1. Introduction

Stable organic chemicals are unfortunately present as pollutants in industrial waste waters and in landfill leachates, and can also diffuse into groundwater, and well and surface water. All such pollutants must be removed to protect our water resources or to achieve drinking water quality. Therefore, many physical and chemical processes have been proposed over the years and are currently being employed for the destruction of these pollutants\(^1\). During the past 20 years, development has been tremendous in the field of heterogeneous photocatalyzed degradation of organic pollutants, as mediated by semiconductors in the presence of light, focusing in particular on mechanistic and kinetic aspects\(^2\).

The molecular transformations or reactions take place on the catalyst surface in a heterogeneous photocatalytic system. Semiconductors (e.g. TiO$_2$, ZnO, CdS, etc.) can act as sensitisers for light induced redox processes, due to their electronic structure which is characterised by a filled valence band and an empty conduction band\(^3\). Absorption of a photon with an energy greater than the bandgap energy leads to the formation of an electron/hole pair. The valence band holes are powerful oxidants (+1.0 to +3.5 V vs. NHE), whereas the conduction band electrons are good reductants (+0.5 to −1.5 V vs. NHE). Such redox potentials can easily achieve the complete degradation of many organic pollutants.

Titanium dioxide is the semiconductor most widely employed as a photocatalyst due to its stability under reaction conditions, low cost, and absence of environmental hazards. The fundamental features of the basic mechanistic steps of the photoinduced process occurring when TiO$_2$ is irradiated with UV light are summarised in Section 2.

This review will describe the molecular phenomena, i.e. adsorption and photoinduced transformations, occurring at the surface of TiO$_2$ in contact with different types of molecules, representative of the common classes of organic chemicals polluting air and water. These phenomena have been studied by IR spectroscopy, to reproduce the interfacial conditions between TiO$_2$ particles and aqueous solutions or wet gaseous streams occurring in solid/liquid and solid/gas systems, respectively, as described in Section 3.

The degradation pathway followed by the adsorbed molecules can be influenced by the specific surface features of the photocatalyst, typically the presence of surface centres able to chemically react (not via photo-stimulated processes) with the original pollutant molecules and/or intermediates. To account for this aspect, some studies were carried out using two types of commercial TiO$_2$ powders, and the differences in surface structure and chemical behaviour are described in...
Section 4.

2. Reaction Mechanisms of Photocatalysis on TiO₂

Most organic photodegradation reactions utilize the oxidising power of the valence band holes either directly or indirectly. In fact, two principal pathways have been proposed for the mineralisation of organic substrates or oxidation of inorganic materials. One pathway involves direct oxidation of organic materials by the holes; the alternative pathway considers the semiconductor surface species, typically hydroxyl groups, as the primary targets of the photogenerated holes.

The surface of TiO₂ is readily hydroxylated when the semiconductor is in contact with water. If a crystal of TiO₂ is formed, the network of Ti⁴⁺ and O²⁻ comes to an abrupt end at the gas-solid or liquid-solid interface. This leads to Ti³⁺ and O₂⁻ species at the surface that are coordinatively unsaturated, that is, there are dangling orbitals (surface states) on the particle surface that can interact with orbitals of other species present at the interfaces. Exposure of a naked TiO₂ crystals to water vapore or to an aqueous medium causes hydroxylation of the surface by dissociative chemisorption of molecular water to satisfy the co-ordination of the surface Ti³⁺ ions.

Dissociation of water on a pure TiO₂ surface forms two distinctive hydroxyl groups: one OH⁻ group bridges two surface vicinal Ti³⁺ ions and the other forms a terminal Ti³⁺–OH⁻ group with basic character. The TiO₂ particle surface also contains the coordinated and physisorbed water of hydration. Temperature programmed desorption experiments have measured the number of surface OH⁻ groups at ca. 7–10 OH⁻/nm² for TiO₂ at ambient temperature, depending on the type of crystal plane examined. Moreover, chemisorbed water amounts to about 2.3 molecules/nm². Thus, most if not all of the TiO₂ sites are occupied[6,5].

In the absence of light, the particle surface will have specific electronic characteristics and a specific number of adsorption sites onto which anions, cations, organics, and other species present can chemisorb or physisorp, reversibly or irreversibly. In the presence of light, the surface electronic properties will undergo dramatic changes, altering as well the nature of the adsorption sites. Thus, different dark adsorption/desorption events will occur, and additional new events will take place arising from the photodesorption/photodesorption equilibria.

The primary photochemical process, subsequent to near-UV light absorption by TiO₂ particles (wavelengths < 380 nm), is the generation of conduction-band electron (e⁻CB) and valence-band hole (h⁺VB) pairs:

\[ \text{TiO}_2 + h\nu \rightarrow \text{TiO}_2(e^- + h^+) \rightarrow e^-\text{CB} + h^+\text{VB} \] (1)

Physically, the hole that is associated with valence-bonding orbitals is constrained at the surface or subsurface sites in the region where light is absorbed. The greater mobility of the electron facilitates its migration across the particle. If both charge carriers are present on the surface, recombination can occur, or they can be ultimately trapped by extrinsic traps via interfacial electron transfer with surface adsorbed electron donors (D_ads) and acceptors (A_ads), respectively:

\[ h^+\text{VB} + D_{\text{ads}} \rightarrow D'_{\text{ads}} \] (2)
\[ e^-\text{CB} + A_{\text{ads}} \rightarrow A'_{\text{ads}} \] (3)

Since OH⁻ groups and water are the most abundant electron donors, the holes are most likely to react with these species. In fact, in the case of a hydrated and hydroxylated TiO₂ surface, hole trapping occurs via Eqs. (4) and (5) to give surface-bound •OH radicals.

\[ [\text{Ti}^{IV}_2\text{O}_2\twoheadleftarrow\text{Ti}^{IV}_2]\text{OH} + h^+\text{VB} \rightarrow [\text{Ti}^{IV}_2\text{O}_2\twoheadleftarrow\text{Ti}^{IV}_2]\text{•OH} \] (4)
\[ [\text{Ti}^{IV}_2\text{O}_2\twoheadleftarrow\text{Ti}^{IV}_2]\text{H}_2\text{O} + h^+\text{VB} \rightarrow [\text{Ti}^{IV}_2\text{O}_2\twoheadleftarrow\text{Ti}^{IV}_2]\text{•OH} + \text{H}^+ \] (5)

On the other hand, adsorbed O₂ molecules are usually recognised as the most efficient electron trappers, giving O₂⁻ species[3,6].

For the oxidation of OH⁻ or H₂O to occur, the oxidation potential for reactions (4) and (5) must lie above (i.e. be more negative than) the position of the semiconductor valence band E_v. The semiconductor band potentials are a function of pH, with the valence band of TiO₂ in the anatase form at about +2.6 eV (vs. NHE) at neutral pH and varying as −0.059 V/pH unit. The oxidation potentials for the reactions of Eqs. (4) and (5) remain above E_v (thermodynamically favourable) throughout the entire pH range, with reaction (4) favoured at high pH and (5) favoured at low pH. Thus, under both acidic and basic conditions, the oxidation of surface-bound OH⁻ and H₂O by TiO₂ valence band holes to form •OH is thermodynamically possible and expected.

The oxidation potentials for many organic compounds are also above the E_v of anatase, so they should be thermodynamically able to interact directly with holes at the photocatalyst surface. However, experiments run in water-free, aerated organic solvents have found only partial oxidation of organics. The complete mineralisation to CO₂, common in aqueous solutions, was not detected, so the presence of water or hydroxyl groups appears to be essential for the complete oxidative destruction of organic reactants. The intermediates detected during the photocatalytic degradation of aromatic compounds typically have hydroxylated structures, and are consistent with those found when similar aromatics are reacted with a known source of hydroxyl radicals, further suggesting that •OH is the primary attacking species[5].

The necessity for preadsorbed D and A for efficient charge carrier trapping emphasises the importance of adsorption-desorption equilibria in photocatalysis. In the case of degradation processes carried out in aqueous media, these equilibria and the extent of adsorption

J. Jpn. Petrol. Inst., Vol. 47, No. 6, 2004
will depend on such factors as the pH of the medium and the point of zero charge (PZC) for the TiO2 used (for anatase PZC = 6.0-6.4\(^{+}\)), which, in turn, is highly affected by the particle environment (nature of ions and ionic strength, among others). At pH < PZC, the particle surface is positively charged which should enhance adsorption of anionic and polar substrates, whereas at pH > PZC the surface charge is negative which should favour adsorption by cationic species.

Conversely, it should be also emphasised that, in the absence of adsorbed species and of suitable conditions, trapped electrons and holes can rapidly recombine on the particle surface. To prevent recombination of holes and electrons, the latter can be effectively scavenged by preadsorbed (and photoadsorbed) molecular oxygen, to give the superoxide radical anion \(\text{O}_2^{-}\) (ads), which can be reduced further to the peroxide dianion \(\text{O}_2^{2-}\) (ads). Alternatively, surface peroxo-species can be formed either by hydroxyl radical (hole) pairing or by sequential two-hole capture by the same \(\text{OH}^{-}\) group or by dismutation of \(\text{O}_2^{2-}\)\(^{+}\).

3. Experimental

Details on the specific experimental conditions adopted in the various reviewed studies are reported in the original paper. Here, the common, general aspects of the procedures adopted are summarised.

3.1. Materials

Two types of polycrystalline TiO2 commercial powders have been considered, produced by Merck (anatase phase, BET specific surface area 10 m\(^2\cdot\text{g}^{-1}\)), and by Degussa (P25 type, 80% anatase, 20% rutile, BET specific surface area 50 m\(^2\cdot\text{g}^{-1}\)). Adsorption and photodegradation experiments used high purity O\(_2\), H\(_2\)O, CO, CO\(_2\) and organics. For these last, details are reported in the section devoted to the various types of compounds.

3.2. Methods

For the IR measurements, TiO2 powders were pressed in the form of self-supporting pellets (ca. 20 mg\cdotcm\(^{-2}\)) and put in a conventional IR quartz cell equipped with CaF\(_2\) windows connected to a vacuum line (residual pressure: 1 \times 10^{-6} \text{Torr}, 1 \text{Torr} = 133.33 \text{ Pa}) which allowed adsorption-desorption experiments to be carried out in-situ. In general, the TiO2 pellets were simply outgassed at room temperature, in order to maintain a full monolayer of hydroxyl groups and water molecules coordinated to the surface Ti\(^{4+}\) ions, which is expected to correspond the first surface hydration layer in both the gas-solid and liquid-solid systems. The FT-IR spectra (4 cm\(^{-1}\) resolution) were recorded with a Bruker spectrophotometer equipped with a MCT detector.

In the photo-oxidation experiments the TiO2 pellets were irradiated in the presence of O\(_2\) (usually 100 Torr) and H\(_2\)O (usually 18 Torr) through the quartz walls of the IR cell by a medium pressure Hg lamp (Model GN ZS Helios Italquartz). A pyrex + water filter was placed between the lamp and the cell, which was also air cooled.

In the case of the studies reported in Section 4, the size and morphology of the TiO2 microcrystals were detected by high resolution transmission electron microscopy (HRTEM) carried out with a Jeol 2000EX microscope equipped with a pole piece and top entry stage. Before introduction into the instrument, the samples were ultrasonically dispersed in isopropyl alcohol, and a drop of the suspension was deposited on a copper grid covered with a lacey carbon film. Chemical features of the surface centres were investigated by FT-IR spectroscopy of adsorbed CO and CO\(_2\). To study the surface properties at different degrees of dehydroxylation, the samples were first outgassed at the desired temperature for 1 h, and then treated in O\(_2\) (150 Torr) at the same temperature for 1 h, cooled to room temperature in O\(_2\) and finally outgassed. After this procedure the samples appeared white, as expected for fully oxidised, stoichiometric TiO2.

4. Lattice Structure and Surface Reactivity of TiO2

Two different forms of TiO2, rutile and anatase, are commonly used in photocatalysis, with anatase showing a higher photocatalytic activity. The structures of rutile and anatase can be described in terms of chains of Ti\(_6\) octahedra. The two crystal structures differ in the distortion of each octahedron and the assembly pattern of the octahedra chains\(^{+}\).

Figure 1 shows the unit cell structures of the rutile and anatase forms. Each Ti\(^{4+}\) ion is surrounded by an octahedron of six O\(^2-\) ions. The octahedron in rutile is not regular, showing a slight orthorhombic distortion. The octahedron in anatase is significantly distorted so that its symmetry is less than orthorhombic. The Ti-Ti distances in anatase are greater (0.379 and 0.304 nm vs. 0.357 and 0.296 nm in rutile), whereas the Ti-O
distances are shorter than in rutile (0.1934 and 0.1980 nm in anatase vs. 0.1949 and 0.1980 nm in rutile). In the rutile structure, each octahedron is in contact with eight neighbours (four sharing an edge and four sharing a corner). These differences in lattice structures result in different mass densities and electronic band structures for the two forms of TiO₂.

Besides differences in the bulk structure, there are differences in the surface structures, resulting from the different morphology of TiO₂ particles, which can be important.

Two commercial photocatalysts were generally examined, TiO₂ P25 from Degussa (80% anatase, 20% rutile, BET specific surface area 50 m²·g⁻¹) and TiO₂ from Merck (pure anatase phase, BET specific surface area 10 m²·g⁻¹).

4.1. Surface Morphology of TiO₂ Particles

TEM images of Merck TiO₂ showed the presence of large particles, with a mean size of ca. 140 nm and characterised by both sharp and roundish edges (Fig. 2). The presence of roundish edged particles prevented crystallographic indexing in many cases, while sharp edges appear parallel to fringes pattern corresponding to the interplanar spacing of (101) planes.

TEM images showed that the Degussa P25 photocatalyst is characterised by the presence of plate-like particles with irregular contours and mean size of ca. 40 nm. HRTEM images revealed the presence of two series of perpendicular interference fringes on most particles (Fig. 3). These fringes are related to the (110) planes of anatase, actually orthogonal to the (001) face, which corresponds to the face lying in the plane of the image. The analysis of fringe patterns revealed that, in other cases, the (010) planes are also exposed at the microcrystal surface, suggesting that the (001) and (010) planes are the more extended faces of the particles and correspond to the more abundant faces exposed at the surface of the microcrystals. Five-coordinated Ti⁴⁺ cations, with a single coordinative unsaturation with respect to the titanium cations in the bulk, are exposed on both these faces, together with oxygen anions bonded to three cations and oxygen anions bridged to two cations.

FT-IR characterisation of the surface active sites was carried out on both photocatalysts to predict and to explain the differences in the chemical and photocatalytic behaviour towards the degradation of the organic compounds considered in this study.

4.2. IR Spectra of Hydroxyl Groups

Figure 4 shows the IR spectra in the νOH region of TiO₂ P25 (Fig. 4A) and TiO₂ Merck (Fig. 4B) in air, which were both significantly more intense than the corresponding spectra recorded after outgassing at room temperature and activation at 873 K (Fig. 4 a, b and c, respectively), which resulted in extensive dehydroxylation. In contrast, after outgassing at room temperature, an almost complete monolayer of hydroxyl groups and water molecules coordinated to surface cations persisted. These conditions are assumed to be representative of the hydration state of the catalyst surface during the photo-oxidative process, carried out in the presence of water vapour at medium temperatures (413 K).

The spectrum of TiO₂ P25 (Fig. 4B) was characterised by a series of narrow components in the 3800-
3600 cm\(^{-1}\) domain, including a dominant peak at 3630 cm\(^{-1}\) with a series of heavily overlapped shoulders on the high frequency side due to the stretching mode (\(\nu\)OH) of different types of free hydroxyl groups\(^{11,13,14}\), and by an intense and broad absorption in the 3600-3200 cm\(^{-1}\) range, with two maxima at 3415 and 3260 cm\(^{-1}\), resulting from the superposition of the \(\nu\)OH mode of bonded hydroxyl groups and the symmetric and antisymmetric \(\nu\)OH modes of molecular water coordinated to Ti\(^{4+}\) ions\(^{11,15,16}\), as cations on the (110) face of microcrystalline rutile\(^{17}\).

The variety of components in the 3800-3600 cm\(^{-1}\) region indicates the great heterogeneity of hydroxyl groups. The origin of this heterogeneity can be ascribed to the different types of planes exposed at the surface of the TiO\(_2\) P25 microcrystals and to the presence of sites in defect positions (steps, edges, corners)\(^{11,13,14}\). Interestingly, the Ti\(^{4+}\) ions on the most abundant, regular faces of TiO\(_2\) P25 microcrystals monitored by CO adsorption appeared highly homogeneous, whereas at least two types of O\(^{2-}\) were suggested on these faces on the basis of the CO\(_2\) adsorption data. Apparently, OH groups, which are formed by dissociation of water molecules on Ti\(^{4+}\)-O\(^{2-}\) pairs, reflect the heterogeneous character of the system.

In contrast, the IR spectrum of TiO\(_2\) Merck was much simpler. A single peak at 3665 cm\(^{-1}\) was observed, slightly asymmetric on the low frequency side, and a weaker broad band was present in the 3500-2800 cm\(^{-1}\) range (Fig. 4A). The main component at 3665 cm\(^{-1}\) and the ill resolved shoulder on the low frequency side should correspond to the stretching vibration of two types of free hydroxyl groups, indicating greater homogeneity of the Ti\(^{4+}\)-O\(^{2-}\) pairs for this type of material. Furthermore, the relatively weak intensity of the broad band in the 3500-2800 cm\(^{-1}\) range, mainly due to the symmetric and asymmetric \(\nu\)OH modes of the coordinated water molecules, indicates that very few Ti\(^{4+}\) ions able to coordinate H\(_2\)O in the undissociated form are present on the surface of the TiO\(_2\) Merck particles.

4. 3. Lewis Acid and Basic Sites Probed by IR Spectroscopy of Adsorbed CO and CO\(_2\)

FT-IR investigation of the adsorption of suitable molecular probes was used to evaluate the nature of the sites on the “naked” surface of the two photocatalysts, after removal of hydroxyl groups. The features of the Lewis acid Ti\(^{4+}\) centres exposed at the surface of the two TiO\(_2\) powders were investigated by CO adsorption at 77 K on the photocatalysts previously outgassed at 873 K to obtain highly de-hydroxylated surfaces (Figs. 5A and 5B)\(^8\).

The spectrum of the TiO\(_2\) Merck photocatalyst in the 3750-3500 cm\(^{-1}\) range before CO admission revealed the presence of a very weak band at 3670 cm\(^{-1}\) (Fig. 5A, inset, curve a). After CO admission, this component was completely depleted and a broad signal at 3575 cm\(^{-1}\) due to CO molecules H-bonded with hydroxyl species was observed (Fig. 5A, inset, curve b), but the original spectrum was fully restored after CO outgassing to 2 Torr of equilibrium pressure (Fig. 5A, inset, curve c), indicating the complete reversibility of CO interaction with OH groups. In the 2300-2100 cm\(^{-1}\) range, at high CO coverage, a main peak was present at 2156 cm\(^{-1}\) (Fig. 5A, curve a), due both to CO molecules coordinated to the most common types of Ti\(^{4+}\) ions (present on the roundish surface of TiO\(_2\) Merck microcrystals) and hydrogen bonded to hydroxyl groups. By decreasing the CO pressure, this main peak shifted to 2159 cm\(^{-1}\) and a signal at 2170 cm\(^{-1}\) was observed, which can be assigned to CO molecules coordinated to Ti\(^{4+}\) ions on the less common (101) planes (Fig. 5A, inset, curve c).

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The spectrum of TiO$_2$ Degussa P25 showed the weak bands at 3720 and 3675 cm$^{-1}$ before exposure to CO (Fig. 5B, inset, curve a) due to the $\nu_{\text{OH}}$ mode of hydroxyl groups left on the surface after activation at 873 K, which were completely depleted after CO adsorption, and a broad absorption at 3570 cm$^{-1}$ was observed (Fig. 5B, inset, curve b). The original spectral profile was completely restored by decreasing the CO pressure in equilibrium with the sample to 2 Torr (Fig. 5B, inset, curve c), indicating that complete desorption of CO from hydroxyl groups also occurs in this case. Correspondingly, in the 2300-2100 cm$^{-1}$ range, a main sharp peak appeared at 2178 cm$^{-1}$ at high CO coverage, which can be assigned to parallel CO oscillators $\sigma$-bonded to the highly acidic pentacoordinate Ti$^{4+}$ cations present on the very extended and regular (010) and (001) planes. The weak signal at 2156 and 2170 cm$^{-1}$ are both located at higher frequency than the corresponding signals on the surface planes of TiO$_2$ Merck.

The greater shift undergone by the main peak caused by decreasing the CO coverage in the case of TiO$_2$ Degussa P25 indicates that the adsorbate-adsorbate interaction is highly effective for this system, suggesting that extended crystal planes are present on the surface of the particles. Moreover, the bands at 2156 and 2170 cm$^{-1}$ are both located at higher frequency than the corresponding signals on the surface planes of TiO$_2$ Merck.

The upward shift of the stretching mode of CO molecules adsorbed on surface cations with respect to CO in the gas phase (2143 cm$^{-1}$) increases as the Lewis acid strength of the adsorbing centres increases, and the difference in the position of the stretching band of CO adsorbed on the two types of TiO$_2$ powders clearly indicates that both types of Ti$^{4+}$ ions exposed on the roundish surfaces and (101) faces of TiO$_2$ Merck have significantly lower acidity than those exposed on the (001) and (010) surfaces of TiO$_2$ Degussa P25 microcrystals.

Since the Ti$^{4+}$ cationic centres are accompanied by O$_2^-$ counter-ions, the difference in Lewis acidity will also depend on the presence of different Lewis basic centres in the two forms of TiO$_2$, resulting in acid-base couples with different Lewis acid-base character. CO$_2$ was used as a probe to test the basic character of the two photocatalysts surface sites. Very similar results were obtained by adsorbing CO$_2$ over samples activated at 423 and 873 K. For the sake of brevity, only the spectra obtained in the case of the sample outgassed at the lowest temperatures are reported.

CO$_2$ adsorption on TiO$_2$ Merck previously activated at 423 K resulted in the spectra reported in Fig. 6A,
which also shows the dependence on pressure (curves a-d). Only the peak at 2347 cm$^{-1}$ was observed, due to the stretching mode of CO$_2$ molecules linearly adsorbed on surface cations, with no significant absorptions in the low frequency range.

In contrast, P25 had a much richer spectrum. Figure 6B shows the spectra after adsorption of an increasing amount of CO$_2$ on TiO$_2$ Degussa P25 previously activated at 423 K. The most intense peak in the spectrum was observed at 2351 cm$^{-1}$ and can be assigned to the stretching mode of $^{12}$CO$_2$ linearly adsorbed on Ti$^{4+}$ on regular faces of the TiO$_2$ P25 microcrystals. The weaker component at 2280 cm$^{-1}$ is the corresponding absorption for $^{13}$CO$_2$ molecules present in natural abundance. Moreover, the signal at 2351 cm$^{-1}$ was located at higher frequency than in the case of TiO$_2$ Merck (2347 cm$^{-1}$), and since the shift of this signal with respect to the gas phase (2343 cm$^{-1}$) increases together with the Lewis acid strength of the cationic adsorbing sites, this difference agrees well with the difference in the Lewis acid strength of the surface Ti$^{4+}$ ions of the two TiO$_2$ powders as shown by the IR spectra of CO adsorbed at 77 K.

At lower wavenumbers, in the 1800-1000 cm$^{-1}$ range, the presence of a complex spectroscopic pattern indicated the formation of various types of carbonate-like species, namely mono- (1578 and 1359 cm$^{-1}$) and bidentate (1672, 1243 and 1053 cm$^{-1}$) carbonates, due to nucleophilic attack of O$_2^-$ anions on the CO$_2$ molecules previously linearly adsorbed on adjacent Ti$^{4+}$ centres. The presence of bands due to carbonate-like groups indicates the presence of Ti$^{4+}$-$O_2^-$ couples, in which the anions are nucleophilic enough to react with CO$_2$. Moreover, signals at 1630, 1430, 1408 and 1221 cm$^{-1}$ are the consequence of bicarbonate group formation, due to the reaction between the OH basic species and adsorbed CO$_2$ molecules. A similar reactivity towards CO$_2$ was found for TiO$_2$ P25 activated at 873 K (spectra not reported). However, the bands due to bicarbonate-like species were strongly reduced in intensity, because of the high degree of dehydroxylation attained, and components due to bidentate carbonate species appeared less intense. Significantly, no bands due to carbonate-like species were detected for TiO$_2$ Merck, indicating that no O$_2^-$ centres could react with CO$_2$ linearly adsorbed on adjacent Ti$^{4+}$ ions on the surface of this system.

The differences in the Lewis acid and base character of Ti$^{4+}$ and O$^{2-}$ sites, respectively, as shown by the experiments reported above, are the basis of the different chemical features of the hydroxyl groups formed by reaction of such centres with H$_2$O molecules, which are naturally formed at the end of the preparation route, when TiO$_2$ powders are stored in air. For the two types of titania powder considered, several studies indicated that hydroxyl groups at the surface of TiO$_2$ P25 are basic enough to react with CO$_2$ to give bicarbonate-like species or with carbonylic compounds and nitrilic compounds. The effect of such specific features on photocatalytic processes are reported in more detail in the sections devoted to the photo-transformation of the various types of organic molecules.

5. Photo-transformation of Organic Pollutants

Adsorption (in the dark) and subsequent exposure to UV light have been investigated for various organic molecules, and the results are described below.
5.1 Phenolic Compounds

Phenolic compounds are among the most refractory pollutants present in industrial waste waters. Their high stability and solubility in water represent the main obstacles to complete removal. Purification of wastewater contaminated with these pollutants is very difficult since they are resistant to conventional treatment techniques.

The largest use of phenol is as an intermediate in the production of phenolic resin. Phenol is also used in the production of caprolactam, which is used in making nylon, and Bisphenol A, which is used in making epoxy and other resins. Moreover, phenol is also used as a fungicide, as a disinfectant, and in medicinal preparations such as over-the-counter treatments for sore throats. The International Agency for Research on Cancer (IARC) does not classify phenol as carcinogenic in humans, but the acidity causes coagulation necrosis as a result of the desiccating action of the acid on proteins in surface tissues and phenol ingestion results in cardiac effects because it blocks cardiac sodium channels.

Nitrophenols are considered priority pollutants by the United States Environmental Protection Agency and the maximum allowed concentrations range from 1 to 20 ppb. Nitrophenols are widely used in the manufacture of explosives, pharmaceuticals, pigments, dyes and rubber chemicals. Among the mononitrophenols, 4-nitrophenol is probably the most important in terms of quantities used and potential environment contamination. It may be produced in the atmosphere by the photochemical reaction between benzene and nitrogen monoxide and has been detected in samples of urban particulate matter. Moreover, a number of widely used pesticides, including parathion, are readily metabolised to 4-nitrophenol in the human body and are believed to be the source of 4-nitrophenol residues in human urine.

The presence and widespread use of chlorinated aromatic solvents, chemical cleaning agents, biocides, preservatives and pesticides in the environment represents a serious problem because of their toxicity and potential for accumulation in plants and animal tissues. Soluble chlorinated organic compounds, like chlorophenols, have recently shown extended potential to enter the food chain. Obviously, the contamination may arise in various ways: runoff from croplands, effluents from industry, and disinfection of drinking water supplies and water treatment with chlorine. In fact, water which is initially free from organochlorine compounds can become contaminated in the chlorination treatment processes as a result of reactions between the chlorine and naturally occurring humic and fulvic acids in the water, leading to the formation of chlorinated organics, like chlorophenols.

5.1.1 Phenol

5.1.1.1 Phenol Adsorption

Standard gas-solid interaction procedures were adopted for the FT-IR measurements and self-supported pellets of TiO_2 were employed for the adsorption and photodegradation of phenol via the vapour phase. Preliminary investigations had shown that standard gas-solid interaction procedures simulate well the adsorption behaviour in an aqueous suspension, although a definitely better signal to noise ratio can be obtained in the solid-gas system. Polycrystalline TiO_2 Degussa P25 was used for the FT-IR measurements and for the phenol adsorption and photodegradation runs.

After phenol adsorption in the presence of 10 Torr of water vapour, intense bands were observed at 1590, 1480, and 1265 cm\(^{-1}\), together with weaker components at 1600, 1490, 1380, 1280, 1240, 1170, and 1160 cm\(^{-1}\) (Fig. 7, curve a). By comparison with the phenol spectra registered in aqueous solution at different pHs, these components can be easily assigned. The molecular form C_6H_5OH (prevailing at low pHs) is mainly responsible for the signal at 1380 and 1170 cm\(^{-1}\) and contributes to the broad absorption bands at 1590 cm\(^{-1}\) with a band at 1595 cm\(^{-1}\) and a shoulder at 1605 cm\(^{-1}\), the two weak bands at 1500 and 1475 cm\(^{-1}\) and the components at 1265 and 1240 cm\(^{-1}\) (Fig. 7, curve b). Conversely, ionic C_6H_5O\(^{-}\) species (prevalent at alkaline pHs) predominantly contribute to the signals at 1585, 1480 and 1270 cm\(^{-1}\). The spectrum of phenolate ions is also characterised by the presence of a weaker components at 1565 and 1150 cm\(^{-1}\), which may also contribute to the spectrum of the adsorbed phenol (Fig. 7, curve c).
The presence of the signals of both undissociated phenol and phenate species in the spectrum of the phenol adsorbed on the catalyst simply outgassed at room temperature clearly suggests that different adsorption processes are occurring. The undissociated phenol molecules are probably stabilised via hydrogen-bonding through their functional group, whereas the presence of basic surface hydroxyls may be responsible for the acid-base reaction which leads to the formation of hydroxyl species.

5.1.2. Phenol Photo-transformation

After phenol adsorption, the TiO₂ pellets were exposed to UV radiation through the quartz walls of the IR cell, maintaining the photocatalyst in contact with water vapour and O₂ during irradiation, to simulate the liquid-solid regime in actual photodegradation systems.

The exposure of the catalyst to UV irradiation for increasing time intervals leads to important modifications in the spectral pattern. In particular, all signals due to adsorbed phenol were progressively depleted, and new components appeared in the spectrum. More specifically, after the first irradiation steps, new bands appeared at 1715, 1645, 1555, 1450, 1325, 1210 and 1105 cm⁻¹ (Fig. 8, curve b). Moreover, the complex absorption in the 1300-1200 cm⁻¹ range evolved with the formation of two peaks at 1265 and 1275 cm⁻¹, and a shoulder at 1305 cm⁻¹, and the composite band centered at 1485 cm⁻¹ was progressively transformed to a simpler peak at 1482 cm⁻¹.

At the end of the complete photodegradation cycle, the signals due to the adsorbed phenol had almost completely disappeared, pointing to complete mineralisation of the organic substrate. In fact, under these conditions, the spectrum was characterised by a new, very broad and complex absorption in the 1800-1500 cm⁻¹ range, with minor peaks at 1445, 1380 and 1360 cm⁻¹, mainly due to the presence of carbonate-like species of various types adsorbed on the surface of TiO₂ (Fig. 8, curve c).

To understand the reaction mechanism of phenol photodegradation, an evaluation of the nature and reactivity of intermediate species was carried out. Poly-hydroxybenzenes had been previously indicated as possible intermediates of phenol photo-oxidation, due to the attack of highly active OH radicals at the activated position of the aromatic ring. Adsorption via the vapour phase of the three isomeric dihydroxybenzenes was attempted, to evaluate the influence of the OH group on the reaction mechanism. The experiments were possible only with pyrocatechol and hydroquinone, and failed with resorcinol, which had an exceedingly low vapour pressure.

The spectrum of pyrocatechol adsorbed on TiO₂ was very similar to that obtained at partial photodegradation of phenol. Some components due either to unreacted phenol or to more oxidised species were present, but further experiments have shown that pyrocatechol undergoes photodegradation on TiO₂, producing carbonate species and water, as found with phenol.

The spectrum of hydroquinone adsorbed on TiO₂ did not indicate the presence of any species detected at the intermediate stages of photodegradation of phenol. However, this observation may be misleading as hydroquinone is very reactive on the surface of TiO₂. In fact, the results showed that adsorbed hydroquinone is converted, by contact with O₂, to benzoquinone which is very quickly transformed to carbonate species and water under UV-Vis irradiation. Therefore, hydroquinone formed during phenol degradation is unlikely to be observed as an intermediate on the surface because of its extremely rapid transformation. The presence of quinones in the bulk of the water suspension during phenol degradation in batch photoreactors suggests that part of the degradation products may desorb from the catalyst and diffuse into aqueous medium, far from the reactive centres at the liquid-solid interface, where quinones would undergo very fast mineralisation.

5.1.2. Nitrophenol

5.1.2.1. Nitrophenol Adsorption

Adsorption and photo-oxidation experiments on nitrophenols were carried out on the TiO₂ Merck photocatalyst for the ortho-isomer (2-nitrophenol), which has a reasonably high vapour pressure at room temperature.

Adsorption of increasing amounts of 2-nitrophenol on the photocatalyst outgassed at room temperature lead to the transmittance spectra reported in Figs. 9A and 9B. New signals appeared in the spectra in the 1600-1200 cm⁻¹ range due to contact with 2-nitrophenol vapour with the TiO₂ surface (Fig. 9A, curves b and c), but the broad band at 1630 cm⁻¹ already present in the spectrum of the catalyst simply outgassed at
room temperature due to the bending mode of water adsorbed in molecular form (Fig. 9A, curve a) was masked by new adjacent components. By comparison with the spectrum of 2-nitrophenol in solution, the main bands at 1612, 1475, 1441, and 1331 cm\(^{-1}\) can be assigned to ring modes, the signals at 1270 and 1255 cm\(^{-1}\) to CO vibrations, and the components at 1348 and 1520 cm\(^{-1}\) to NO\(_2\) symmetric and asymmetric stretching.

In the high wavenumber region, the signal due to the stretching mode of free hydroxyl groups (3680 cm\(^{-1}\)) was progressively depleted by contact with increasing doses of 2-nitrophenol (Fig. 9B, curves b and c), indicating that surface OH groups are certainly involved in the adsorption of 2-nitrophenol. Simultaneously, a new broad absorption increased in the 3600-3200 cm\(^{-1}\) range, with two superimposed signals at 3125 and 3085 cm\(^{-1}\) due to CH stretching.

5.1.2.2. Nitrophenol Photo-transformation

After 2-nitrophenol adsorption, oxygen was allowed into the cell and the sample was UV irradiated. Figure 10 shows the spectra corresponding to the catalyst in contact with the highest amount of nitrophenol before (curve a) and after irradiation for 2 h (curve b).

All components due to adsorbed 2-nitrophenol were depleted after UV irradiation, indicating that the adsorbed species were progressively destroyed during the photodegradation process, and simultaneous formation of new signals was indicated. Conclusive identification of intermediates and by-products was not possible, but a tentative reaction mechanism may be suggested, based on parallel photocatalytic runs carried out in batch reactors and the formation of highly oxidised species by reaction with the holes\(^{30}\):

\[
\begin{align*}
\text{TiO}_2\text{(substrate)}\text{OH}^- + h^+ & \rightarrow \text{TiO}_2\text{(substrate)}\text{OH}^\cdot \\
\text{O}_2\text{N-C}_6\text{H}_4\text{OH}\text{(ads)} + h^+ & \rightarrow \text{O}_2\text{N-C}_6\text{H}_4\text{O}^\cdot + \text{H}^+ \\
\text{and/or} & \\
\text{O}_2\text{N-C}_6\text{H}_4\text{OS}^- + h^+ & \rightarrow \text{O}_2\text{N-C}_6\text{H}_4\text{O}^\cdot + \text{H}^+ \\
\text{O}_2\text{N-C}_6\text{H}_4\text{OH}\text{(ads)} + \text{OH}^\cdot & \rightarrow \text{O}_2\text{N-C}_6\text{H}_4\text{(OH)}_2 + \text{other intermediates} \\
& \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{H}^+ + \text{NO}_2^-/\text{NO}_3^- 
\end{align*}
\]

5.2. Volatile Organic Compounds (VOCs)

Volatile Organic Compounds (VOCs) in the urban and industrial atmosphere mainly originate from motor vehicle exhausts and other combustion processes utilizing fossil fuels, solvent usage and other industrial processes. The most important emitters among industrial
processes are petroleum refineries and petrochemical plants, and their operations are generally associated with the emission of various organic compounds into the atmosphere, mainly originating from the production processes, the storage tanks and the waste areas. In the petrochemical industries, most of the organic compounds are derived from light petroleum fractions, and essentially from hydrocarbons such as methane, ethane, propane, benzene, toluene and xylene.

Several effects of VOCs are recognised, such as stratospheric ozone depletion, toxic and carcinogenic effects, and enhancement of the global greenhouse effect. Studies on the carcinogenicity of certain classes of hydrocarbons indicate that some cancers appear to be caused by exposure to aromatic hydrocarbons in combination with NO\textsubscript{x} which, in the presence of sunlight, undergo photochemical oxidation, producing a photochemical smog that is environmentally hazardous.

Regulations on controlling organic vapour pollutants in air have been issued worldwide. The ambient air quality standards of the US Environmental Protection Agency require that the maximum 3-h hydrocarbon content should not exceed \(5.0 \times 10^{-4}\) kg/m\(^3\) (0.24 ppm) for more than a year. The recently passed European Community stage emission limit is 35 g total organic carbon per cubic meter gasoline loaded. Similarly, the US Environmental Protection Agency Standard 40 CFR Part 63 has established an emission limit of 10 g TOC/m\(^3\).

5. 2. 1. Example of VOCs: Toluene

5. 2. 1. 1. Toluene Interaction with TiO\textsubscript{2} Surface

Toluene and toluene/water adsorption experiments were carried out on TiO\textsubscript{2} Merck samples pre-outgassed at room temperature, with a monolayer of hydroxyl groups and water molecules still covering the surface of the TiO\textsubscript{2} microcrystals.

The corresponding IR spectra are shown in Fig. 11. Curve a is the spectrum of the catalyst powder pre-outgassed at room temperature for 45 min, and the high wavenumber region is reproduced (in absorbance mode) of the spectrum already reported as curve a of Fig. 9B. In the low wavenumber range, bands at 1620, 1455 and 1360 cm\(^{-1}\) were observed (curve a). The bending mode of water molecules produces the band at 1620 cm\(^{-1}\), and the components at 1455 and 1360 cm\(^{-1}\) might be due to some residual carbonate-like groups, produced by reaction of CO\textsubscript{2} with basic centres on the TiO\textsubscript{2} surface during the storage of the catalyst powder in air.

In contact with toluene, the signal at 3680 cm\(^{-1}\) due to the free hydroxyl group was completely depleted, indicating that OH species act as effective Lewis acid adsorption sites for toluene, and a new broad adsorption appeared at lower wavenumbers, the observed shift resulting from the interaction between the OH groups and the \(\pi\)-electrons of the aromatic molecules. At lower frequencies, peaks due to adsorbed toluene appeared in the 3100-2800 cm\(^{-1}\) (CH stretching) and 1610-1360 cm\(^{-1}\) (ring stretching, CH deformation) ranges.

After simply outgassing at room temperature, all components due to adsorbed toluene completely disappered, and the original spectral features of the free OH species were completely restored (curve c), indicating that the interaction between aromatic molecules and hydroxyl group is quite weak and fully reversible.

5. 2. 1. 2. Toluene Photo-transformation

To evaluate the role of OH groups in the photodegradation of toluene, two series of FT-IR experiments were carried out on TiO\textsubscript{2} Merc.

The first series of investigations evaluated the differences in the catalyst surface behaviour of two TiO\textsubscript{2} samples with different surface hydration states: pre-outgassed at room temperature and other pre-outgassed at 873 K, the highest temperature attainable without the occurrence of the anatase-rutile phase transition.

Figure 12 shows the spectra obtained after admission of the toluene/H\textsubscript{2}O/O\textsubscript{2} mixture (curve a) and exposure to 10 min of UV irradiation and subsequent outgassing at room temperature for 45 min on the fully hydrated sample (curve b). After exposing the photocatalyst surface to the toluene/H\textsubscript{2}O/O\textsubscript{2} mixture, signals due to adsorbed water (main peak at 1640 cm\(^{-1}\)) and aromatic molecules (signals at 1600, 1496 and 1460 cm\(^{-1}\)) were observed (curve a). By exposing the system to UV light for 10 min, a slight decrease in the toluene bands was observed, and new components appeared (spectrum not shown), indicating that a fraction of toluene molecules were transformed into new species and that partial photo-oxidation of toluene occurred on the fully hydrated sample even under the
model conditions employed.

The subsequent outgassing at room temperature completely removed the absorptions due to physisorbed water molecules and unreacted toluene, and the signals at 1690, 1645, and 1580 cm\(^{-1}\) due to the newly formed species became clearly evident (curve b). To identify the nature of the intermediate formed after the UV irradiation step, the spectrum corresponding to the catalyst simply outgassed at room temperature before the admission of the toluene/H\(_2\)O/O\(_2\) mixture was subtracted using the spectrum of curve b in Fig. 12. In this way, the spectral pattern mainly containing the bands due to the species formed during the UV irradiation was obtained (curve not shown) and was found to correspond to the spectrum of benzaldehyde adsorbed onto the catalyst (Fig. 12, curve c).

After this stage, H\(_2\)O and O\(_2\) were re-admitted onto the catalyst (Fig. 13, curve b) and the sample was exposed to the UV light for another 10 min and then outgassed at room temperature for 45 min. Under these conditions, only the weak and broad band at 1640 cm\(^{-1}\) due to molecular water coordinated to surface Ti\(^{IV}\) remained, whereas the bands due to adsorbed benzaldehyde were strongly reduced in intensity (Fig. 13, curve c), indicating further transformation under UV irradiation in the presence of H\(_2\)O and O\(_2\), but no bands due to newly formed species were observed.

In parallel catalytic runs carried out in batch reactors, benzene and CO\(_2\) were detected among the products of the photoreaction, resulting from the photodecarboxylation of benzoic acid produced by oxidation of benzaldehyde. Presumably the same reactions occurred in the model conditions employed in the IR cell, so the observed behaviour could be explained by assuming that, in the presence of water vapour, the bands due to the species derived from the benzaldehyde reaction may not be observed due to the predominant intensity of the signals due to physisorbed water, so water and products from the benzaldehyde transformation are desorbed from the catalyst during outgassing at room temperature and so could not be observed.

As described above, after outgassing at high temperature, the absorptions due to hydroxyl groups and water molecules disappear, except for a very weak band at 3665 cm\(^{-1}\) (Fig. 4A, curve c), indicating that almost complete dehydration of the catalyst occurred, leaving only a negligible fraction of free OH groups on its surface. By exposing this highly dehydrated sample to water vapour, the spectral pattern characteristic of water molecules physisorbed onto the catalyst was obtained, but subsequent simple re-outgassing at room temperature fully restored the spectrum observed after treatment at 873 K. These results indicate that dehydroxylation at high temperature is irreversible and that irradiation of the catalyst pre-outgassed at 873 K would actually occur in the absence of surface OH groups, even if water vapour is present in the reaction mixture.

Exposure of the dehydroxylated catalyst to the toluene/H\(_2\)O/O\(_2\) mixture resulted in observation of the bands due to physisorbed H\(_2\)O and toluene molecules (Fig. 14, curve a). Nevertheless, after 10 min of UV irradiation and subsequent outgassing of the reaction mixture at room temperature for 45 min, few traces of bands due to photoproduced benzaldehyde were recog-
nizable in the spectrum (Fig. 14, curve b), pointing to highly reduced photocatalytic activity of the highly dehydroxylated catalyst with respect to the fully hydroxylated catalyst, clearly confirming the involvement of surface OH groups in the photooxidative process.

The second series of experiments investigated the phenomena occurring on the surface of the catalyst during the photo-oxidation process in both hydrated and dry conditions\(^{33}\). The results previously obtained for toluene photodegradation carried out in presence of H\(_2\)O were compared with the same experiment carried out with the photocatalyst exposed to a toluene/O\(_2\) mixture, but in the absence of H\(_2\)O.

By exposing the catalyst to the toluene/O\(_2\) mixture, the features of the adsorbed toluene molecules were clearly observed at 1600, 1496 and 1460 cm\(^{-1}\) (Fig. 15, curve b). After 10 min of UV irradiation and subsequent outgassing of the unreacted toluene at room temperature, a decrease in the toluene bands was observed, and signals at 1690, 1645, 1600 and 1580 cm\(^{-1}\) due to newly formed species appeared (Fig. 15, curve c). This behaviour clearly indicates that benzaldehyde is formed photochemically on the catalyst surface even in the absence of H\(_2\)O.

Photocatalytic experiments carried out in a photo-reactor showed that, in the solid/gas system, TiO\(_2\) Merck exhibited stable activity in the presence of water vapour, which was greatly decreased in a dry gas stream. In contrast, TiO\(_2\) P25 Degussa produced CO\(_2\) and traces of benzaldehyde but was continuously deactivated, even in the presence of water vapour\(^{20}\).

An IR investigation of the toluene adsorption and phototransformation on TiO\(_2\) P25 surface was then carried out. The disappearance of the OH bands in the 3700-3600 cm\(^{-1}\) range after exposure to toluene and their transformation to an intense and broad components centered at ca. 3500 cm\(^{-1}\) clearly indicates that vibrationally free hydroxyls act as effective Lewis acid adsorption sites for toluene, the observed shift resulting from the interaction between such OH groups and the \(\pi\)-electrons of the aromatic molecules. At lower frequencies, peaks due to adsorbed toluene appeared in the 3100-2800 cm\(^{-1}\) (CH stretching) and 1610-1360 cm\(^{-1}\) (ring stretching, CH deformation) ranges (Fig. 16, curve b), but disappeared after outgassing at room temperature, whereas the signals due to vibrationally free OH groups were completely restored (Fig. 16, curves c), indicating that, for this system also, the interaction between the aromatic molecules and hydroxyl groups is very weak.

In contrast, the interaction of benzaldehyde with the surface of the photocatalyst exhibits a significant dependence on the type of TiO\(_2\) photocatalyst. In the case of TiO\(_2\) Degussa P25, the adsorption of benzaldehyde resulted in the spectra in Fig. 17. In this case the components due to benzaldehyde molecules adsorbed in an unperturbed form were observed as
minor features and the FT-IR spectrum was dominated by an intense peak at 1650 cm\(^{-1}\) and a series of bands at 1518, 1495, 1451 and 1413 cm\(^{-1}\) (Fig. 17, curves b and c). These components can be assigned to hemiacetal-like species formed by nucleophilic attack of the basic oxygen of the hydroxyl groups on the carbon atom of the carbonyl group of the adsorbed aldehyde molecules, as in the first step of the Cannizzaro reaction.

Such different behaviour also affects the reactivity of the hydroxyl groups, under high hydration conditions, which exhibit a nucleophilic character (through the O atom) for TiO\(_2\) Degussa P25, but as an electron acceptor (through the H atom) for TiO\(_2\) Merck, and could well account for the different photocatalytic behaviours exhibited by the two types of TiO\(_2\) powders in parallel batch reactor experiments.

As discussed above, in the case of TiO\(_2\) Merck, benzaldehyde molecules resulting from the photo-oxidation of toluene weakly interact with the catalyst surface and can be easily released to the gas phase. In contrast, the present results for TiO\(_2\) P25 indicate that the hydroxyl groups on the surface can react with benzaldehyde formed photochemically, which is then retained on the catalyst surface. Subsequently, the benzaldehyde can be converted to other products, such as benzoic acid, strongly adsorbed on the TiO\(_2\) surface leading to the progressive deactivation of the catalyst in the gas-solid system.

5.3. Acetonitrile

Acetonitrile (methyl cyanide, CH\(_3\)CN) has been the focus of several recent studies in atmospheric, marine, chemical and biological science. Acetonitrile is strongly and predominantly emitted from biomass burning. Since the atmospheric lifetime of acetonitrile is long in comparison with regional and hemispheric transport processes, it can serve as a characteristic global marker of biomass burning. In the future, if increasing global temperatures cause increased aridity, then increased incidence of biomass burning, and hence acetonitrile emissions, can be expected. Recently, revised global OH estimates have increased its importance as a removal mechanism, although the main sink for acetonitrile is presently thought to be uptake in the ocean.

Direct industrial emissions and indirect production from the agricultural fumigant methyl isothiocyanate via methyl isocyanide (CH\(_3\)NC) seem to be less important than that from automobiles. The reaction rates and products of acetonitrile with other atmospheric species such as ozone, bromine and iodine are still unknown\(^{34}\).

5.3.1. Acetonitrile adsorption

To investigate the molecular mechanisms of the interaction between acetonitrile (using deuterated acetonitrile to avoid the Fermi resonance effect, which perturbs the determination of the \(\nu(CN)\) mode) and the photocatalyst surface, CD\(_3\)CN adsorption and desorption were carried out on TiO\(_2\) Merck and TiO\(_2\) Degussa P25 simply outgassed at room temperature (after isotopic exchange with D\(_2\)O).

Exposure of the TiO\(_2\) Merck sample to CD\(_3\)CN at room temperature resulted in a main peak at 2270 cm\(^{-1}\) in the IR spectra, due to the \(\nu(CN)\) mode of acetonitrile molecules D-bonded to surface deuterated hydroxyl groups, and a shoulder at 2305 cm\(^{-1}\) (Fig. 18, curve a). Finally, the weaker components at 2215 and 2113 cm\(^{-1}\) corresponded to a combination band (2\(\nu_{\text{sym}}(CC) + \delta_{\text{asym}}(C\equiv C\equiv N)\)) and to the \(\nu_{\text{sym}}(CD_3)\) mode, respectively.

At the higher wavenumbers, an asymmetric peak at 2670 cm\(^{-1}\), and a broad shoulder at 2707 cm\(^{-1}\), due to the stretching mode of isolated deuteroxyl groups (inset in Fig. 18, curve a'), completely disappeared, whereas a broad component in the 2650-2200 cm\(^{-1}\) range appeared due to the overlap of the bands due to the stretching mode of D-bonded OD groups and of D\(_2\)O.
molecules co-ordinated to surface Ti⁴⁺ cations (inset in Fig. 18, curve b'). This behaviour indicates that deuteroxyl groups also act as effective adsorption sites for CD₃CN molecules, through D-bonding between the lone-pair on the nitrogen atom and the D atom of the OD groups.

No changes in the spectrum were observed by increasing the contact time with acetonitrile vapour (spectrum not shown). By simply outgassing at room temperature, all CD₃CN bands disappeared, indicating complete desorption of the adsorbed species (Fig. 18, curve b) and restoration of the peaks due to the isolated deuteroxyls (inset in Fig. 8, curve c').

Since CD₃CN interaction with the Merck photocatalyst surface is completely reversible by simply outgassing at room temperature, UV irradiation for increasing time (up to 17 h) in the presence of O₂ and D₂O was carried out on the total amount of adsorbed CD₃CN. At the end of each irradiation step, O₂ and D₂O were outgassed, and the IR spectrum of the sample was recorded.

5.3.2. Acetonitrile Photo-transformation

After irradiation for 17 h, the intensity of the peaks at 2270, 2215 and 2113 cm⁻¹ decreased, and the shoulder at 2305 cm⁻¹ completely disappeared (Fig. 19A, curve b), indicating almost complete consumption of adsorbed and physisorbed CD₃CN. Correspondingly, in the 1750-1100 cm⁻¹ range, a complex pattern was formed (Fig. 19B, curve b), in particular, weak components were recognised at 1720, 1692, 1620, 1476, 1428 and 1350 cm⁻¹, and a predominant band at 1175 cm⁻¹.

This behaviour indicates the photostimulated conversion of adsorbed CD₃CN molecules into new species. More specifically, the 1720 cm⁻¹ peak can be ascribed to formyl groups³⁵), and the absorption signals at 1692, 1428 and 1350 cm⁻¹ suggest the formation of NₓOᵧ compounds³⁶). The assignment of the band at 1175 cm⁻¹ is not straightforward, and additional investigations are in progress.

Exposure of TiO₂ Degussa P25 to acetonitrile at room temperature resulted in peaks at 2291 and 2264 cm⁻¹ (ν(CN)) and at 2215 (2νₚₛₜₜ(CC) + δₚₛₜₜ(C≡C=N)) and 2113 cm⁻¹ (νₚₛₜₜ(CD₃)) due to adsorbed acetonitrile in the 2350-2075 cm⁻¹ range (Fig. 20A, curve a). Correspondingly, in the 1750-1150 cm⁻¹ range, a weak negative band at 1195 cm⁻¹ was observed due to the
deformation mode of D\textsubscript{2}O molecules coordinated to surface Ti\textsuperscript{4+} ions and results from the displacement by acetonitrile of D\textsubscript{2}O molecules previously coordinated to these stronger Lewis acid sites (Fig. 20B, curve a).

This band was not detectable for TiO\textsubscript{2} Merck (expected at ca. 1200 cm\textsuperscript{-1}), because it falls at a frequency lower than the catalyst cut-off (ca. 1250 cm\textsuperscript{-1}).

CD\textsubscript{3}CN adsorption on Degussa P25 resulted in the asymmetric peak at 2685 cm\textsuperscript{-1} with two shoulders at higher wavenumbers (2715 and 2754 cm\textsuperscript{-1}), due to the more heterogeneous isolated OD groups, and the peak at 2533 cm\textsuperscript{-1} due to the stretching mode of D\textsubscript{2}O molecules co-ordinated to Ti\textsuperscript{4+} sites disappeared and was substituted by a broad absorption (inset of Fig. 20A, curve b'). This behaviour confirms the formation of D-bonding between the OD groups and the N-lone pair of CD\textsubscript{3}CN molecules.

By increasing the time of contact with adsorbed CD\textsubscript{3}CN on the photocatalyst surface, a considerable evolution of the spectral pattern was observed in the 2350-2075 cm\textsuperscript{-1} (Fig. 20A, curve b) and 1750-1150 cm\textsuperscript{-1} ranges (Fig. 20B, curve b), unlike that observed for TiO\textsubscript{2} Merck.

After 12 h of contact, all peaks decreased in intensity in the 2350-2075 cm\textsuperscript{-1} range, particularly evident for the signal at 2291 cm\textsuperscript{-1} (Fig. 20A, curve b). Correspondingly, a large and complex absorption pattern was observed in the 1750-1300 cm\textsuperscript{-1} range (Fig. 20B, curve b), indicating the formation of acetamide-like species due to the reaction of acetonitrile molecules initially adsorbed on Ti\textsuperscript{4+} cations with surface basic centres (O\textsuperscript{2-} anions or OD groups). This behaviour was not observed for TiO\textsubscript{2} Merck because the surface species are not basic enough to allow nucleophilic attack on CD\textsubscript{3}CN to form acetamide-like species.

After subsequent outgassing at room temperature, the spectral pattern of acetamide-like species in the 1750-1300 cm\textsuperscript{-1} range was slightly modified (Fig. 20B, curve c), possibly due to D\textsubscript{2}O and physisorbed CD\textsubscript{3}CN desorption, also indicating that these species are irreversibly adsorbed on the surface of the photocatalyst.

In the 2350-2075 cm\textsuperscript{-1} range, further depletion of the 2264 and 2215 cm\textsuperscript{-1} peaks and further decrease in the intensity of the 2113 cm\textsuperscript{-1} peak were observed, due to the desorption of acetonitrile molecules from surface OD groups and physisorbed CD\textsubscript{3}CN, respectively (Fig. 20A, curve c). Moreover, the increase in intensity of the 2291 cm\textsuperscript{-1} band indicates the loss of D\textsubscript{2}O co-ordinated to the CD\textsubscript{3}CN molecules absorbed on Ti\textsuperscript{4+} ions, (contributing, when in such form, to the 2264 cm\textsuperscript{-1} peak), which are converted into CD\textsubscript{3}CN− Ti\textsuperscript{4+} adducts.

In the case of TiO\textsubscript{2} Degussa P25, UV irradiation for increasing times (up to 17 h) in the presence of O\textsubscript{2} and D\textsubscript{2}O was carried out after outgassing the reversible fraction of adsorbed CD\textsubscript{3}CN (step corresponding to curve c of Fig. 20A). After 17 h of UV irradiation, the decrease of the 2291, 2215 and 2113 cm\textsuperscript{-1} signals and the corresponding formation of new components in the 2350-2075 cm\textsuperscript{-1} (Fig. 21A, curve b) and 1750-1150 cm\textsuperscript{-1} ranges suggest the photo-induced conversion of the irreversibly adsorbed CD\textsubscript{3}CN into other species. Moreover, the growth of absorptions due to the acetamide-like species indicates that at least part of the...
photo-converted CD$_3$CN molecules contribute to the formation of new adducts. New components appeared, assignable to cyanate (2234 cm$^{-1}$)\textsuperscript{41}, isocyanate (2189 cm$^{-1}$)\textsuperscript{42}, formyl (1720 cm$^{-1}$)\textsuperscript{35}, carbonate and bicarbonate (1700-1450 cm$^{-1}$ range)\textsuperscript{8},18) and nitrate (1560-1500 cm$^{-1}$ and 1300-1250 cm$^{-1}$ ranges)\textsuperscript{36}) species, which resulted from the photo-oxidation of CD$_3$CN coordinated to Ti$^{4+}$ ions. Moreover, the weak band at 2161 cm$^{-1}$ is likely due to polymerized CD$_3$CN\textsuperscript{39}).

This behaviour indicates that acetamide-like species are less sensitive to photo-oxidation than acetonitrile adsorbed in molecular form. Thus, these species can exhibit a poisoning effect towards part of the photocatalytic surface sites, accounting for the lower initial reaction rate observed for TiO$_2$ Degussa P25 compared to TiO$_2$ Merck, as observed in parallel experiments carried out in typical batch reactors.

6. Conclusions

Insights on the nature of the species adsorbed on the surface of TiO$_2$ photocatalysts in the dark and their evolution under UV irradiation can be easily obtained from FT-IR spectra collected under simulated operating photocatalytic conditions. This kind of investigation is also very useful to differentiate between reactions in which intermediates evolve until complete mineralisation and processes in which the initial photoreaction products are stable and produce irreversible quenching of the catalyst, thus allowing identification of the causes of the deactivation.

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TiO₂粉末上における有機化合物の光触媒分解
—FT-IRによる表面の反応性と反応機構の解析—

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空気および水中を汚染する有機化合物（たとえばフェノール、VOCs、アセトニトリル）の光触媒分解過程において、暗所およびUV照射下、TiO₂表面で起こる現象を分子レベルで調べた一連の研究がまとめられている。分析手法として、FT-IR分光法を模擬操作条件で利用し、さらにTiO₂粒子の表面構造と形態の解明に高分解能透過電子顕微鏡を用いた。得られた結果は、UV照射下における吸着／反応サイトとして表面水酸基が重要な役割を示すこと、および塩基性表面サイト（TiO₂格子中の水酸基あるいは表面O²⁻）も表面の化学反応過程に影響を与える可能性があることを示している。