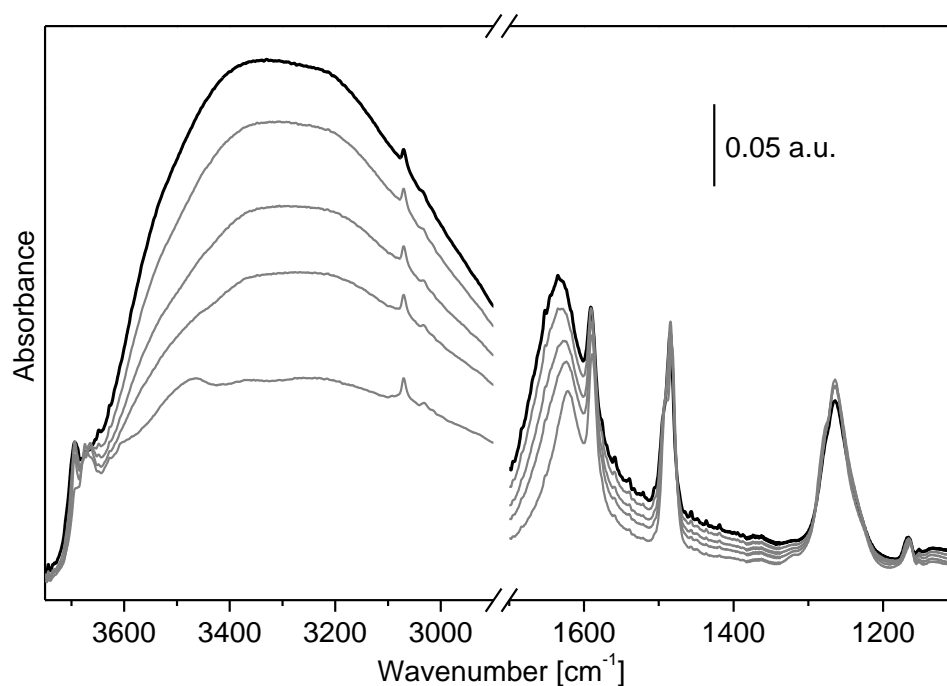


Figure 3. FTIR spectra of increasing water pressures (up to 15 mbar, black curve) on phenol pre-adsorbed on activated TiO_2 P25. The spectrum of the activated material has been subtracted from all spectra.

After UV irradiation of the TiO_2 /phenol/ H_2O system for increasing times up to 30 minutes (Figure 4), we can see that again the phenol signals do not decrease significantly. We can also note that there is an increase of the IR absorbance during the irradiation, but considerably smaller with respect to the case of the TiO_2 /phenol in vacuum. This finding is in agreement with literature data which show that water chemisorption reduces the concentration of conduction band electrons [14].

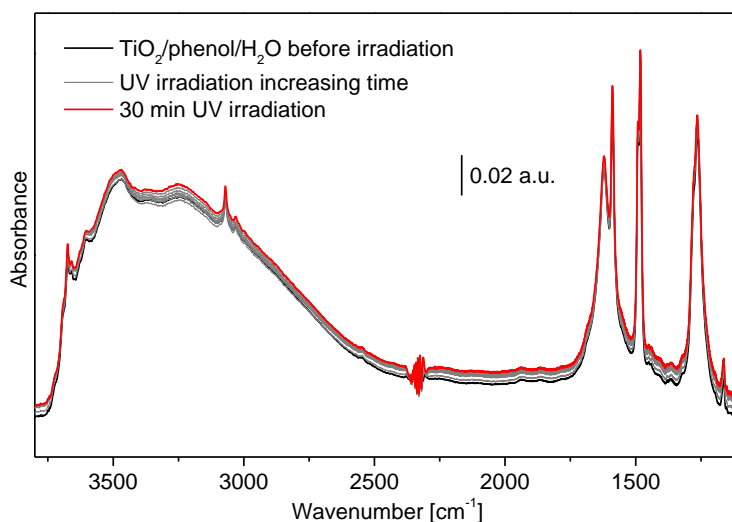


Figure 4. FTIR spectra at increasing irradiation time (up to 30 min, red curve) of activated TiO_2 P25 with co-adsorbed phenol and molecular water. The black curve refers to the TiO_2 /phenol/ H_2O system before starting UV irradiation. The spectrum of the activated material has been subtracted from all spectra.

Photodegradation of phenol on TiO_2 P25 surfaces

Since also the TiO_2 /phenol/ H_2O system without O_2 showed a negligible photocatalytic activity, we decided to prepare a new model surface by adsorbing less than half monolayer of phenol on activated P25 and saturating the surface by co-adsorbed water (see Figure 5a for a pictorial representation of the TiO_2 surface conditions), then we added to the reaction cell 100 mbar of O_2 . From Figure 5b, we can see that the addition of an electron scavenger (O_2) dramatically improves the photocatalytic activity. In particular, the main phenol bands, i.e. the $\nu(\text{C-H})$ at 3070 cm^{-1} , the $\nu(\text{C=C})$ at 1590 and 1484 cm^{-1} and the $\nu(\text{C-O})$ at 1265 cm^{-1} , progressively disappear, while new signals related to the products raise. Conversely, the $\nu(\text{O-H})$ band of hydrogen bonded water in the $3600\text{--}3100\text{ cm}^{-1}$ spectral region and the signal at 1625 cm^{-1} , associated to the water bending mode, experience a small increase. Meanwhile, new bands, highlighted by black arrows in Figure 5b, are formed around 1700 and 1400 cm^{-1} . The former can be likely ascribed to $\nu(\text{C=O})$ stretching modes of carboxylic acids [4], while the latter to the formation of surface carbonates [15, 16].

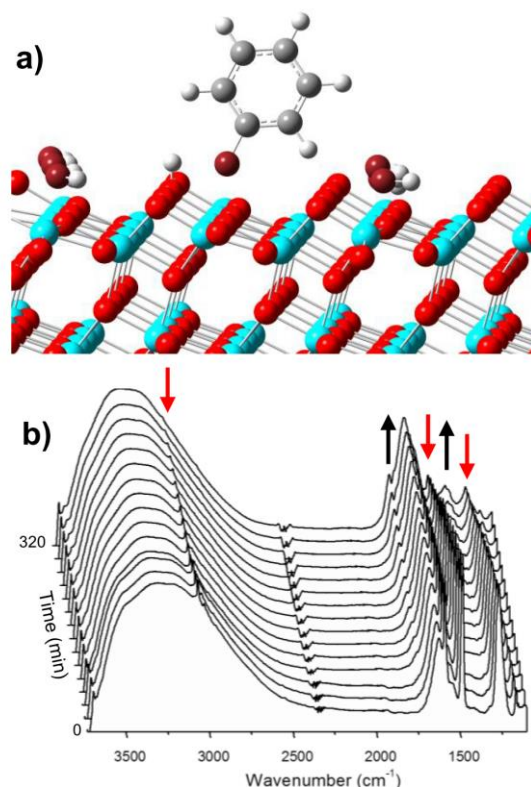


Figure 5. a) Pictorial representation of the initial TiO₂ surface conditions adopted for phenol photodegradation. Titanium, carbon, hydrogen and surface oxygen atoms are represented in cyan, gray, light gray and red, respectively; while water and phenol oxygen atoms are represented in dark red. b) Photodegradation of phenol adsorbed on activated P25 in presence of co-adsorbed water and 100 mbar of O₂. Red arrows highlight the phenol bands, which progressively decrease during the photodegradation, while black arrows highlight the products signals.

Phenol photodegradation intermediates: oxalic acid

As introduced in the previous section, the two bands around 1700 cm⁻¹, which are progressively formed during phenol photodegradation and are clearly visible in the magnification of the low frequency region reported in Figure 6a, could be ascribed to short chain carboxylic acids. The absence of the $\nu(\text{C-H})$ stretching modes in the 3000-2800 cm⁻¹ spectral region (see Figure 5b) suggests that the main carboxylic acid formed during the photodegradation could be oxalic acid, which does not contain C-H bonds and it is often reported as a common intermediate in literature [13]. To further confirm this assignment we adsorbed oxalic acid on the surface of P25 in the same hydration conditions used for phenol photodegradation: considering the black curve in Figure 6b, we can see that the two main bands at 1718 and 1690 cm⁻¹, related to the $\nu(\text{C=O})$ mode of chemisorbed oxalates, appear at the same frequency observed during phenol photodegradation.

The IR spectra at increasing UV irradiation times (grey curves in Figure 6b) show that the bands of oxalic acid progressively disappear and no other evident signals are formed, suggesting that the final mineralization of the organic compounds leads to the formation of H₂O and CO₂.

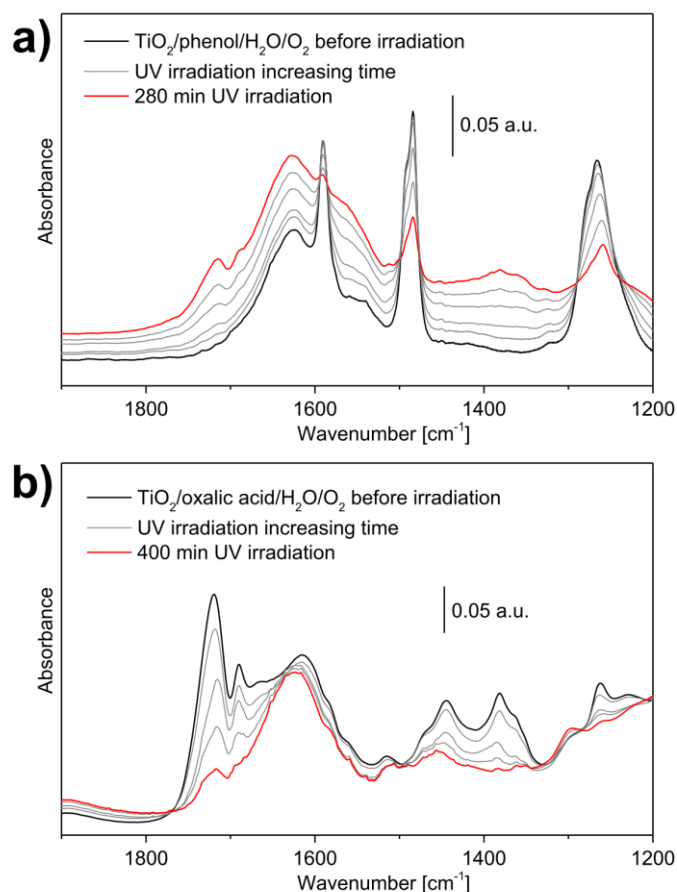


Figure 6. a) Photodegradation of phenol (up to 280 minutes of UV irradiation, red curve) adsorbed on activated P25 in presence of co-adsorbed water and 100 mbar of O_2 . The black curve refers to the TiO_2 /phenol/ H_2O/O_2 system before starting UV irradiation. The spectrum of the activated material has been subtracted from all spectra. b) Photodegradation of oxalic acid (up to 400 minutes of UV irradiation, red curve) adsorbed on P25 in presence of co-adsorbed water and 100 mbar of O_2 . The black curve refers to the TiO_2 /oxalic acid/ H_2O/O_2 system before starting UV irradiation.

Conclusions

The use of a new transmission FTIR set-up allowed us to study in controlled atmosphere the photodegradation of phenol and oxalic acid, overcoming some of the limitations which are encountered with the ATR-FTIR approach.

The study of the phenol mechanism of adsorption on TiO_2 P25 showed that the activated oxide surface is able to dissociate the molecule forming an OH group and an adsorbed phenolate, while, at higher phenol doses, a surface multilayer of undissociated phenol is present. The addition of molecular water to a low coverage of adsorbed phenol converts back some phenate species to molecular phenol.

The UV irradiation of the TiO_2 /phenol system (with or without co-adsorbed molecular water) in absence of O_2 showed no relevant photocatalytic activity, but the rise of a monotonic IR absorption, starting at *ca.* 4000 cm^{-1} and increasing exponentially toward 1000 cm^{-1} , due to the IR absorption by the UV-generated free conduction electrons.

The addition of both O_2 and H_2O to the TiO_2 /phenol system allowed us to achieve an efficient photodegradation reaction. In parallel to the decrease of the phenol bands, we highlighted the formation of new bands ascribed to carboxylic acids and adsorbed carbonates. The study of the photodegradation of oxalic acid showed that the two main bands, observed at 1718 and 1690 cm^{-1} during phenol photodegradation, are due to chemisorbed oxalates, which can be finally mineralized to H_2O and CO_2 by UV irradiation. This finding confirmed that oxalic acid is one of the most important intermediates in phenol photodegradation, in agreement with the most common reaction mechanism proposed in literature.[13]

Acknowledgements. The financial support of the FP7 European project SETNanoMetro - Shape-engineered TiO₂ nanoparticles for metrology of functional properties: setting design rules from material synthesis to nanostructured devices - (Project number 604577) is gratefully acknowledged.

References

1. A. Fujishima; X. T. Zhang; D. A. Tryk. *Surf. Sci. Rep.* **63** (2008) 515-582
2. P. Z. Araujo; C. B. Mendive; L. A. G. Rodenas; P. J. Morando; A. E. Regazzoni; M. A. Blesa; D. Bahnemann. *Colloid Surf. A-Physicochem. Eng. Asp.* **265** (2005) 73-80
3. C. B. Mendive; D. W. Bahnemann; M. A. Blesa. *Catal. Today* **101** (2005) 237-244
4. I. Dolamic; T. Burgi. *J. Catal.* **248** (2007) 268-276
5. L. Palmisano; M. Schiavello; A. Sclafani; G. Martra; E. Borello; S. Coluccia. *Appl. Catal. B-Environ.* **3** (1994) 117-132
6. S. M. Jain; J. J. Biedrzycki; V. Maurino; A. Zecchina; L. Mino; G. Spoto. *J. Mater. Chem. A* **2** (2014) 12247-12254
7. L. Mino; A. M. Ferrari; V. Lacivita; G. Spoto; S. Bordiga; A. Zecchina. *J. Phys. Chem. C* **115** (2011) 7694-7700
8. L. Mino; G. Spoto; S. Bordiga; A. Zecchina. *J. Phys. Chem. C* **116** (2012) 17008-17018
9. L. Mino; G. Spoto; S. Bordiga; A. Zecchina. *J. Phys. Chem. C* **117** (2013) 11186-11196
10. J. C. Evans. *Spectrochim. Acta* **16** (1960) 1382-1392
11. D. A. Panayotov; S. P. Burrows; J. R. Morris. *J. Phys. Chem. C* **116** (2012) 4535-4544
12. M. Bertelli; E. Selli. *J. Hazard. Mater.* **138** (2006) 46-52
13. E. Grabowska; J. Reszczynska; A. Zaleska. *Water Res.* **46** (2012) 5453-5471
14. D. A. Panayotov; J. T. Yates. *Chem. Phys. Lett.* **410** (2005) 11-17
15. G. Martra. *Appl. Catal. A-Gen.* **200** (2000) 275-285
16. L. Mino; G. Spoto; A. M. Ferrari. *J. Phys. Chem. C* **118** (2014) 25016-25026