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IR spectroscopy as a tool to investigate photocatalytic reactions at oxide surfaces

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Abstract

In the last years *in situ* and *operando* IR spectroscopy is emerging as a powerful tool to directly investigate the processes occurring at the surface of oxide particles during photocatalytic reactions. This paper provides a concise overview of the most used acquisition modes (transmission, ATR and DRIFT) and the related experimental setups available to study reactions under UV irradiation. Subsequently a selection of significant applications will be presented, including photocatalytic reactions in gas phase and at the solid-liquid interface. The selected examples will highlight the effectiveness of IR spectroscopy in monitoring the evolution of the reaction intermediates and products at the photocatalyst surface. This approach allows to better understand the reaction mechanism and to derive the kinetic laws, expressed in terms of surface concentrations.

Keywords: ATR-IR; DRIFT; VOC photodegradation; organic pollutants photocatalysis; TiO₂; degradation kinetics.

1. Introduction

Infrared spectroscopy has been widely employed to unravel structure and reactivity of surface sites in oxides (Zaera 2014). In particular, in the last decades a lot of information about the nature, strength, local arrangement, and amount of surface sites has been obtained by employing suitable probe molecules (Busca 1999; Hadjiivanov and Klissurski 1996; Jain et al. 2014). The interpretation of the experimental data has been further facilitated by the parallel development of first principles calculations, which can evaluate the interaction energy and the vibrational frequencies of the probe molecules adsorbed on different surface sites (Deiana et al. 2013; Mino et al. 2011; Mino et al. 2013; Scaranto and Giorgianni 2008).

More recently, IR spectroscopy is emerging as a powerful tool to investigate the surface processes occurring during photocatalytic reactions at oxides surfaces. Indeed, the majority of the studies devoted to the photodegradation of organic substrates are focused on aqueous suspensions containing the photocatalyst and the pollutant which has to be mineralized. These investigations often employ chromatographic separation techniques coupled to mass spectrometry (HPLC/GC-MS) (Grabowska et al. 2012), which are extremely useful to detect the intermediates and products present in solution, but cannot provide direct information about the processes occurring at the oxide surface. In this respect, infrared spectroscopy is particularly appealing owing to its ability to identify specific functional groups and its sensitivity to adsorbed surface species. These features make it a perfect tool to directly investigate the intermediates and products evolution at the photocatalyst surface, thus helping to clarify the reaction mechanism.

This paper will provide a brief overview of the IR setups employed to study photocatalytic reactions and will discuss some selected examples to highlight the potentialities of IR spectroscopy in this field.

2. Experimental setups

Figure 1 shows the two most common experimental setup employed to study photocatalytic reaction by IR spectroscopy. Attenuated total reflection infrared spectroscopy (ATR-IR) exploits the evanescent wave formed at the interface between an internal reflection element (IRE) and the sample, which is deposited on the IRE as a thin film (see Figure 1a). The exact cell design to perform an ATR-IR experiment depends on the reaction and catalyst under study. Moreover, the selected IRE material determines the range of applicable temperature, pressure and pH. The penetration depth into the sample depends on the wavelength, the angle of incidence and the indices of refraction of the sample and the IRE and it is generally of few micrometers (Mojet et al. 2010). This feature makes ATR-IR particularly suitable to directly investigate solid-liquid interfaces since the limited penetration depth of the evanescent wave allows to probe also liquids with significant extinction coefficients, like water.

In a typical setup for transmission IR spectroscopy (Figure 1b) the sample is pressed in a thin self-supported wafer or deposited on a Si wafer and placed inside a cell equipped with IR-transparent windows (often KBr) to operate in controlled atmosphere either in static conditions or in flow. The radiation emitted by a UV lamp is focused on the oxide surface using a liquid light guide, which allows to obtain an intense UV beam in the same position probed by the IR beam. This setup is not suitable to directly study solid-liquid interfaces, but can have some advantages in terms of sensitivity, quantification and spectral quality. Moreover, it allows to activate the oxide surface before performing the photocatalytic reaction and to dose precise amounts of reactants from the gas phase.

Finally, it is worth mentioning that some studies employed also the diffuse-reflectance (DRIFTS) acquisition mode. In this case, the oxide powder is loosely placed in a sample cup inside the reaction cell and illuminated by the IR beam, then the scattered (rather than transmitted) IR radiation is collected with appropriate optics. In these setups, a dome with three windows usually covers the sample cup: two of the windows are IR transparent, while the third is made of quartz to allow UV irradiation of the catalyst.

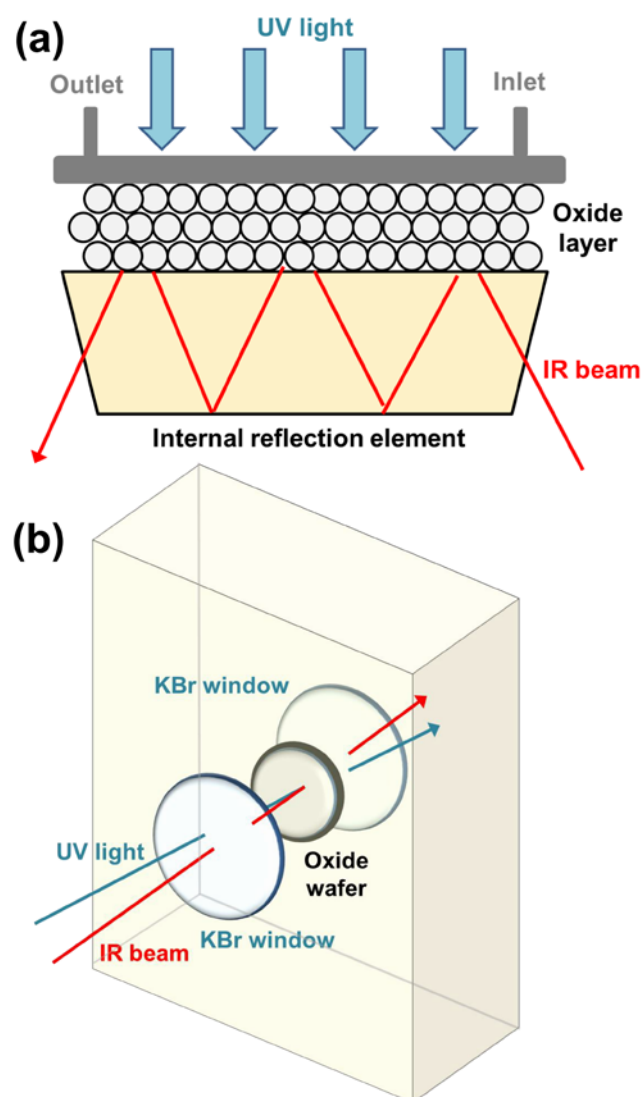


Figure 1. (a) Scheme of a typical ATR-IR setup in which the oxide photocatalyst is deposited as a thin layer on the internal reflection element and it is illuminated from the top by UV light. (b) Scheme of a typical transmission IR setup in which the oxide photocatalyst is placed in form of wafer inside a cell equipped with KBr optical windows, which allow both the IR and UV beams to be focused on the wafer in controlled atmosphere.

3. Gas phase photocatalytic reactions

Several *in situ* IR spectroscopy studies have been devoted to the investigation of the photodegradation of volatile organic compounds (VOCs) which have attracted special attention because of their economic and health impacts. These pollutants are emitted from different sources such as office equipment, combustion by-products, cooking, and construction materials. A long-term exposure to VOCs is detrimental to human health, resulting in sick building syndrome.

Heterogeneous photocatalysis is a promising technology for the degradation of VOCs. Indeed, using a semiconductor photocatalyst irradiated with UV or visible light, the VOCs can be mineralized into carbon dioxide, water and mineral compounds at room temperature.

Zhu *et al.* (Zhu et al. 2010) studied by transmission IR spectroscopy the photodegradation of gaseous benzene under UV irradiation by TiO₂ P25 and by TiO₂ nanoballs obtained by hydrothermal treating of P25 in alkaline solution. The IR spectra indicated that weakly adsorbed phenol is formed as the reaction progresses. Hydroxyl groups on the surface of TiO₂ nanoballs are able to react with photo-produced phenol, which is then retained on the catalyst surface leading to the progressive deactivation of the catalyst in the gas-solid system.

El-Roz *et al.* (El-Roz et al. 2012) developed a setup to study the VOCs photodegradation by time-resolved transmission IR spectroscopy coupled with mass spectrometry (MS), which allows a surface study of the photocatalyst with on-line analysis of the products. They studied the photo-oxidation of methanol (see Figure 2a), n-hexane, and carbon dioxide by TiO₂ P25 and TiO₂ nanotubes (TNTs). The TNT catalyst was found to be 1.5 – 2 times more active and selective than TiO₂ P25 in methanol photo-oxidation with improved results at higher temperature, higher UV light intensity, or lower methanol concentration. A negative influence of temperature was observed for n-hexane photo-oxidation and attributed to surface poisoning by unsaturated species (coke). The TNT material was also more active and selective than TiO₂ P25 for the photooxidation of CO into CO₂, with a negative influence of CO concentration. In conclusion, the TNT material was generally found to be more active and selective than the reference TiO₂ P25 because of its higher surface area. In a more recent paper (El-Roz et al. 2015), they also proposed a global mechanism for methanol photo-oxidation (Figure 2b). The main pathway for methanol photo-oxidation goes through the chemisorption of methanol as surface methoxy species, then their oxidation into formates and, finally, into carbon dioxide. In parallel, neighboring adsorbed formates and methoxy groups can give rise to methylformates, as secondary species.

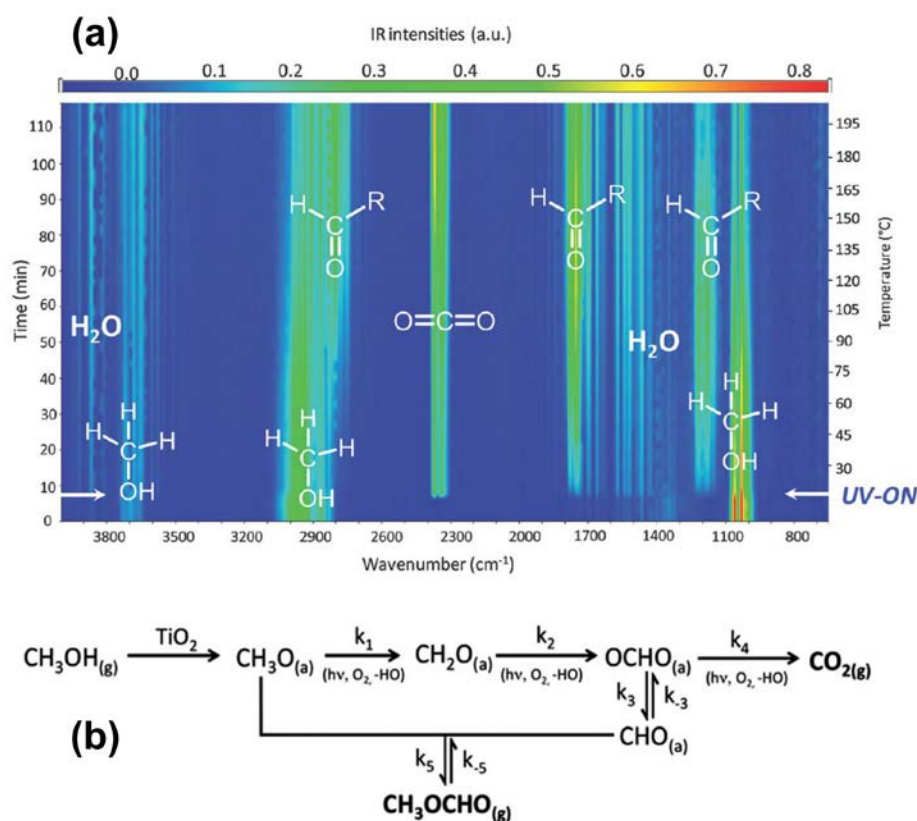


Figure 2. (a) Transmission IR spectra versus time (and temperature) of the gas phase during the photooxidation of methanol by TiO₂ nanotubes (TNTs) at different temperatures. The arrow corresponds to the turn-on time of the UV lamp. (b) Mechanism of methanol photooxidation into CO₂ and CH₃O-CHO obtained from the *operando* IR data. The k_i parameters represent the apparent kinetic constants of each reaction step. Part (a) adapted with permission from Ref. (El-Roz et al. 2012), Copyright ACS (2012); part (b) adapted with permission from Ref. (El-Roz et al. 2015), Copyright Owner Societies (2015).

Sun *et al.* (Sun et al. 2010) investigated the adsorption and photocatalytic oxidation of formaldehyde on TiO₂ P25 under dry and humid conditions by DRIFTS. It was found that the formaldehyde is adsorbed on the OH groups of the catalyst surface via hydrogen bonding. Under UV irradiation, the adsorbed formaldehyde rapidly converts to formate species at room temperature and atmospheric pressure. In dry conditions, the superoxide radical anion O₂^{•-}, formed by electron transfer to the adsorbed oxygen, is suggested to play an important role in the formaldehyde oxidation. The introduction of water vapor increases the amount of hydroxyl groups and molecular water adsorbed on the catalyst surface (Mino et al. 2012) and has a positive effect on the degradation kinetics. Indeed, oxidation of water and hydroxyl groups by the photogenerated holes produces very active OH• radicals, which take part in the redox reactions and, owing to their high redox potential, improve significantly the conversion rate.

Mino *et al.* (Mino *et al.* 2016a; Mino *et al.* 2016b) developed a transmission IR setup allowing to monitor the processes occurring at the oxide surface during photocatalytic reactions under *in situ* UV-Vis irradiation and in controlled atmosphere. They employed this system to study the pseudo-gas phase photocatalytic degradation of phenol on TiO₂ P25. It was highlighted that the activated TiO₂ surface is able to dissociate phenol forming a hydroxyl group and an adsorbed phenolate, then, after completion of the monolayer, undissociated phenol is adsorbed forming a multilayer. Experiments under UV irradiation showed no relevant photocatalytic activity in absence of oxygen, 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. During UV-Vis irradiation in presence of O₂ the main phenol signals progressively decrease, while new bands appear, ascribed to the formation of carboxylic acids (mainly oxalic acid) and of surface carbonates (Mino *et al.* 2014) (see Figure 3). Also the presence of small quantities of catechol and hydroquinone, often reported in the reaction mechanisms discussed in the literature (Grabowska *et al.* 2012), as reaction intermediates can be supposed, although the main IR bands of these compounds fall in the same spectral region of the most intense phenol signals. A quantitative analysis of the phenol photodegradation kinetics at different coverages of co-adsorbed water was performed by considering the variation of the main phenol signals at increasing irradiation times. The pseudo-first order rate constants resulted to be strongly dependent on the surface hydration conditions and increase of one order of magnitude moving from a nearly dehydrated surface to a surface in equilibrium with 10 mbar of H₂O in the gas phase (i.e. in presence of a multilayer of liquid-like adsorbed water).

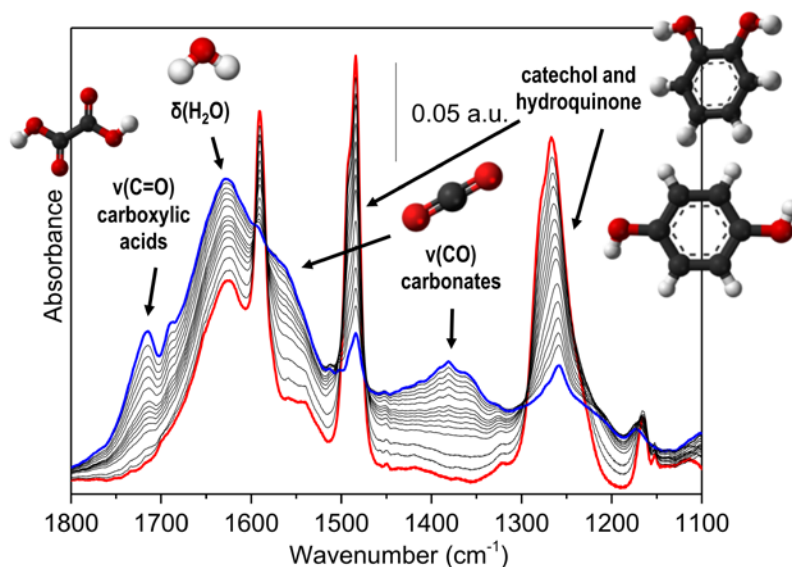


Figure 3. Photodegradation of phenol adsorbed on TiO₂ P25 (previously outgassed at 773 K) in presence of 500 mbar of a 20% O₂ – 80% N₂ mixture and of a monolayer of co-adsorbed water. The red spectrum refers to the TiO₂/phenol system before starting UV irradiation, while the other spectra are recorded at increasing UV-Vis

irradiation times (up to 320 minutes, blue spectrum). The bands of the different intermediates and products are highlighted. Unpublished figure reporting data published in Ref. (Mino et al. 2016b).

4. Photocatalysis at the solid-liquid interface

Attenuated total reflectance infrared (ATR-IR) spectroscopy is an ideal tool to investigate solid-liquid interfaces of powders *in situ*, i.e. during illumination and in the presence of liquid water (see also Section 2). It has been employed to study the surface processes occurring at the oxide surface immersed in water during the degradation of several water pollutants including carboxylic acids, aldehydes and alcohols.

For instance, Gong *et al.* (Gong et al. 2011) investigated by ATR-IR the photo-oxidation of ethanol, acetaldehyde, and acetic acid over pristine and platinized TiO₂ P25. They demonstrated that ethanol photo-oxidation over pure P25 is quite slow and associated with accumulation of free electrons with their associated quasi-continuum absorption, implying that photoreductive activation of oxygen does not proceed at a significant rate in aerated ethanol water solutions. Platinization leads to a significant increase in activity with reduced build-up of negative charge, suggesting that the noble metal acts as a “reactive sink” for electrons. Acetaldehyde and acetic acid were identified as the two key intermediates in ethanol conversion. The rate-determining step was found to be photodecomposition of adsorbed acetate.

Araujo *et al.* (Araujo et al. 2005) analyzed the photocatalytic degradation of oxalic acid at pH 3.7 and of catechol at pH 6.2 by TiO₂ P25. In the case of oxalate photo-oxidation, no intermediates are expected to be formed since the product formed upon hole capture, the radical anion C₂O₄^{•-}, rapidly injects an electron into the conduction band of TiO₂, yielding two CO₂ molecules. However the broad feature at *ca.* 1610 cm⁻¹ present in the ATR-IR spectra during UV irradiation (Figure 4) might contain a contribution from adsorbed carbonates. In the case of catechol, both IR and HPLC demonstrate the formation of an intermediate, the accumulation of carbonate, and the depletion of the ligand on the illuminated surface. Concerning the kinetics aspects, the systems behave as expected for low degrees of coverage, determined by fast surface reactions, $k_2\{h^+\} \gg k_{-1}$, where k_2 is the rate constant for hole trapping by the adsorbed ligand, k_{-1} the rate constant for ligand desorption, and $\{h^+\}$ is the effective hole concentration, determined by the intensity of light. The rate law then turns out to be $R = k_1 N_S [HL]$, where R is the reaction rate, k_1 the adsorption rate constant, N_S the surface site density, and $[HL]$ is the bulk ligand concentration.

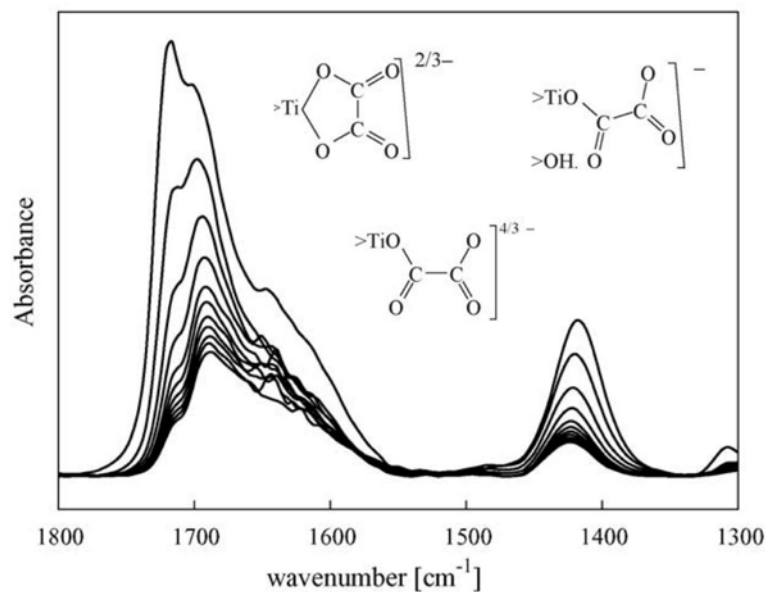


Figure 4. Time evolution of the ATR-IR spectra of oxalate adsorbed at 6.5×10^{-4} M initial concentration and pH 3.7 on TiO₂ P25 under 0.6 mW cm^{-2} UV light irradiation. The spectrum in bold line corresponds to equilibrated dark adsorption, for the following descending spectra the time axis is read downwards; spectra were recorded successively at 3.56 min intervals. The postulated surface species are also represented. Adapted with permission from Ref. (Araujo et al. 2005).

Borer *et al.* (Borer et al. 2007) studied the photodegradation of citrate adsorbed on γ -FeOOH (lepidocrocite) by ATR-IR and by batch photodissolution experiments. Batch photodissolution experiments showed that the R-hydroxycarboxylic acid functional group of citrate was selectively photo-oxidized at pH 4 and pH 6. ATR-IR spectra acquired under irradiation of γ -FeOOH-layers with adsorbed citrate revealed that the primary photoproduct of citrate was acetonedicarboxylic acid. In the presence of excess citrate, the adsorbed photoproduct was exchanged in a ligand-exchange reaction indicating that citrate forms stronger surface complexes than acetonedicarboxylic acid. Moreover, ATR-IR spectroscopy provided key information to show that that only at pH 4 the proposed photoproduct, acetonedicarboxylic acid, is further decomposed to acetoacetic acid. Therefore, the photo-oxidation of citrate at the surface of lepidocrocite follows the same photo-oxidation route of dissolved Fe(III) - citrate complexes.

Dolamic *et al.* (Dolamic and Burgi 2007) combined ATR-IR spectroscopy, modulation excitation spectroscopy and isotope labeling to study the mineralization of malonic acid over TiO₂ P25. ATR-IR spectra of normal and ¹³C-labeled malonic under UV irradiation (Figure 5a) show that the central (labeled) carbon atom of the malonate ends up in an oxalate. The enhanced sensitivity achieved by the phase-sensitive detection of periodically varying signals made the observation of dissolved carbon dioxide possible. From the relative signals of CO₂ and ¹³CO₂ measured during the mineralization of

selectively labeled malonic acid, it was determined that half of the adsorbed malonate was completely converted to CO₂ via oxalate, whereas half of the C₂ intermediates, generated after the first photo-Kolbe reaction, initiated by a photogenerated hole, were desorbed from the surface and washed away without being oxidized (see Figure 5b). Modulation experiments highlighted also the presence of carbonates on the TiO₂ surface under irradiation. Experiments performed with labeled ¹⁸O₂ revealed that the ¹⁸O is incorporated into the adsorbed oxalate. However, oxalate was also formed from irradiated malonate in absence of dissolved oxygen. Therefore at least two different pathways, characterized by different oxygen sources, lead from the carbon-centered radical to the oxalate after the first photo-Kolbe reaction. Moreover, dissolved oxygen influences the rates of the different reaction steps, acting as an electron acceptor and preventing electron-hole recombination. The crucial role of oxygen and water in the photocatalytic degradation of carboxylic acids has been also highlighted in a very recent ATR-IR study (Hu and Bürgi 2016) by the same group devoted to the catalytic photo-oxidation of 3,4-dihydroxybenzoic acid on TiO₂ P25.

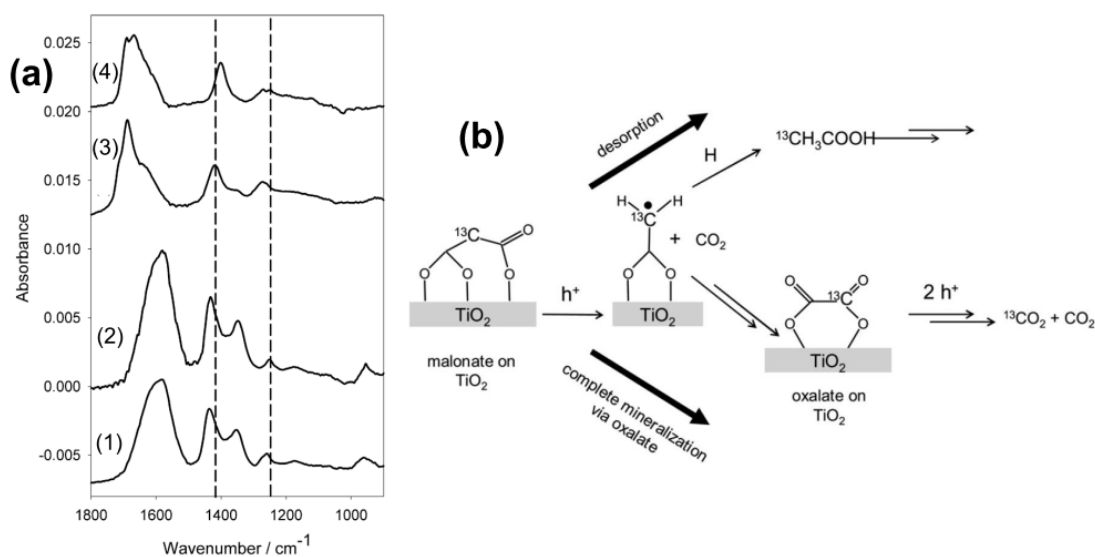


Figure 5. (a) ATR-IR spectra of (1) malonic acid and (2) ¹³C-labeled malonic acid adsorbed from aqueous solutions (1.5×10^{-4} mol/L) on TiO₂ P25 in the dark and of the corresponding adsorbed unlabeled (3) and ¹³C-labeled (4) reaction products after illumination for 7 min and flowing neat water for 14 min. Malonic acid was allowed to adsorb for 30 min before recording the spectra. Only the central C atom of malonic acid was labeled. (b) Proposed mechanism of photocatalytic mineralization of malonic acid over TiO₂ P25. Adapted with permission from Ref. (Dolamic and Bürgi 2007)

4. Conclusions

The discussed examples highlight that *in situ/operando* IR spectroscopy is a valuable tool to characterize in detail the surface state of solid particles, unravelling surface processes which will be difficult to investigate using conventional (*ex situ*) surface analytical techniques.

Different detection modes are available including transmission, diffuse-reflectance (DRIFT) and attenuated total reflectance (ATR). The latter acquisition mode is particularly suitable to directly probe solid-liquid interfaces since the limited penetration depth of the evanescent wave allows to study also liquids with high extinction coefficients, like water.

IR spectroscopy can provide precise information about the time evolution of the species present at the photocatalytic surface during illumination. Therefore accumulation of intermediates and reaction products can be monitored and the kinetic laws, expressed in terms of surface concentrations, can be derived. This approach helps to better understand the photocatalytic mechanisms and facilitates the improvement of the photomineralization processes.

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