

**SELECTIVE PHOTOCATALYTIC
OXIDATION OF AROMATIC ALCOHOLS
WITH TITANIUM DIOXIDE**

**Sedat YURDAKAL
Ph.D. Dissertation**

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ABSTRACT
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SELECTIVE PHOTOCATALYTIC OXIDATION OF AROMATIC
ALCOHOLS WITH TITANIUM DIOXIDE

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Home-prepared (HP) TiO₂ catalysts were prepared by sol-gel process and characterized by using XRD, SEM and BET methods. They were used in a batch photoreactor for performing the selective oxidation of 4-methoxybenzyl alcohol to 4-methoxybenzaldehyde in water. Then by using the most selective photocatalyst, 4-substitute aromatic alcohols were oxidised to corresponding aldehydes in order to investigate the influence of the substituent group on the reaction rate and selectivity. Commercial TiO₂ catalysts were also used for comparison. HP TiO₂ catalysts showed selectivity 3-8 times higher than commercial catalysts. The Hammett relationship well describes the influence of substituent group on the kinetic constant of partial oxidation to aldehydes. Moreover a continuous annular fixed bed photoreactor containing Pyrex beads covered by HP TiO₂ was investigated for the same reaction. The Langmuir-Hinshelwood approach was satisfactorily applied for modelling the photoreactivity results and the values of all the model parameters were determined.

Selectivity enhancement by aliphatic alcohols was investigated; the addition of an aliphatic alcohol in small amounts decreased the overall oxidation rate but enhanced the selectivity for aldehyde formation up to 1.5 times. The values of band gap, valence band and conduction band edges are similar for all the samples. The ATR-FTIR investigation indicates that HP and Degussa P25 TiO₂ surfaces show a very dissimilar hydrophilicity and different ability for adsorbing the organic compounds deriving from benzyl alcohol oxidation.

Finally, this thesis presents a quantitative method which enables to determine the amount of substrate photoadsorbed onto the catalyst surface in the same reaction conditions. The method is applied to oxidation of phenol in the presence of Degussa P25 and oxidation of benzyl alcohol in the presence of a HP catalyst. The influence of substrate concentration, catalyst amount and irradiation power on photoadsorption is investigated by using Langmuir, Freundlich, and Redlich-Peterson isotherms. All the parameters of kinetic model are favorably affected by an increase of the photon flow absorbed per unit mass of catalyst.

Keywords: Aromatic alcohols, selective oxidation, photocatalysis, TiO₂, photoadsorption determination, continuous annular fixed bed photoreactor.

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ÖZET
Doktora Tezi
AROMATİK ALKOLLERİN TİTANYUM DİOKSİT
KATALİZÖRLERİYLE SEÇİCİ FOTOOKSİDASYONLARI
Sedat YURDAKAL
Anadolu Üniversitesi
Fen Bilimleri Enstitüsü
Kimya Anabilim Dalı
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Laboratuvar sentezi (HP) TiO_2 katalizörleri için sol-jel yöntemi kullanılmıştır. Bu katalizörler XRD, SEM ve BET yöntemleriyle karakterize edilmiş ve kesikli fotoreaktörde ve sulu ortamda, 4-metoksibenzil alkolün seçici olarak 4-metoksibenzaldehide oksidasyonu için kullanılmıştır. Daha sonra en seçici katalizörün kullanılmasıyla, bu substitüye grupların tepkime hızı ve seçiciliğe etkisini incelemek amacıyla, 4-substitüye aromatik alkoller aldehytlere yükseltgenmişlerdir. Ticari TiO_2 katalizörler de kıyaslama amaçlı kullanılmıştır. HP TiO_2 katalizörleri ticari katalizörlerden 3-8 kat daha fazla seçicilik göstermişlerdir. Hammett bağıntısı, aldehide seçici oksidasyonun kinetik sabiti ile substitüye grubun etkisinin oldukça uyumlu olduğunu göstermiştir. Ayrıca, bu tepkime için HP TiO_2 ile kaplanmış Pyrex boncuk içeren sürekli silindirik sabit yataklı bir fotoreaktör geliştirilmiştir. Fotoaktivite sonuçlarının modellenmesinde Langmuir-Hinshelwood yaklaşımı başarılı bir şekilde uygulanmış ve model parametreleri belirlenmiştir.

Seçicilik artışı alifatik alkollerle geliştirilmiştir; küçük miktarlarda bir alifatik alkolün ilave edilmesiyle toplam reaksiyon hızı düşmüş, ancak aldehyt oluşumu seçiciliği 1,5 kata kadar artmıştır. Bant aralığı, temel hal bandı ve iletkenlik bandı değerleri tüm katalizörler için benzerdir. ATR-FTIR analizlerinden HP ve Degussa P25 TiO_2 yüzeylerinin oldukça farklı hidrofilisiteye sahip oldukları ve benzil alkol oksidasyonundan oluşan türlere karşı farklı adsorpsiyon yatkınlığı gösterdikleri anlaşılmıştır.

Son olarak, bu çalışma aynı reaksiyon koşullarında katalizör yüzeyine fotoadsorbe olabilen substrat miktarını belirleyebilen bir kantitatif metod sunmuştur. Bu metod Degussa P25 varlığında fenol oksidasyonuna ve bir HP katalizörü varlığında benzil alkol oksidasyonuna uygulanmıştır. Substrat derişimi, katalizör miktarı ve ışın şiddetinin fotoadsorpsiyona etkisi Langmuir, Freundlich ve Redlich-Peterson izotermi ile geliştirilmiştir. Kinetik modelin tüm parametreleri, birim miktar katalizöre absorbe olan foton şiddetinin artışına paralel olarak bağımlıdır.

Anahtar Kelimeler: Aromatik alkoller, seçici oksidasyon, fotokataliz, TiO_2 , fotoadsorpsiyon belirlenmesi, sürekli silindirik sabit yataklı fotoreaktör.

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We shall overcome...

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LIST OF SYMBOLS and ACRONYMS

ATR-FTIR:	Attenuated total reflectance - Fourier transform infrared spectroscopy
BA:	Benzyl alcohol
BAD:	Benzaldehyde
C_{AA} :	Aromatic alcohol concentration
C_{ALD} :	Aldehyde concentration
Cat:	Photocatalyst
C_{CD} :	Carbon dioxide concentration
C_{MBA} :	MBA concentration in the aqueous phase
C_{MBAD} :	MBAD concentrations in the aqueous phase
$C_{MBA,I}$:	Molar concentration of MBA at the inlet of the photoreactor
$C_{MBA,O}$:	Molar concentrations of MBA at the outlet of the photoreactor
C_L :	Concentration in the liquid phase
$(C_{Ox})_{AIR}$:	Oxygen saturation concentration obtained by bubbling air in water
$(C_{Ox})_{OX}$:	Oxygen saturation concentration obtained by bubbling pure oxygen in water
C_{Ox} :	Oxygen concentration in the aqueous phase
CSTR:	Continuous-flow stirred tank reactor
C_T :	Total concentration of the species
dS_{PO} :	Irradiated surface area of the photocatalyst for partial oxidation sites in the control volume
dS_{MIN} :	Irradiated surface area of the photocatalyst for mineralisation sites in the control volume
e^- :	Electron pair
E:	Energy of exciting light
$E_{MV^{2+}/MV^{+\bullet}}^0$:	Redox potential of the $MV^{2+}/MV^{+\bullet}$ couple
EA:	Ethanol
EDAX:	Energy dispersive X-ray spectroscopy
E_{fb} :	Quasi-Fermi level of electrons
f:	Temkin constant

GC-MS:	Gas chromatography- Mass spectroscopy
h:	Planck's constant
h^+ :	Hole pair
$HO^\bullet$:	Hydroxyl radical
$HO_2^\bullet$:	Hydroperoxyl radical
HP:	Home prepared
HP1/20:	The home-prepared rutile TiO_2 catalyst prepared at room temperature by using 1:20 volumetric ratios of $TiCl_4$ and H_2O
HP1/35:	The home-prepared rutile TiO_2 catalyst prepared at room temperature by using 1:35 volumetric ratios of $TiCl_4$ and H_2O
HP1/50:	The home-prepared rutile TiO_2 catalyst prepared at room temperature by using 1:50 volumetric ratios of rutile $TiCl_4$ and H_2O
HP1/75:	The home-prepared rutile TiO_2 catalyst prepared at room temperature by using 1:75 volumetric ratios of $TiCl_4$ and H_2O
HP1/100:	The home-prepared rutile TiO_2 catalyst prepared at room temperature by using 1:100 volumetric ratios of $TiCl_4$ and H_2O
HP0.5:	The home-prepared anatase TiO_2 catalyst prepared at 373K for 0.5h
HP2:	The home-prepared anatase TiO_2 catalyst prepared at 373K for 2h
HP4:	The home-prepared anatase-rutile TiO_2 catalyst prepared at 373K for 4h
HP6:	The home-prepared anatase-rutile TiO_2 catalyst prepared at 373K for 6h
HP8:	The home-prepared rutile TiO_2 catalyst prepared at 373K for 8h
HP298:	The home-prepared amorphous TiO_2 catalyst prepared at 298K
HP333:	The home-prepared rutile TiO_2 catalyst prepared at 333K temperature by using 1:50 volumetric ratios of $TiCl_4$ and H_2O
HP333D:	The dialysed HP333
HP673:	The calcined HP333 at 673K for 6h
HP973:	The calcined HP333 at 973K for 6h
$H_3PW_{12}O_{40}$:	Phosphotungstic acid

I :	Absorbed light intensity
IR:	Infrared spectroscopy
k :	Pseudo-first-order rate constant
K :	Shape factor, a typical value of about 0.9
k'' :	Second-order rate constant
k_1 :	A constant assumed equal to 0.059 V
k_D :	First order kinetic constant of overall degradation reaction
K_F^* :	Freundlich isotherm constant
K_L^* :	Langmuir photoadsorption equilibrium constant
K_{MIN} :	Equilibrium adsorption constant of MBA and MBAD on mineralising sites
$k_{1,Min}$:	First order kinetic constant of mineralization reaction
$k_{2,MIN}$:	Second order rate constants for mineralization
K_{Ox} :	Equilibrium adsorption constant of oxygen
K_{PO} :	Equilibrium adsorption constant of MBA and MBAD on partial oxidising sites
$k_{1,PO}$:	First order rate constant for partial oxidation
$k_{1,PO}^0$:	First order rate constant of the partial oxidation reaction of the unsubstituted reactant
$k_{2,PO}$:	Second order rate constant for partial oxidation
K_{R-P}^* :	Redlich-Peterson isotherm constant
K_T^* :	Temkin equilibrium adsorption constant
LH:	Langmuir-Hinshelwood
M:	Substrate in the fluid phase
MBA:	4-Methoxybenzyl alcohol
MBAD:	4-Methoxybenzaldehyde
MeBA:	4-Methylbenzyl alcohol
M_{P-ads} :	Photoadsorbed substrate
MPSD:	Marquardt's percent standard deviation
MV:	Methyl viologen
NBA:	4-Nitrobenzyl alcohol
NMR:	Nuclear magnetic resonance

n :	Freundlich parameter
n_L :	Number of moles in the fluid phase
n_{MBA} :	Moles of MBA
n_{MBAD} :	Moles of produced MBAD
n_{MIN} :	MBA moles oxidised to CO_2
n_{PO} :	MBA moles partially oxidised to MBAD
n_S :	Number of moles photoadsorbed on the solid phase
N^*_S :	Maximum capacity of photoadsorbed moles of substrate
$n_{S,Ox}$:	Oxygen moles photoadsorbed on the solid
$N^*_{S,Ox}$:	Maximum capacity of photoadsorbed moles of oxygen
n_T :	Total number of moles present in the photoreactor
OX_2 :	Electron acceptor
$O_2^{\bullet-}$:	Superoxide ion
P :	Reaction product
$P25$:	Degussa P25 TiO_2
PFR :	Plug flow reactor
POM :	Polyoxometalate
PSH :	Superhydrophilicity
PSS :	Pseudo steady state
Q :	Volumetric flow rate
R :	Reactant
$(-r)$:	Reaction rate
$(-r_{AA})$:	Disappearance rate of aromatic alcohol
Red_1 :	Electron donor
$R-P$:	Redlich-Peterson
$(r_{PO}+r_{MIN})_{OX}$:	Disappearance rate of MBA in the presence of pure oxygen
$(r_{PO}+r_{MIN})_{AIR}$:	Disappearance rate of MBA in the presence of air
r_{MIN} :	MBA mineralization rate
r_{PO} :	MBA partial oxidation rate
r_T :	Total disappearance rate of substrate per unit surface area
S :	Catalyst surface area
S^* :	Active state of photoadsorption center

SA:	Sigma Aldrich TiO ₂
S _e :	Electron trap surface
S _e [*] :	Electron trapped surface
SEM:	Scanning electron microscope
S _h :	Hole trap surface
S _h [*] :	Hole trapped surface
S _{MIN} :	Catalyst surface area on which mineralization occur
S _{PA} :	Photoadsorption center
S _{PO} :	Catalyst surface area on which partial oxidation occur
S _s :	Surface area per unit mass of catalyst
SSA:	Specific surface area
S _S :	Catalyst specific surface area
t:	Time
TOC:	Total organic carbon
V:	Volume of the liquid phase
VB:	Valance band
W:	Mass of catalyst
X:	Conversion
XPS:	X-ray photoelectron spectroscopy
XRD:	X-ray diffraction
Y:	Selectivity
α:	Fraction of the total surface area of catalyst
α _{R-P} [*] :	Redlich-Peterson isotherm constant
β:	Redlich-Peterson heterogeneity factor
γ:	(I ^γ) The value between 0.5 to 1
θ:	Bragg angle
θ _{Ox} :	Oxygen fractional coverage of the surface
θ _{Sub} :	Substrate fractional coverage of the surface
θ _{PO} :	Fractional coverage of MBA on sites determining its partial oxidation to MBAD
θ _{MIN} :	Fractional coverage of MBA on sites determining its mineralization to CO ₂

$(\theta_{\text{Ox}})_{\text{Ox}}$:	the oxygen fractional coverage obtained by bubbling pure oxygen in water
$(\theta_{\text{Ox}})_{\text{AIR}}$:	the oxygen fractional coverage obtained by bubbling air in water
λ :	X-ray wavelength
ν :	Radiation wavenumber
$\Delta\nu$:	Difference between the frequencies of asymmetric and symmetric group vibrations
ν_{as} :	Frequencies of asymmetric group vibrations
ν_{s} :	Frequencies of symmetric group vibrations
ξ :	Line broadening at half the maximum intensity in radians
ρ :	Reaction constant
σ :	Substituent constant which is related to the electron orientation effect of the specific substituent
τ :	Mean crystallite dimension

1. INTRODUCTION

1.1. Fundamentals of Photocatalysis

Photocatalysis term is a combination of photochemistry and catalysis, and implies that light and a catalyst are needed to bring about a chemical change to accelerate (Serpone and Pelizzetti 1989).

Among the advanced oxidation processes investigated in the last decades, photocatalysis in the presence of irradiated semiconductor has shown to be very effective in the field of environment remediation. The use of irradiation to initiate chemical reactions is the principle on which heterogeneous photocatalysis is based; in fact, when a semiconductor oxide is irradiated with suitable light, excited electron-hole (e^-h^+) pairs result that can be applied in chemical processes to modify specific compounds. The main advantage of heterogeneous photocatalysis, when compared with the chemical methods, is that in most cases it is possible to obtain a complete mineralization of the toxic substrate even in the absence of added reagents. The radical mechanism of photocatalytic reactions, which involve fast attacks of strongly oxidant hydroxyl radicals (Schiavello 1995) determines their unselective features. Additional advantages are: i) its non-specificity; ii) the possibility of treating effluents having very low concentrations of contaminants without lowering the reaction rate to negligible values; iii) the possibility of operation at ambient temperature and pressure; iv) the use of a cheap oxidant as molecular oxygen.

The knowledge of the main thermodynamic and kinetic factors influencing the photoreactivity is essential in order to make predictions on the feasibility of photoprocesses and to explain why some solids are active and others not (Schiavello 1997). Moreover the same solids can be active in a particular system for a particular photoreaction and not active in different experimental conditions or for different reactions. Therefore, thermodynamic and kinetic factors governing the photocatalytic processes should be carefully considered in order to choose the best experimental conditions for their occurrence.

1.2. Thermodynamics of Heterogeneous Photocatalytic Processes

When an n-type semiconductor is illuminated by light of suitable energy, electrons are promoted from the valence band to the conduction band and positive holes are created in the valence band (Schiavello 1997). The occurrence of the above charge separation is one of the first essential steps of a photocatalytic reaction.

From a physical point of view, light absorption, therefore, induces the formation of electron-hole pairs (Augugliaro et al. 2006). Both reductive and oxidative processes can occur at/or near the surface of the photoexcited semiconductor particle. In aerated aqueous suspensions, oxygen is able to scavenge conduction band electrons forming superoxide ions ($O_2^{\bullet-}$) and its protonated form, the hydroperoxyl radical ($HO_2^{\bullet}$):



In this way, electron/hole recombination can be effectively prevented and lifetime of holes is prolonged. $HO_2^{\bullet}$ can lead to the formation of H_2O_2 :



Photo-generated holes can react with adsorbed water molecules (or hydroxide anions) to give hydroxyl radicals:



or they can also be filled by an adsorbed organic donor. Controversy still exists in the literature about the oxidative species; even if the photogenerated hole has the potential to oxidize several substrates by electron transfer, in aqueous solutions oxidation of water to hydroxyl radical seems to be the predominant pathway.

Superoxide anion can also act as an oxidant. The whole process can end in the complete mineralization of organic compounds.

The potential energy of the photogenerated electrons and holes can be given up to a redox couple with suitable redox potential, i.e. less positive than that of the valence band of the semiconductor (holes oxidise the reduced species of the couple) and more positive than that of the conduction band of the semiconductor (electrons reduce the oxidised species of the couple), as can be seen in Fig. 1.1 (Schiavello 1997). In this figure the position of the band edges of some semiconductors are reported by using as reference the normal hydrogen electrode (NHE) scale.

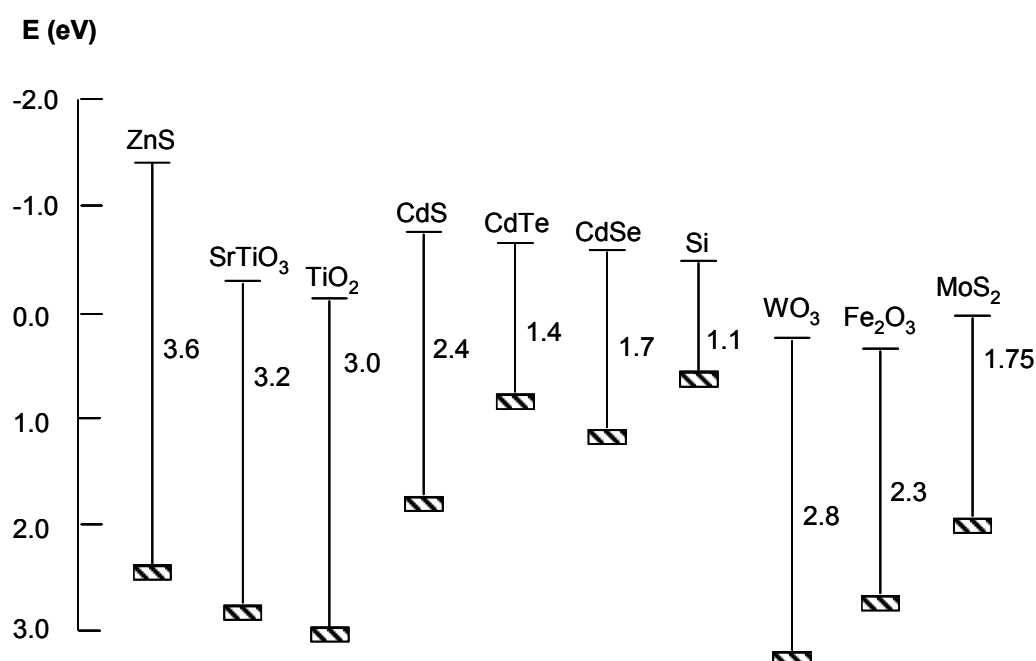


Figure 1.1. Positions of the band edges for some semiconductors in contact with aqueous electrolyte at pH = 0

More than one couple, of course, can be involved in a photocatalytic process, and electrons and holes can reduce and oxidise, respectively, species belonging to different redox couples contemporaneously present in the reacting system.

The above phenomena, by means of which the semiconductor converts light energy in chemical energy, are of fundamental importance in photocatalysis.

A prevalence, of course, of the occurrence of redox processes on the recombination of pairs enhances the photocatalytic activity of the semiconductor.

When the same redox couple is considered, different reaction pathways could be observed in the presence of two different semiconductors with similar gaps, depending on the position of their conduction and valence bands.

Hence, for instance, photooxidation of water in the presence of MoS₂ (band gap 1.75 eV) is possible from a thermodynamic point of view, but the same reaction is not possible in the presence of CdSe (band gap 1.70 eV) due to the position of the valence band of this solid. The photoreduction of water, instead, could occur more easily in the presence of CdSe (Fig. 1.1), due to the position of its conduction band.

In addition, even if some catalysts have low band-gap energies, and so they need irradiation with light of low energy, these catalysts show photocorrosive effect under light during the reaction so that they get inactive (Schiavello 1997).

1.3. Photocatalysis in the Presence of TiO₂

Various semiconductor materials have been tested as oxidation photocatalysts, but it is generally accepted that anatase TiO₂ is the most reliable material due to its low cost, high photostability and its ability to be activated by near UV-light and also by the UV portion of solar radiation (Fujishima et al. 1999). Among the crystalline phases of TiO₂ (anatase, rutile and brookite), anatase, pure or in mixture with rutile, shows the highest activity.

TiO₂ anatase and rutile phases have similar band-gap values (3.2 and 3.0 eV, respectively) and, consequently their different photoactivities cannot be explained by taking into account only these small differences (Schiavello 1997). On the other hand, the recombination rates of the photoproduced electrons and holes are significantly different for the two phases and, in particular, the rate is higher for rutile. This parameter could play a negative role for the occurrence of some photoreactions in the case of rutile as, the recombination rate of the pairs being high, they would be less available for the adsorbed reagent species. Among the physico-chemical parameters, the surface hydroxylation of the catalyst particles is

one of the most important; it is well known, indeed, the major role played by surface hydroxyls as primary oxidant species for photocatalytic reactions (Pelizzetti and Serpone 1986; Ollis and Al Ekabi 1993; Schiavello 1997). The presence of surface OH groups favours the O₂ adsorption (Primet et al. 1971; Munuera et al. 1979) and, consequently, its reducibility by photoproduced electrons.

Rutile, which is the most thermodynamically stable phase, usually shows scarce photo-activity. Likely reasons invoked to explain the poor performance of rutile with respect to anatase phase are that it shows a very low hydroxyl group surface concentration and a high recombination rate of the photogenerated e^-h^+ pairs (Yang et al 2003; Kawaguchi 1984; Augugliaro et al 1988). However, while rutile produced at very high temperature (ca. 1000 K) (Sclafani et al 1990) shows a poor photoreactivity, rutile home prepared (HP) at low temperature exhibits a certain photocatalytic activity (Nag et al. 2007; Yin et al. 2002; Li et al. 2006).

The catalyst particle size also plays an essential role in determining the optical properties of the suspension and consequently the radiant field inside the photoreactor (Romero et al. 1997). In water the TiO₂ catalyst is not dispersed as primary particles but as solid aggregates (Alfano et al. 1994), called secondary particles; in fact, regardless of the primary particle size, there is particle aggregation (Pirkanniemi et al. 2002) which depends on catalyst concentration and on factors such as the charge density of the particle surfaces and van der Waals forces. Indeed the presence of small catalyst particles suspended in the liquid phase causes scattering and absorption phenomena (van de Hulst 1981) whose extent depends not only on catalyst concentration (Yang et al. 2005) but also on physical and chemical properties of the catalyst powders. The kinetics of photocatalytic reaction is affected in a complex way both by the reactant and product concentrations and by the distribution of the radiant field inside the system (Brandi et al. 2000), so it may be concluded that the optical properties of the suspension eventually affects the performance of the photocatalytic process (Yurdakal et al. 2007).

1.4. Preparation of TiO₂ Catalysts

Sol-gel method is widely employed for the preparation of nanoparticles, due to the inexpensive equipment required and the low temperatures involved. The properties of the sol-gel derived samples are strongly dependent not only on the composition, but also on the preparation conditions including the starting materials and solvents, the solution preparation sequence and various processing conditions as (precursor)/(solvent) ratio, temperature, stirring and aging time (Addamo et al. 2005a). Moreover, pH, the kind and amount of additive and pressure must be considered as other important parameters.

Recently, various nanostructured TiO₂ catalysts have been prepared by hydrolysis of titanium isopropoxide or titanium tetrachloride (Addamo et al. 2004). The samples derived from TiCl₄ were the most photoactive and neither filtration nor calcination was needed to obtain a highly efficient anatase phase.

The samples deriving from TiCl₄ show a significant amount of rutile phase, with anatase, after thermal treatments in air of their precursor solids at only 673-823K for 3-24 hours (Schiavello 1997). By raising the temperature (up to 873K) and/or the duration of the thermal treatment, rutile phase becomes the unique phase or the dominant one. In addition, the samples obtained using TiCl₄ as starting reagent and containing mainly or exclusively rutile phase are the most photoactive when the thermal treatment does not exceed 973K (3 hours).

The preparation of photo-active rutile samples is generally carried out at room temperature in highly concentrated acidic solutions. Yin et al. (2002), for instance, crystallized TiO₂ at room temperature in the presence of HCl, HNO₃ or H₂SO₄ by using titanium tetraisopropoxide as the precursor. It is worth noting that in the absence of acids they obtained amorphous TiO₂. Yang et al. (2003) used Ti(SO₄)₂ as the precursor but the crystallization occurred after a long time and in HNO₃ solution. Fei et al. (2006) prepared rutile nanorods photo-active for the degradation of harmful molecules, starting from titanium isopropoxide solution at room temperature in a concentrated HNO₃ solution.

1.5. Heterogeneous Photocatalytic Reactors

The main components of a photocatalytic process are indeed the photoreactor and the radiation source (Schiavello 1997). For thermal and catalytic processes the reactors are generally chosen on the basis of the mode of operation, the phases present in the reactor, the flow characteristics, the need of heat exchange, the composition and the operative conditions of the reaction mixture, which affect the selection of materials of construction. For selecting the type of heterogeneous photoreactor additional parameters must be considered owing to the fact that photons are needed for the occurrence of photoreaction. The selection of the construction material for the photoreactor must be generally done in order to allow the penetration of radiation into the reacting mixture. The choice of the radiation source is easier than that of the photoreactor. In principle, in order to improve the economics of the photocatalytic process, the radiation spectrum of the lamp used should coincide with the absorption spectrum of the reacting system. In the case of photocatalytic systems utilising semiconducting solids, the absorbed radiation energy should be equal to or higher than band gap.

The utilisation of radiation and solid catalysts in a synergic effect for performing chemical transformations of species present in liquid or gaseous mixtures makes the heterogeneous photocatalytic process much more complex than the homogenous photochemical one as another phase is added to the system. For instance, when stirred dispersions are used, the presence of suspended solid particles determines not only fluidodynamic complications, since the solid affects momentum transfer, but also questions of opacity, scattering and depth of radiation penetration are to be taken into account.

The main difficulties present in heterogeneous photocatalytic reactor engineering are linked to the fact that (i) the fluidodynamics of a fluid-solid system is highly non-ideal so that modelling of the specific system is generally needed: and (ii) the kinetic of a heterogeneous photocatalytic reaction is affected in a complex way by the concentration and the radiation fields which are affected by the fluidodynamics. The coupling of models that describe the radiation emission, the volumetric radiation absorption and the fluidodynamics of the

reacting system in the reactor determines that the design of a heterogeneous photoreactor is a very difficult task. Generally the set of conversion equations which model the photoreactor can be solved only numerically.

1.5.1. Radiation Sources

The light source is a very important factor to be considered as the performance of a photoreactor is strongly dependent on the irradiation source (Schiavello 1997). Different type of lamps allow generation of radiation with different ranges of wavelengths. As reported before, the choice of a particular lamp is made on the basis of the reaction energy requirements.

There are four main types of radiation sources: (a) arc lamps; (b) fluorescent lamps; (c) incandescent lamps; (d) lasers.

In arc lamps the emission is obtained by a gas activated by collisions with electrons accelerated by an electric discharge. The activated gases are mercury and/or xenon vapours.

In fluorescent lamps the emissions is obtained by exciting an emitting fluorescent substance, deposited in the inner side of a cylinder, by an electric discharge occurring in the gas filling the lamps. Generally these lamps emit in the visible region, but the “actinic” type ones have emission in the near-UV region. Of course the emission spectrum depends on the nature of the mixture of fluorescent substances used. Their power is quite small (up to 150 W).

In incandescent lamps, the emission is obtained by heating at very high temperature suitable filaments, of various nature, by current circulation.

The features of lasers are well known, especially for their frequent use in photochemistry and in many other fields. They produce coherent radiation of very high intensity.

In general, in photocatalysis arc and fluorescent lamps are used for carrying out various reactions.

For arc lamps and in particular for mercury lamps, a classification based on the pressure of Hg is made and it is as follows:

(a) Low-pressure Hg lamps: This type of lamp contains Hg vapour at a pressure of about 0.1 Pa at 25 °C, emitting mainly at 253.7 and 184.9 nm.

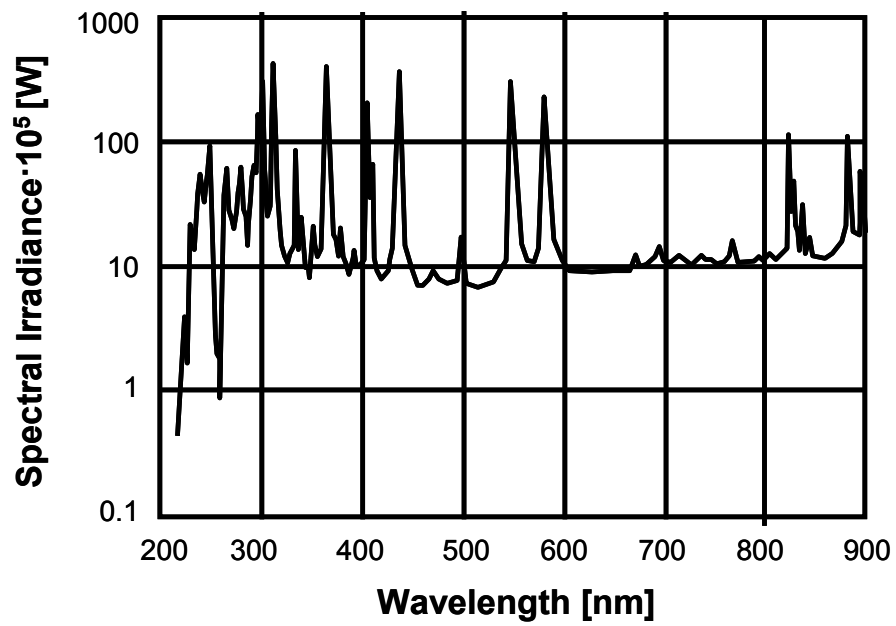
(b) Medium-pressure Hg lamps: This kind of lamp has a radiation source containing mercury vapour at pressures ranging from 100 to several hundreds kPa. Emission is mostly from 310 to 1000 nm with most intense lines at 313, 366, 436, 576 and 578 nm.

(c) High-pressure Hg lamps: This type of lamp has a radiation source containing mercury at a pressure of 10 MPa or higher, which emits broad lines and a background continuous between about 200 and 1000 nm.

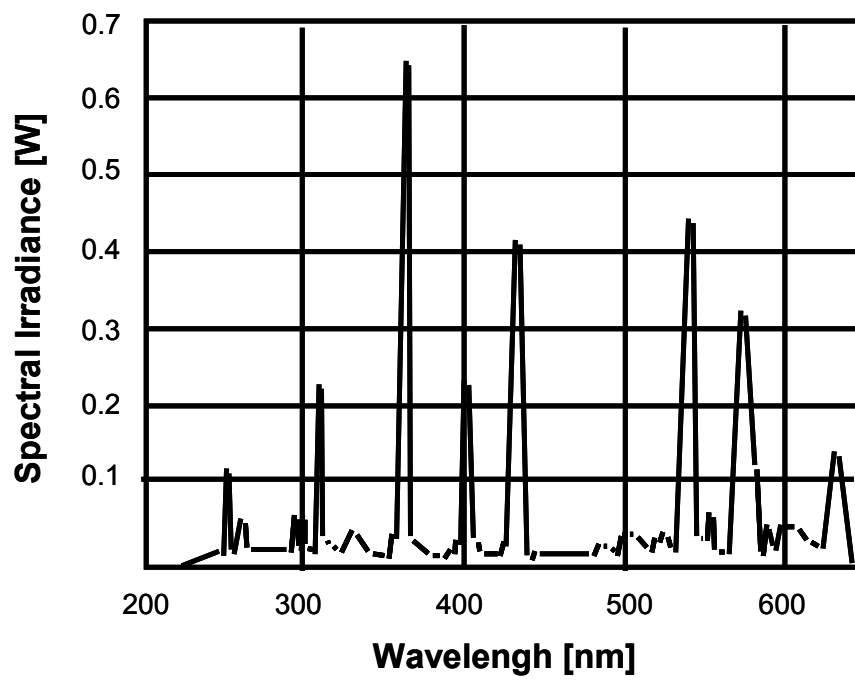
(d) Xenon and Hg-Xenon lamps. In this type of lamp an intense source of ultraviolet, visible and near-IR radiation in a mixture of Hg and Xe vapours under high pressure is obtained. Xenon lamps are used to simulate the solar irradiating spectrum and the presence of Hg vapour increases the radiation intensity in the UV region.

Typical emission spectra are shown in Fig. 1.2.

These lamps are usually cylindrical, with arc length increasing as pressure decreases and power increase. Power ranges from a few watts to 60000 W. Generally medium and higher-pressure mercury lamps need to be cooled by circulating suitable liquids around them. Filtering solutions and glass filters can be used with the aim of absorbing the wavelengths that should not reach the reacting medium.



A



B

Figure 1.2. Emission spectra for higher and medium pressure arc lamp: (A) 1000 W high-pressure Hg-Xe lamp; (B) 125 W medium pressure Hg lamp

1.5.2. Features of Heterogeneous Photoreactors

Three types of ideal reactors are assumed in chemical engineering: the batch reactor, the plug flow reactor (PFR) and the continuous-flow stirred tank reactor (CSTR) (Schiavello 1997). A batch reactor has no input or output of mass; the stirring of the reactor ensures that there are no temperature or concentration gradients within the system volume. The concentration and the temperature will change with time due to the reaction, but at any time they are everywhere uniform. The reaction rate is also uniform and it is considered everywhere equal to the average.

A PFR is usually visualised as a long tubular reactor. For the tube to be a PFR, three conditions must be satisfied: (i) the axial velocity profile is flat; (ii) there is complete mixing across the tube section so that all the reactor variables are a function of the axial dimension of the reactor and (iii) there is not diffusional mass transfer in the axial direction. PFRs have spatial variations in concentration and temperature. Such systems are called distributed and analysis of their steady-state performance requires solution of differential equations.

The CSTR is a flow reactor in which the contents are mechanically agitated. If mixing caused by the agitator is adequate, the entering feed will be quickly dispersed through the vessel and the composition and temperature at any point will approximate the average composition and temperatures. Perfect mixers have no spatial distribution of compositions and temperatures. Such systems are called lumped. The steady-state performance of lumped systems is determined by algebraic equations rather than the differential equations needed for distributed systems such as PFR.

For treating high-volume chemicals, flow reactors are usually preferred to batch reactors. Flow reactors are operated continuously; that is, at steady-state with reactants continuously entering the vessel and with products continuously leaving.

1.5.2.1. Fixed Bed Photoreactors

In photocatalytic processes at laboratory scale, the semiconductor catalyst is generally applied in the form of powder suspended in slurry (Dieckmann and Gray 1996). For large-scale applications of photocatalytic slurries, the catalyst particles must be filtered before the discharge of the treated water, even though TiO_2 is harmless to environment. Besides, the penetration depth of UV light in slurry is limited due to the strong absorption by TiO_2 and dissolved organic species. These problems can be eliminated by immobilizing TiO_2 catalyst over suitable supports; the use of particles completely constituted by active material is avoided owing to the fact that the penetration depth of radiation inside a semiconductor solid is a few microns (Loddo et al. 2007). The main advantages of catalyst immobilization are that (i) it eliminates the need for separation of catalyst particles from treated liquid and enables the contaminated water to be treated continuously; (ii) the catalyst film is porous and, therefore, it can provide a large surface area for the degradation of contaminant molecules; and (iii) the catalyst film, if supported on a conductive material, can be connected to an external potential to reduce electron–hole recombination, thereby significantly improving the quantum efficiency. The problems arising from immobilization are (i) the accessibility of the catalytic surface to photons and reactants and (ii) the influence of external mass transfer due to the diffusional length of reactant from bulk solution to the catalyst surface (Chen et al. 2001).

The immobilization of thin TiO_2 films on the outer surface of suitable support is a procedure largely reported in the literature (Byrne et al. 1998; Serrano and de Lasa 1997; Al-Ekabi and Serpone 1988; Feitz et al. 2000; Arabatzis et al. 2005; Turchi and Ollis 1989; Loddo et al. 2007). Immobilized TiO_2 anchored on fibreglass mesh was used in the Photo-CREC-Water I photoreactor (Byrne et al. 1998) and TiO_2 supported on compact particles has been used in fixed-bed photocatalytic reactors for investigating the degradation of aqueous solutions of phenolic compounds (Al-Ekabi and Serpone 1988). The guidelines for optimal design of fixed-bed photocatalytic reactors both in liquid and gas phase for

destruction of organic compounds (Arabatzis et al. 2005; Turchi and Ollis 1989) have been recently discussed.

The radiation field inside a photocatalytic fixed bed continuous reactor has been recently modelled (Loddo et al. 2007) by applying the Monte Carlo method; it was found that the radiation intensity profile sharply decreases inside the bed so that an important aliquot of the bed is not active for the photoreaction occurrence. The main drawback of a fixed bed is that, if the catalyst layer is able to absorb all the incident radiation, the rear particles are not irradiated and, therefore, an aliquot of the fixed bed photoreactor is not working. To avoid this problem it is important that the support material is transparent to the radiation used; moreover, the thickness of catalyst layer must be optimized in order that radiation reaches all the packed bed. The solution of this optimization problem is not straightforward owing to the fact that radiation propagation in the fixed bed is not a linear phenomenon (Cassano et al. 1995; Imoberdorf et al. 2007).

The Langmuir-Hinshelwood kinetics have been applied to rationalize the first-order behaviour in solid-liquid reactions and to argue in favour of a degradation reaction occurring on the TiO_2 particle surface. Feitz et al. (2000) evaluated two designs of solar pilot scale fixed-bed photocatalytic reactor by assessing the processing rate for phenol solutions. They found that the photonic efficiencies for removal of organic contaminant using the packed-bed reactor are only 40% lower than ideal suspension systems suggesting that fixed-bed photocatalysis is highly suitable for degradation of contaminated water. The guidelines for optimal design of fixed-bed photocatalytic reactors for destruction of liquid (Alexiadis and Mazzarino 2005) and volatile organic compounds (Arabatzis et al. 2005) have been recently discussed. The modelling of radiation-field for an annular packed-bed photocatalytic oxidation reactor has been also carried out by introducing some simplifying assumptions such as that the system is pseudo-homogeneous and that the reaction takes place only on the catalyst's external surface (Raupp et al. 1997; Alexiadis et al. 2001).

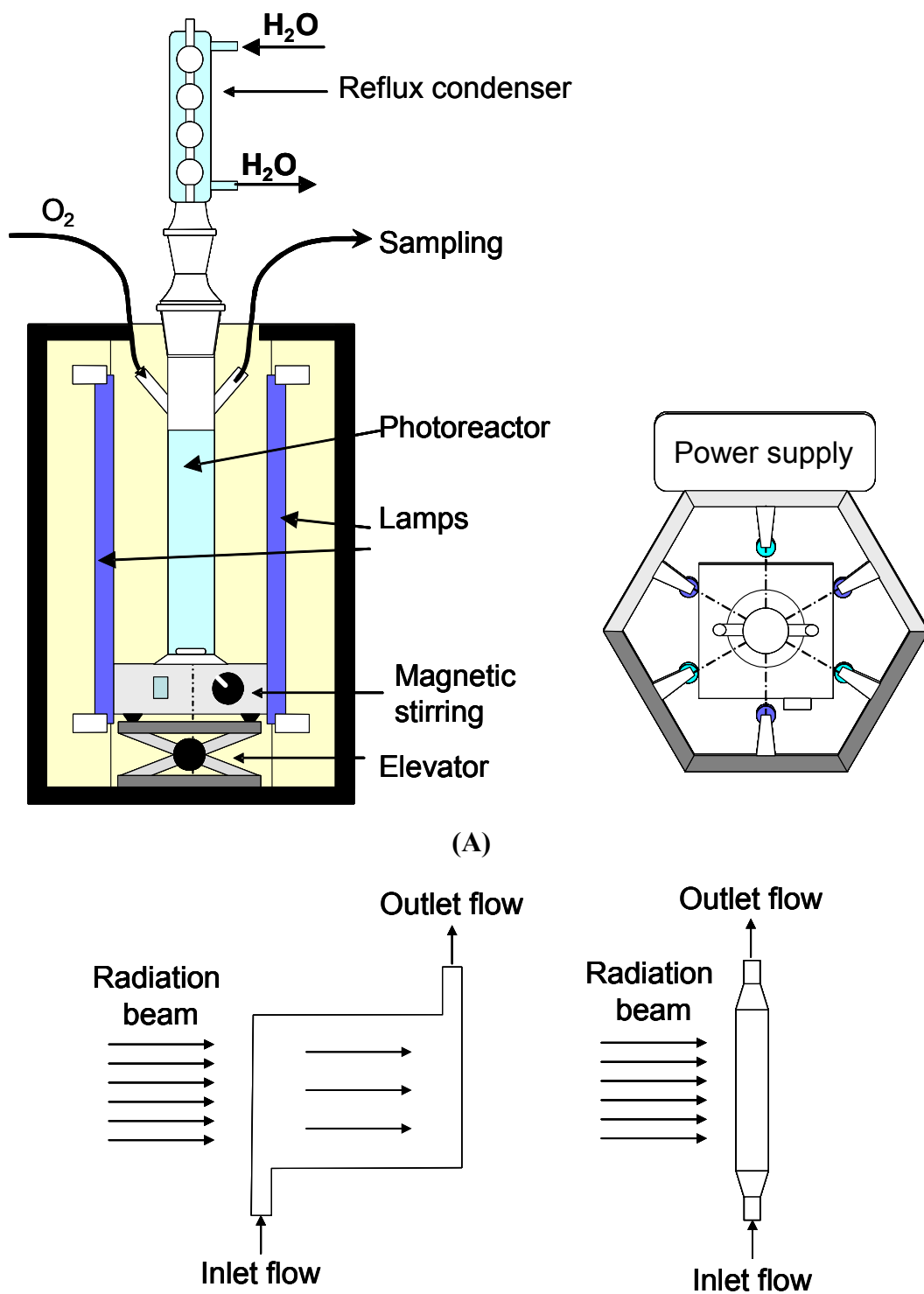
1.5.3. Photoreactor Geometries

For photoreactors, the geometry and the spatial relation between reactor and light source are very important factors (Schiavello 1997). The reason for that lies in the fact that geometry plays an important role in determining reaction yields as well as reactor operability. The geometrical configuration of a photoreactor is usually chosen to derive the maximum benefit from the pattern of irradiation taking into account shape and cooling requirements of available commercial lamps useful for wavelength required by the reaction.

The most usual photoreactors geometries are cylindrical (Fig. 1.3a), parallel plate (1.3b) and annular (see Figs. 2.1 and 2.3).

The irradiation may be normal or parallel to the reactor surface. In selecting the reactor geometry configuration it is necessary to determine the optical path of the light which will be obtained within the reactor. It is, in fact, the most important factor affecting the irradiation absorption by the reacting mixture and therefore it determines the efficiency of the photoprocess.

The choice of the best photoreactor for a certain application must take into consideration some important points such as scale and purposes of the operation, available lamps, phases involved and thickness of the reacting medium. It is obvious that laboratory and industrial applications have different purposes. In the first case the target is to obtain reproducible results that have to be interpreted in terms of fundamental quantities, while in the last case the purpose is to obtain a certain product with minimum cost and maximum reliability. The lamps needed to carry out the process (number and geometry) often restrict photoreactor choice while when a solid phase is present, as in the case of photocatalysed reactions, to keep the solid phase in suspension, mechanical agitation as well as fluidisation can be used. The optical thickness of the reacting medium is of great importance, in fact it gives an idea of the thickness of the layer of the irradiation medium. It is a guide for the choice of photoreactor type together with the knowledge of the average life of the intermediates.



(I) Axially irradiated photoreactor (II) Cross-flow photoreactor

(B)

Figure 1.3. Cylindrical (A) and parallel plate (B) photoreactors

While a lot of photocatalytic reactor geometries are used in the literature we will mention about annular photoreactors as they were used in this thesis investigation. In this kind of reactor the reaction zone is delimited by two coaxial cylinders. The lamp is placed on the symmetry axis. It can operate in batch or continuous way. Practically all the photons emitted by the lamp reach the reacting medium. In the case of low thickness of suspension in which a relevant quantity of photons reach the outer wall of the photoreactor, an outer mirror can be used.

1.6. Heterogeneous Photocatalysis for Partial Oxidation of Aromatic Alcohols

The partial oxidation of $-CH_2OH$ to $-CHO$ group is a key reaction step throughout many organic syntheses; this process is of great industrial importance as it is commonly used in the preparation of many organic products, due to the wide use of aldehyde derivatives in the flavour, confectionary, and beverage industries (Mao and Bakac 1996; Pillai and Demessie 2002).

The selective oxidation of alcohols to carbonyl compounds is generally carried out in environmentally harmful organic solvents at high temperature and pressure by employing stoichiometric oxygen donors (such as chromate and permanganate) that not only are expensive and toxic compounds but also produce high amounts of dangerous wastes (ten Brink et al. 2000; Sheldon et al. 2002; Enache et al. 2006; Li and Chen 2006; Ohkubo et al. 2006). To overcome these drawbacks, a major goal of the chemistry research during the last decade has been that of developing clean catalytic processes with high conversion and selectivity and also of using aqueous solvents such as water and supercritical CO_2 for safety and environmental reasons.

For the selective catalytic oxidation of alcohols in water a soluble palladium(II) bathophenanthroline complex was used as catalyst at a pressure of 30 bar and a temperature of 373.16 K (ten Brink et al. 2000). The conversion was almost complete and the yield was in the 79-90% range depending on the substrate, but no oxidation of di-substituted aromatic was reported.

Recently Enache et al. (2006) reported the catalytic oxidation of various alcohols by means of $Au-Pd/TiO_2$ catalysts: in the case of benzyl alcohol

oxidation to benzaldehyde the reached conversion was 74.5% and the selectivity 91.6%, benzyl benzoate being the only detected byproduct.

A interesting and environmentally friendly work was performed for oxidation of aliphatic and aromatic alcohols to the corresponding aldehydes and ketones derivatives in supercritical carbon dioxide medium (Jenzer ve ark. 2000). In this study, a fixed bed reactor, containing Pd-Pt-Bi/C catalyst, was used and very high selectivity was obtained.

Homogenous photocatalytic oxidation of primary and secondary benzyl alcohols to corresponding benzaldehydes or acetophenones was performed by using 10-methylacridium perchlorate or 9-phenyl-10-methyl-acridinium perchlorate as photocatalyst, under visible light irradiation at room temperature (Xu et al. 2007). No conversion was observed in water and very low conversion was observed in ethanol, however in other organic solvents (such as chloroform, dimethyl sulfoxide or toluene), especially in acetonitrile yield of 90% was obtained.

In literature, there are also heterogenous photocatalytic reactions for oxidation of aromatic alcohols by using polyoxometalates (POMs) as catalysts that show very high activity and selectivity (Rüther et al. 2003; Farhadi et al. 2005; Shen et al. 2007). Substitute benzyl alcohols were oxidized to corresponding aldehyde or ketone with high efficiency and selectively by using a decatungstate (a POM complex) catalyst supported on silica and γ -alumina (Trizakis et al. 2007). All the reactions were performed in organic solvents and it was shown that the activity results were low in acetone and acetonitrile, but were high in dichloromethane, diethyl ether or ethyl acetate. In addition, it was observed in that investigation that silica supported decatungstate is more active than unsupported decatungstate, however less active than γ -alumina supported decatungstate and unsupported one. Moreover, photocatalytic oxidation of primary and secondary benzyl alcohols to the corresponding aldehydes and ketones carbonyl derivatives was succesfully achieved by using silica-encapsulated $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (phosphotungstic acid) as a recyclable heterogenous photocatalyst in acetonitrile under oxygen as oxidant (Farhadi et al. 2005). As expected, the reaction of benzyl alcohols containing electron withdrawing groups

was slow and showed low selectivity with respect to benzyl alcohols containing electron donor groups. Another POM complex, Wells-Dawson anion, $[R_3N]_4[S_2M_{18}O_{62}]$, (M:W,Mo), was used as catalyst in acetonitrile for photocatalytic oxidation of benzyl alcohol under sun light (Rüther et al. 2003). 29% conversion was observed after 25 days of irradiation with 85% selectivity to benzaldehyde; small amounts of benzoic acid were also produced. Aliphatic and aromatic alcohols were selectively oxidized to the corresponding aldehydes and ketones derivatives (90-99%) using $H_3PW_{12}O_{40}/MCM-41$ as a photocatalyst in ionic liquids, $[bmim]BF_6$ (1-butyl-3-methylimidazolium hexafluorophosphate), $[omim]BF_4$ (1-octyl-3-methylimidazolium tetrafluorophosphate) and $[hmin]BF_4$ (1-hexyl-3-methylimidazolium tetrafluorophosphate), and in the presence of molecular oxygen (Shen et al. 2007). Among these surfactants, $[omim]BF_4$ showed very high conversion per unit time with respect to others, and the reactions in all the surfactants were much more efficient than the reaction going on in acetonitrile.

Heterogeneous photocatalysis has been also used for performing selective oxidations. Hydrocarbons were oxidised in aqueous TiO_2 suspensions to obtain alcohols and carbonyl compounds in the presence of artificial irradiation (Gonzalez et al. 1999), whereas sunlight induced functionalisation of some heterocyclic bases in the presence of polycrystalline TiO_2 in water/acetonitrile solvents (Caronna et al. 2003). Selective oxidation of alcohols to the corresponding aldehydes and ketones in the presence of TiO_2 was performed either in gas phase (Pillai and Sahle-Demessie 2002) or in liquid phase using acetonitrile as solvent (Mohamed et al. 2002a) in some cases affording high yields.

Photocatalytic oxidation of some fluorenols in oxygen saturated TiO_2 suspensions in acetonitrile or acetone was carried out and corresponding ketones were formed in a high yield with a small amount of reduction product (fluorene) and other oxidation products (Mohamed 2002b). Until recently, attempts of performing selective photocatalytic oxidation of alcohols to aldehydes in organic-free water were not reported in the literature.

Photocatalytic degradation of 2-phenylphenol on TiO_2 (Degussa P25) and ZnO in aqueous suspensions was carried out by Khosja et al. (2001); they

observed that the reaction is slower with TiO_2 than ZnO . Similar reactions were observed on both catalysts, but the mass balance was satisfied only with ZnO . Hydroxylations occurred preferentially in ortho and para position in good agreement with the electrophilic properties of hydroxyl radicals. If a lot of intermediates were considered, it could be evident that the photocatalytic oxidation reactions carried on in water are unselective.

1.7. Photoadsorption Phenomenon

In the field of heterogeneous catalysis the need of kinetic investigation is strictly connected to the main task of an investigator in the chemical field, i.e. designing properly a chemical reactor. A successful reactor design should thus starts from reliable kinetic models that describe the rate of catalytic reactions and, therefore, from the reaction mechanisms, which means understanding reactions at a molecular level. In catalysis, due to the complex nature of this phenomenon, adsorption and desorption of reactants as well as several steps for surface reactions must be taken into account. For heterogeneous photocatalysis, which may be considered a special case of heterogeneous catalysis, the previous considerations hold true with the added difficulty that the light absorbed by the photocatalyst affects both adsorption (photoadsorption) and surface reactions.

The use of irradiation to initiate chemical reactions is the principle on which heterogeneous photocatalysis is based. When a wide-band gap semiconductor like titanium dioxide (Carp et al. 2004) is irradiated with suitable light, excited electron-hole pairs result that can be applied in chemical processes to modify specific compounds. If recombination or lattice reaction do not involve all the photogenerated pairs, the conduction band electrons participate in reduction reactions on the catalyst surface while positive holes are involved in oxidation reactions. Suitable substrates must be adsorbed on the catalyst surface for the occurrence of a photoreaction process which always starts with the substrate(s) adsorption and eventually ends with the product(s) desorption. On these grounds heterogeneous photocatalysis is defined as follow: (Braslavsky 2007): “*Change in the rate of a chemical reaction or its initiation under the action of ultraviolet,*

visible, or infrared radiation in the presence of a substance, the photocatalyst, that absorbs light and is involved in the chemical transformation of the reaction partners.” Symbolically overall photocatalytic reaction is expressed by the Equation:



where R and P are reactants and reaction products, respectively, present in the gas or liquid phase, Cat is the solid photoadsorbent (photocatalyst) and $h\nu$ is the symbol of photons able to be absorbed by the photocatalyst.

The knowledge of heterogeneous photocatalytic systems has grown very much since the pioneering work on water photolysis carried out with a semiconductor electrode (Fujishima and Honda 1972). The basic principles of heterogeneous photocatalysis are now well established (Schiavello 1997; Fujishima et al. 1999; Kaneko and Okura 2002) and also the applicative aspects of this technology are being investigated in the fields not only of environment remediation (Mills and Le Hunte 1997; Fujishima et al. 2000; Augugliaro et al. 2006) but also of green chemistry (Gonzalez et al. 1999; Mohamed et al. 2002a). There are however, many important aspects waiting to be investigated. One of these is the correct approach for the determination of the photoadsorption capacity under photoprocess occurrence, i.e. of the amount of substrate adsorbed on the surface of a photocatalyst which is being irradiated.

Photon absorption by photocatalyst is regarded as the first stage of photoexcitation of heterogeneous system; the photoexcitation pathways of wide band gap solids may involve photogeneration of excitons and/or free charge carriers, depending on photocatalyst features such as fundamental absorption band, extrinsic/intrinsic defect absorption bands, or UV-induced colour centers bands. Independently of photoexcitation type, photon absorption has two main effects: (i) it changes the characteristics of photocatalyst surface; and (ii) it generates active photoadsorption centers. A typical case of the first effect is that band gap irradiation induces superhydrophilicity (photoinduced superhydrophilicity, PSH) on the TiO_2 surface, which shows hydrophobic features under dark conditions

(Wang et al. 1997; Fujishima et al. 2000; Fujishima and Zhang 2006). This PSH is accompanied by photocatalytic activity, as both phenomena have a common ground; so that the surface adsorbed compounds may be either photooxidised or washed away by water.

The second important effect is that irradiation absorption generates active states of the photoadsorption centers with trapped electrons and holes. By definition (Serpone and Emeline 2002) *“the photoadsorption center is a surface site which reaches an active state after photoexcitation and then it is able to form photoadsorbed species by chemical interaction with substrate (molecules, or atoms, or ions) at solid/fluid interface.”* In turn, the active state of a surface photoadsorption center is *“an electronically excited surface center, i.e. surface defect with trapped photogenerated charge carrier that interacts with atoms, molecules or ions at the solid/gas or solid/liquid interfaces with formation of chemisorbed species.”*

Adsorption initiated by light absorbed by the solid surface (photoadsorption) can be expressed by the following simple mechanism (Ryabchuk 2004):



where S_{PA} is the photoadsorption center, S_{PA}^* the active state of photoadsorption center, M the substrate in the fluid phase and M_{p-ads} the photoadsorbed substrate. Equation 1.7 describes the photoexcitation of adsorbent with formation of active S_{PA}^* centers and Equation 1.9 the adsorption of molecule M or “chemical decay” of the active states S_{PA}^* , while Equation 1.8 depicts the “physical decay” of S_{PA}^* state.

For a liquid-solid catalytic reaction the common technique for determining the adsorbed amount of a species dissolved in the solution is that of performing experiments in a batch not-reacting system and of measuring: (i) the volume of liquid solution; (ii) the concentration of the adsorbing species in the starting solution; and (iii), after that a known mass of catalyst is added to the liquid and

steady state conditions are reached, the concentration decrease determined in the starting solution due to the added catalyst. This procedure is based on the adequate assumptions that the catalyst superficial features are not affected by the composition of the surrounding fluid phase and that the measured decrease of the species amount in the solution is equal to the amount of species adsorbed on the catalyst. The same procedure cannot be applied for the photoadsorption determination; in fact, photoadsorption occurs under the simultaneous presence of irradiation and of reducing and oxidising species needed for charge carriers to be trapped on the semiconductor surface. Under these conditions the photoreaction also starts so that the measured decrease of species in the batch irradiated slurry is determined both by photoadsorption and reaction, these contributions being indistinguishable from the solution side.

This complexity determines that investigations on heterogeneous photocatalytic processes sometimes report information only on dark adsorption and use this information for discussing the results obtained under irradiation. This extrapolation is not adequate as the characteristics of photocatalyst surface change under irradiation and, moreover, active photoadsorption centers are generated. Nowadays very effective methods allow a sound characterisation of bulk properties of catalysts and powerful spectroscopies give valuable information on surface properties. Unfortunately information on the photoadsorption extent under real reaction conditions, i.e. at the same operative conditions at which the photoreactivity tests are performed, are not available. For the cases in which photoreaction events only occur on the catalyst surface, a critical step to affect the effectiveness of the transformation of a given compound is to understand the adsorption process of that compound on the catalyst surface. The study of the adsorbability of the substrate allows one to predict the mechanism and kinetics that promote its photoreaction and also to correctly compare the performance of different photocatalytic systems.

1.7.1. TiO₂ Surface Modifications Under Irradiation

For gas-solid and liquid-solid systems the interaction of a species with the solid surface depends on the chemical nature of the species and on the chemical and physical nature of the solid. For nonilluminated surface of semiconductor oxides a thermodynamic equilibrium between a species and the solid is established only when the electrochemical potential of the electrons in the entire system is uniform. When the adsorption-desorption equilibrium is established, an aliquot of the species is located in an adsorbed layer, held at the surface by either weak or strong bonding forces.

When a photocatalyst goes from dark conditions into irradiated ones, the radiation absorption determines that its surface undergoes a series of changes needed for eventually allowing the occurrence of photoprocesses (Bickley 1985a; Bickley 1985b). Essentially the interaction of a photon with a solid semiconductor gives rise to an increase of the vibrational state of the lattice or the number of quasi-free charge carriers, i.e. it generates an excited state of the solid. The illumination with band gap (or greater) energy creates a perturbation to this adsorption-desorption equilibrium established in the dark; under irradiation the previous equilibrium is displaced determining a net photoadsorption or photodesorption of species. A new equilibrium is achieved when the species and the solid acquire the same electrochemical potential (Bickley 1988a; Bickley 1988b).

Direct observation of photosorption phenomena at the TiO₂ surface has been reported in several earlier studies, focussing on the role played by surface OH groups in the photoadsorption of oxygen and therefore in regulating the TiO₂ photoactivity. For example, UV illumination stimulates desorption of oxygen and water molecules adsorbed at the TiO₂ surface (Meriaudeau and Vedrine 1976; Murphy et al. 1976; Sakai et al. 1998; Wang et al. 1999; Wu et al. 2000) while studies by IR (infrared spectroscopy) and XPS (X-ray photoelectron spectroscopy) reveal that the amount of OH groups on the TiO₂ surface increases by UV illumination (Linsebigler et al. 1995; Hoffmann et al. 1995; Asakuma et al. 2003; Ignatchenko et al. 2006; Mori et al. 2007). These changes are generally fast

and reversible, i.e. once irradiation is stopped the surface recovers its previous features, at equal initial conditions. A well recognized indication of the fact that irradiation modifies the surface of wide band gap solids is the post-sorption or memory effect, i.e. the adsorption in the dark caused by the pre-irradiation of solid surface (Solonitzyn and Terenin 1959; Solonitzyn et al. 1982).

A more recent and clear evidence of this behaviour is the phenomenon of induced superhydrophilicity, i.e. the generation of a highly hydrophilic TiO_2 surface by UV illumination (Wang et al. 1997; Sakai et al. 1998; Watanabe et al. 1999; Nakajima et al. 2001; Miyauchi et al. 2002; Lee et al. 2003; Takeuchi et al. 2005). Superhydrophilic property of the TiO_2 surface allows water to spread completely across the surface rather than remaining as droplets. In the case of a film which consists of only TiO_2 , the contact angle of water almost becomes zero during UV irradiation. However, it is found that the contact angle goes up and is restored comparatively quickly in a dark place. One of the most interesting aspects of TiO_2 is that photocatalysis and induced hydrophilicity can take place simultaneously on the same surface even though the mechanisms are different. In the case of photocatalysis UV light excites the catalyst and pairs of electrons and holes are generated; the photogenerated electrons then react with molecular oxygen to produce superoxide radical anions and the photogenerated holes react with water to produce hydroxyl radicals. These two types of rather reactive radicals then work together to carry out redox reactions with species adsorbed on the TiO_2 surface. On the other hand, surface hydroxyl groups can trap more photogenerated holes and improve the separation of electrons and holes which results in the enhancement of photocatalysis.

In the case of superhydrophilicity electrons and holes are still produced, but they react in a different way. The electrons tend to reduce the Ti(IV) cations to the Ti(III) state, and the holes oxidize the oxygen anions. In the process, oxygen atoms are ejected, creating oxygen vacancies. Water molecules can then occupy these oxygen vacancies, producing adsorbed OH groups, which tend to make the surface hydrophilic. Depending upon the composition and the processing, the surface can have more photocatalytic character and less superhydrophilic character, or vice versa. In spite of the different mechanism of photocatalytic and

hydrophilic effect, they behave synergetically. Because more OH groups can be adsorbed on the surface due to hydrophilicity, the photocatalytic activity is enhanced; so hydrophilicity can improve photocatalysis. On the other hand, the surface can adsorb contaminated compounds which tend to turn the hydrophilic surface to hydrophobic surface. Photocatalysis can decompose the organic compounds on the surface resulting in the restoration of hydrophilicity. From this point, photocatalysis can improve hydrophilicity and maintain this characteristic for a long time. The proposed mechanism means that the surface structure changes during the reaction. In other words, the rate of photo-induced hydrophilicity may depend on the history of the sample.

Specifically for liquid-solid systems, adsorption phenomena involving ions occur with a transfer of electric charge, causing a significant variation of the electronic band structure of the surface. The charge transfer is responsible for the formation of the so-called space-charge layer where the potential difference between surface and bulk creates an electric field that can play a beneficial role in the further adsorption steps. Most photons are absorbed in the superficial layer of the solid where the space-charge exists and the photoelectrons straightforwardly interact with the electric field here present. The consequence is a more efficient separation of the electrons and holes within the space-charge layer, i.e. the increase of their mean lifetime.

Photoadsorbed species can act (i) as surface-hole trapping and photoelectrons can be trapped in the bulk of the solid or (ii) as surface-electron trapping and holes can react with OH surface groups and/or H₂O. Both the alternatives depend on the chemical nature of the molecule to be adsorbed and on the type of the solid adsorbent. It is worth noting that in the gas-solid regime only gaseous species or lattice ions can be involved, whereas in the liquid phase also the interaction with the solvent (often H₂O) should be also considered.

All the above considerations allow to conclude that the electronic surface modifications created under irradiation eventually induce photoadsorption both in gas-solid and in liquid-solid regimes, being the photoadsorption phenomenon strictly related with the photoactivity of the solid photocatalysts. When light is switched off, a reversal of the process could be observed, although rarely the

reversibility is complete and the achievement of a new equilibrium depends mainly on kinetics rather than thermodynamic factors.

1.7.2. Photoadsorption Determination

For heterogeneous photocatalytic processes it is generally agreed that the expression for the degradation rate of organic substrates on TiO₂ surfaces in the presence of oxygen follows (with minor variations) the Langmuir–Hinshelwood (LH) model, which is widely used in liquid- and gas-phase systems (Turchi and Ollis 1989; Vorontsov et al. 1999; Ibrahim and de Lasa 2004; de Lasa et al. 2005; Murzin and Salmi 2005; Gora et al. 2006; Palmisano et al. 2007a). This model successfully explains the kinetics of reactions that occur between two adsorbed species, a free radical and an adsorbed substrate, or a surface bound radical and a free substrate. In the LH model adsorption equilibrium is assumed to be established at all times so that the rate of reaction is taken to be much less than the rate of adsorption or desorption. Reaction is assumed to occur between adsorbed species whose coverage on the catalyst surface is always in equilibrium with the species concentration in the fluid phase so that the rate determining step of the photocatalytic process is the surface reaction. The concentrations of adsorbed species are therefore determined by adsorption equilibrium as given by the suitable isotherm. It is useful to report that the simple rate form of the LH approach may have origins which take into account different photoreaction mechanisms (Demeestere et al. 2004; Minero and Vione 2006; Krýsa et al. 2006).

In batch photocatalytic reactors working in liquid-solid regime the depletion of a species is the combined result of photoadsorption and photoconversion processes. To describe this depletion, a mole balance applied to the species at whatever time (de Lasa et al. 2005) can be represented as:

$$n_T = n_L + n_S \quad (1.10)$$

where n_T is the total number of moles present in the photoreactor, n_L the number of moles in the fluid phase and n_s the number of moles photoadsorbed on the solid. When eq 1.10 is divided by the volume of the liquid phase, V , one obtains:

$$C_T = C_L + \frac{n_s}{V} \quad (1.11)$$

where C_T is the total concentration of the species and C_L the concentration in the liquid phase.

By considering that both substrate and oxygen must be present in the system for the occurrence of photoreaction, it is assumed that the total disappearance rate of substrate per unit surface area, r_T , follows a second order kinetics of first order with respect to the substrate coverage and of first order with respect to the oxygen coverage:

$$r_T \equiv - \frac{1}{S} \frac{dn_T}{dt} = k'' \theta_{Sub} \theta_{Ox} \quad (1.12)$$

in which S is the catalyst surface area, t the time, k'' the second order rate constant and θ_{Sub} and θ_{Ox} are the substrate and oxygen fractional coverages of the surface, respectively. θ_{Sub} and θ_{Ox} are defined in the following way:

$$\theta_{Sub} \equiv \frac{n_s}{W N_s^*} \quad (1.13)$$

$$\theta_{Ox} \equiv \frac{n_{s,Ox}}{W N_{s,Ox}^*} \quad (1.14)$$

where $n_{s,Ox}$ is the number of oxygen moles photoadsorbed on the solid, N_s^* and $N_{s,Ox}^*$ are the maximum capacity of photoadsorbed moles of substrate and oxygen, respectively, on the unit mass of irradiated solid and W the mass of catalyst.

By considering that in the course of the runs the oxygen bubbling in the dispersion is not stopped, its concentration in the liquid phase does not change during the occurrence of substrate degradation and, moreover, it is always in

excess. Then the θ_{Ox} term of eq 1.12 does not depend on time, i.e. it is a constant. By putting $k = k'' \cdot \theta_{Ox}$, equation 1.12 turns a pseudo-first order rate equation:

$$r_T \equiv - \frac{1}{S} \frac{dn_T}{dt} = k \theta_{Sub} \quad (1.15)$$

in which k is the pseudo-first order rate constant. Introducing in eq 1.15 the liquid volume, V , and the surface area per unit mass of catalyst, S_s , one obtains:

$$r_T \equiv - \frac{1}{S} \frac{dn_T}{dt} = - \frac{1}{S_s W} V \frac{dC_T}{dt} = k \theta_{Sub} \quad (1.16)$$

By considering that the kinetic information on the photoprocess consists on the knowledge of substrate concentration values in the liquid phase, C_L , as a function of irradiation time, the C_T and θ_{Sub} variables of eq 1.16 must to be transformed as a function of C_L . As to concern θ_{Sub} it is necessary to choose an adsorption isotherm, i.e. a relationship between θ_{Sub} (and therefore n_s , see eq 1.13) and C_L , while for C_T equation 1.11 coupled with the chosen isotherm may be used. Therefore equation 1.16 may be formally written in the following way:

$$- \frac{1}{S_s W} V \frac{d}{dt} C_T (C_L) = k \theta_{Sub} (C_L) \quad (1.17)$$

It is important to remind that the kinetic modelling is carried out by assuming that the main assumptions of the LH model hold; it means that equation 1.17 gives the evolution with irradiation time of the concentration in the liquid phase, C_L , of a species which is in photoadsorption equilibrium on the catalyst surface over which the species undergoes a slow transformation process. The main implication of the previous statement is that for a batch photocatalytic run the substrate concentration values measured in the liquid phase at a certain time represent the substrate concentration in equilibrium with an (unknown) substrate amount photoadsorbed on the catalyst surface. This feature belongs to all the measured values of substrate concentration except to the initial one. The substrate

concentration measured at the start of a photoreactivity run is characteristic of a system without irradiation. As a consequence, when a kinetic model is fitted to the experimental data, the regression analysis must be done with the concentration values measured in the course of the run excluding the value of initial substrate concentration because the condition of the initial concentration value (dark) is not that of the other ones (irradiated).

1.7.2.1. Langmuir Isotherm

The Langmuir isotherm theory (Satterfield 1980) assumes a monolayer coverage of adsorbate over a homogenous adsorbent surface. A plateau characterizes the Langmuir isotherm; therefore, a saturation point is reached where no further adsorption can occur. Adsorption is assumed to take place at specific homogeneous sites within the adsorbent. Once a molecule occupies a site, no further adsorption can take place at that site. The Langmuir model assumes that the catalyst surface is completely uniform, i.e. (i) the adsorption onto the surface of each molecule has equal activation energy; and (ii) no transmigration of adsorbate in the plane of the surface occurs. Those assumptions are here hypothesized to be suitable to describe also photoadsorption. The Langmuir adsorption isotherm is described by the following relationship:

$$\theta_{\text{Sub}} \equiv \frac{n_s}{W N_s^*} = \frac{K_L^* C_L}{1 + K_L^* C_L} \quad (1.18)$$

where K_L^* is the photoadsorption equilibrium constant, which is related to the free energy of photoadsorption, and N_s^* the monolayer adsorption capacity. K_L^* may be considered a measure of the intrinsic photoreactivity of the catalyst surface. By solving eq 1.18 with respect to n_s and substituting in eq 1.11, the result is:

$$C_T = C_L + \frac{W N_s^*}{V} \frac{K_L^* C_L}{1 + K_L^* C_L} \quad (1.19)$$

Substituting in eq 1.16 the Langmuir relationship (eq 1.18) produces

$$-\frac{V}{W S_s} \frac{dC_T}{dt} = k \frac{K_L^* C_L}{1 + K_L^* C_L} \quad (1.20)$$

Taking the derivative of eq 1.19 with respect to time, it yields:

$$\frac{dC_T}{dt} = \left[1 + \frac{W N_s^* K_L^*}{V} \frac{1}{(1 + K_L^* C_L)^2} \right] \frac{dC_L}{dt} \quad (1.21)$$

Substituting eq 1.21 into the left hand side term of eq 1.20, one obtains:

$$-\frac{V}{W S_s} \left[1 + \frac{W N_s^* K_L^*}{V} \frac{1}{(1 + K_L^* C_L)^2} \right] \frac{dC_L}{dt} = k \frac{K_L^* C_L}{1 + K_L^* C_L} \quad (1.22)$$

and, rearranging and separating the variables, the following differential equation is obtained:

$$-\frac{V}{W S_s} \frac{1}{k K_L^*} \frac{dC_L}{C_L} - \frac{V}{W S_s} \frac{1}{k} dC_L - \frac{1}{S_s} \frac{N_s^*}{k} \frac{dC_L}{C_L (1 + K_L^* C_L)} = dt \quad (1.23)$$

As outlined before, equation 1.23 gives the evolution with irradiation time of the concentration in the liquid phase of a species which is in photoadsorption equilibrium on the catalyst surface over which the species undergoes a slow transformation process. On this ground, the integration of eq 1.23 must be performed with the condition that at $t=0$ the substrate concentration in the liquid phase is that in equilibrium with the initial photoadsorbed amount, $C_{L,0}$; this initial concentration is unknown but it may be determined by the regression analysis carried out with the experimental data obtained after the start of irradiation. The integration yields:

$$\frac{V}{W S_s} \frac{1}{k K_L^*} \ln \frac{C_{L,0}}{C_L} + \frac{V}{W S_s} \frac{1}{k} (C_{L,0} - C_L) + \frac{1}{S_s} \frac{N_s^*}{k} \ln \left(\frac{1 + K_L^* C_L}{1 + K_L^* C_{L,0}} \frac{C_{L,0}}{C_L} \right) = t \quad (1.24)$$

Equation 1.24 contains four unknown parameters, K_L^* , N_s^* , k and $C_{L,0}$, whose determination may be carried out by a best fitting procedure.

Asymptotic cases of Langmuir photoadsorption isotherm

A straightforward determination of K_L^* , N_s^* , k and $C_{L,0}$ parameters can be done in the following way. k and $C_{L,0}$ may be easily determined by considering two asymptotic situations of Langmuir adsorption isotherm, i.e. very high or very low substrate concentration. At very high concentrations of substrate the following inequality may be assumed to hold:

$$K_L^* C_L \gg 1 \quad (1.25)$$

In this case from eq 1.18 one obtains:

$$\theta_{\text{Sub}} \equiv \frac{n_s}{W N_s^*} = \frac{K_L^* C_L}{1 + K_L^* C_L} \approx 1 \quad (1.26)$$

and equation 1.19 transforms in:

$$C_T = C_L + \frac{W N_s^*}{V} \quad (1.27)$$

The total disappearance rate of substrate per unit surface area, r_T , gets of zero order so that eq 1.20 can be written as:

$$-\frac{V}{W S_s} \frac{dC_T}{dt} = k \quad (1.28)$$

Taking the derivative of eq 1.27 with respect to time, it yields that $dC_T/dt = dC_L/dt$. Substituting this equality in eq 1.28 and rearranging, one obtains:

$$-\frac{dC_L}{dt} = \frac{W S_s}{V} k \quad (1.29)$$

Integration of eq 1.29 with the condition that $C_L = C_{L,0}$ for $t = 0$ yields the following relationship:

$$C_L = C_{L,0} - \frac{W S_s}{V} k t \quad (1.30)$$

which is a linear relationship between the concentration values measured in the solution and the irradiation time. The intercept and slope values allow to determine the $C_{L,0}$ and k values.

At very low concentrations of substrate the following inequality may be assumed to hold:

$$K_L^* C_L \ll 1 \quad (1.31)$$

In this case from eq 1.18 one obtains:

$$\theta_{\text{Sub}} \equiv \frac{n_s}{W N_s^*} = \frac{K_L^* C_L}{1 + K_L^* C_L} \approx K_L^* C_L \quad (1.32)$$

and from eq 1.19 one obtains:

$$C_T = C_L + \frac{W N_s^* K_L^*}{V} C_L \quad (1.33)$$

The total disappearance rate of substrate per unit surface area, r_T , turns of first order with respect to the substrate concentration and eq 1.20 can be written as:

$$-\frac{V}{W S_s} \frac{dC_T}{dt} = k K_L^* C_L \quad (1.34)$$

Taking the derivative of eq 1.33 with respect to time, it yields:

$$\frac{dC_T}{dt} = \left(1 + \frac{W N_S^* K_L^*}{V} \right) \frac{dC_L}{dt} \quad (1.35)$$

Substituting this equality in eq 1.34 and rearranging, one obtains:

$$- \frac{dC_L}{dt} = \frac{W S_s k K_L^*}{V + N_S^* K_L^*} C_L \quad (1.36)$$

By integrating with the condition that $C_L = C_{L,0}$ for $t = 0$, one obtains:

$$\ln C_L = \ln C_{L,0} - \frac{W S_s k K_L^*}{V + W N_S^* K_L^*} t \quad (1.37)$$

which is a linear relationship in a semilogarithmic plot of concentration values versus the irradiation time. The intercept value allows to determine the $C_{L,0}$ value while the slope contains two parameters, K_L^* and N_S^* , that may be determined in the following way.

From the photoreactivity runs for which the inequalities 1.25 and 1.31 hold, the values of $C_{L,0}$ may be determined. Applying to the substrate the molar balance expressed by eq 1.11 at the start of irradiation, i.e. the zero time, yields:

$$C_{T,0} = C_{L,0} + \frac{n_{S,0}}{V} \quad (1.38)$$

in which $C_{T,0}$ is the total concentration of substrate and coincides with the concentration of initial solution and $n_{S,0}$ is the number of photoadsorbed moles in equilibrium with the solution at $C_{L,0}$ concentration. In the statement of eq 1.38 it is assumed that only photoadsorption can occur on the surface of irradiated particles of catalyst and that the whole particles are irradiated. Equation 1.38 allows to determine the $n_{S,0}$ value corresponding to a certain $C_{L,0}$:

$$n_{S,0} = V(C_{T,0} - C_{L,0}) \quad (1.39)$$

All the $n_{S,0}$ - $C_{L,0}$ couples of values are related by the Langmuir model (eq 1.18):

$$\frac{n_{S,0}}{W N_S^*} = \frac{K_L^* C_{L,0}}{1 + K_L^* C_{L,0}} \quad (1.40)$$

Inverting the terms of eq 1.40 and rearranging, one has:

$$\frac{1}{n_{S,0}} = \frac{1}{W N_S^* K_L^* C_{L,0}} + \frac{1}{W N_S^*} \quad (1.41)$$

Introducing eq 1.39 into eq 1.41 and multiplying eq 1.41 by $C_{L,0}$ yield eq 1.42, which is the linear form of eq 1.40:

$$\frac{C_{L,0}}{C_{T,0} - C_{L,0}} = \frac{V}{W N_S^* K_L^*} + \frac{V}{W N_S^*} C_{L,0} \quad (1.42)$$

where $C_{L,0}/(C_{T,0} - C_{L,0})$ is a dependent variable, $C_{L,0}$ an independent variable, $V/W K_L^* N_S^*$ the linear coefficient and $V/W N_S^*$ the angular coefficient of the straight line. Thus, by plotting $C_{L,0}/(C_{T,0} - C_{L,0})$ versus $C_{L,0}$ one can determine the maximum adsorption capacity, N_S^* , and photoadsorption equilibrium constant, K_L^* , respectively, through the slope and linear coefficient of the straight line.

The determination of the value of K_L^* allows checking the inequalities expressed by eqns. 1.25 and 1.31. For the runs for which the previous inequalities do not hold, equation 1.24 must be used for determining the only unknown parameter contained in it, i.e. the $C_{L,0}$ value.

1.7.2.2. Freundlich Isotherm

The Langmuir theory of adsorption is an approximation of the real surfaces as surface reconstruction frequently occurs. An assumption generally used for the description of the physical chemistry of real adsorbed layers is that surface sites

are different, the so called biographical nonuniformity (Murzin and Salmi 2005). By applying the Langmuir adsorption isotherm to a distribution of energies among the sites such that the heat of adsorption decreases logarithmically with coverage, the Freundlich isotherm is derived (Satterfield 1980); it is described by the following relationship:

$$\theta_{\text{Sub}} \equiv \frac{n_s}{W N_s^*} = K_F^* C_L^{1/n} \quad (1.43)$$

where K_F^* is the Freundlich isotherm constant indicative of the relative adsorption capacity of the adsorbent and n a dimensionless parameter indicative of the intensity of the adsorption. The n parameter represents the mutual interaction of adsorbed species; a value of n greater than unity is interpreted to mean that adsorbed molecules repulse one another. The Freundlich expression is an exponential equation and therefore it assumes that as the adsorbate concentration in the liquid phase increases, the concentration of adsorbate on the adsorbent surface also increases. Using the empirical form of Freundlich isotherm, an infinite amount of adsorption can occur, what is contrary to chemisorption. The statistical derivation of this isotherm, however, sets a value of the Freundlich maximum adsorption capacity, N_s^* . By solving eq 1.43 with respect to n_s and substituting in eq 1.11, the result is:

$$C_T = C_L + \frac{W N_s^*}{V} K_F^* C_L^{1/n} \quad (1.44)$$

Substituting in eq 1.16 the Freundlich relationship (eq 1.43) produces

$$- \frac{V}{W S_s} \frac{dC_T}{dt} = k K_F^* C_L^{1/n} \quad (1.45)$$

Taking the derivative of eq 1.44 with respect to time, it yields:

$$\frac{dC_T}{dt} = \left[1 + \frac{W N_S^* K_F^*}{V} \frac{1}{n} C_L^{\frac{1-n}{n}} \right] \frac{dC_L}{dt} \quad (1.46)$$

Substituting eq 4.46 into the left hand side term of eq 1.45, one obtains:

$$-\frac{V}{W S_s} \left[1 + \frac{W N_S^* K_F^*}{V} \frac{1}{n} C_L^{\frac{1-n}{n}} \right] \frac{dC_L}{dt} = k K_F^* C_L^{1/n} \quad (1.47)$$

and, rearranging and separating the variables, the following differential equation is obtained:

$$-\frac{V}{W S_s} \frac{1}{k K_F^*} \frac{dC_L}{C_L^{1/n}} - \frac{1}{S_s} \frac{N_S^*}{k n} \frac{dC_L}{C_L} = dt \quad (1.48)$$

As done in the case of Langmuir adsorption isotherm, integration of eq 1.48 is performed with the condition that at $t=0$ the substrate concentration in the liquid phase is that in equilibrium with the initial photoadsorbed amount, $C_{L,0}$; this initial concentration is unknown but it may be determined by the regression analysis carried out with the experimental data obtained after the start of irradiation. The integration yields:

$$\frac{V}{W S_s} \frac{1}{k K_F^*} \frac{n}{n-1} \left(C_{L,0}^{(n-1)/n} - C_L^{(n-1)/n} \right) + \frac{1}{S_s} \frac{N_S^*}{k n} \ln \frac{C_{L,0}}{C_L} = t \quad (1.49)$$

Equation 1.49 contains five unknown parameters, K_F^* , N_S^* , n , k , and $C_{L,0}$, whose determination may be carried out by a best fitting procedure.

1.7.2.3. Redlich-Peterson Isotherm

Since in heterogenous catalysis most of the adsorbents follow Langmuir or Freundlich models, much better than Temkin model (see Section 1.7.2.4), an attempt is made here to test the photoadsorption validity with respect to Redlich–Peterson (R-P) model (Redlich and Peterson 1959). The R-P isotherm model

combines elements from both the Langmuir and Freundlich equation and the mechanism of adsorption is a hybrid one and it does not follow ideal monolayer adsorption. The R-P isotherm is an empirical equation, designated the “three parameter equation”, which may be used to represent adsorption equilibria over a wide concentration range (Matthews and Weber 1976; Allen et al. 2004; Ahmaruzzaman and Sharma 2005; Kumar and Sivanesan 2005). The R-P adsorption isotherm is described by the following relationship:

$$\frac{n_s}{W} = \frac{K_{R-P}^* C_L}{1 + \alpha_{R-P}^* C_L^\beta} \quad (1.50)$$

where K_{R-P}^* and α_{R-P}^* are R-P isotherm constants which refer to the adsorption capacity and the surface energy, respectively. The exponent β is the heterogeneity factor which lies between 1 and 0. The equation can be reduced to the Langmuir equation as β approaches 1 while it becomes the Henry's law equation when $\beta = 0$. By solving eq 1.50 with respect to n_s and substituting in eq 1.11, the result is:

$$C_T = C_L + \frac{W}{V} \frac{K_{R-P}^* C_L}{1 + \alpha_{R-P}^* C_L^\beta} \quad (1.51)$$

In the cases of Langmuir and Freundlich isotherms it has been assumed that the total disappearance rate of substrate per unit surface area, r_T , follows a pseudo-first order kinetics with respect to the substrate concentration which is expressed by its fractional coverage. The same assumption is made for R-P isotherm; however, as the R-P isotherm relates an adsorbed amount (and not a fractional coverage) with the equilibrium concentration in the liquid phase, the r_T term is written as:

$$r_T \equiv - \frac{V}{W S_s} \frac{dC_T}{dt} = k C_{Surface} = k \frac{n_s}{W S_s} \quad (1.52)$$

in which C_{Surface} is the surface concentration of adsorbed species (adsorbed moles/catalyst surface area) (Minero and Vione 2006). Substituting in eq 1.52 the R-P relationship (eq 1.50) produces:

$$-\frac{V}{W} \frac{dC_T}{dt} = k \frac{K_{R-P}^* C_L}{1 + \alpha_{R-P}^* C_L^\beta} \quad (1.53)$$

Taking the derivative of eq 1.51 with respect to time, it yields:

$$\frac{dC_T}{dt} = \left[1 + \frac{W K_{R-P}^*}{V} \frac{1 + \alpha_{R-P}^* C_L^\beta (1 - \beta K_{R-P}^*)}{(1 + \alpha_{R-P}^* C_L^\beta)^2} \right] \frac{dC_L}{dt} \quad (1.54)$$

Substituting eq 1.54 into the left hand side term of eq 1.53, one obtains:

$$-\frac{V}{W} \left[1 + \frac{W K_{R-P}^*}{V} \frac{1 + \alpha_{R-P}^* C_L^\beta (1 - \beta K_{R-P}^*)}{(1 + \alpha_{R-P}^* C_L^\beta)^2} \right] \frac{dC_L}{dt} = k \frac{K_{R-P}^* C_L}{1 + \alpha_{R-P}^* C_L^\beta} \quad (1.55)$$

and, rearranging and separating the variables, the following differential equation is obtained:

$$-\frac{V}{W k K_{R-P}^*} \frac{dC_L}{C_L} - \frac{\alpha_{R-P}^* V}{W k K_{R-P}^*} C_L^{\beta-1} dC_L - \frac{1}{k} \frac{dC_L}{C_L (1 + \alpha_{R-P}^* C_L^\beta)} +$$

$$-\frac{V \alpha_{R-P}^* (1 - \beta K_{R-P}^*)}{W k K_{R-P}^*} \frac{C_L^{\beta-1} dC_L}{1 + \alpha_{R-P}^* C_L^\beta} = dt \quad (1.56)$$

As done in the case of previous adsorption isotherms, integration of eq 1.56 is performed with the condition that at $t=0$ the substrate concentration in the liquid phase is that in equilibrium with the initial photoadsorbed amount, $C_{L,0}$; this initial concentration is unknown but it may be determined by the regression analysis carried out with the experimental data obtained after the start of irradiation. The integration yields:

$$\begin{aligned}
& \frac{V}{W k K_{R-P}^*} \ln\left(\frac{C_{L0}}{C_L}\right) + \frac{\alpha_{R-P}^* V}{W k \beta K_{R-P}^*} (C_{L0}^\beta - C_L^\beta) + \frac{1}{k \beta} \ln\left(\frac{1 + \alpha_{R-P}^* C_L^\beta}{1 + \alpha_{R-P}^* C_{L0}^\beta} \frac{C_{L0}^\beta}{C_L^\beta}\right) + \\
& + \frac{V (1 - \beta K_{R-P}^*)}{W k \beta K_{R-P}^*} \ln\left(\frac{1 + \alpha_{R-P}^* C_{L0}^\beta}{1 + \alpha_{R-P}^* C_L^\beta}\right) = t
\end{aligned} \tag{1.57}$$

Equation 1.57 contains five unknown parameters, K_{R-P}^* , α_{R-P}^* , β , k and $C_{L,0}$, whose determination may be carried out by a best fitting procedure.

1.7.2.4. Temkin Isotherm

The Temkin isotherm model assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent–adsorbate interactions, and that the adsorption is characterized by a uniform distribution of the binding energies, up to some maximum binding energy. By applying the Langmuir adsorption isotherm to this distribution of energies, the Temkin isotherm equation is derived (Satterfield, 1980):

$$\theta_{\text{Sub}} \equiv \frac{n_s}{W N_s^*} = \frac{1}{f} \ln(K_T^* C_L) \tag{1.58}$$

where f is a constant related to the differential heat of adsorption at zero surface coverage, and K_T^* the Temkin equilibrium adsorption constant. By solving eq 1.58 with respect to n_s and substituting in eq 1.11, the result is:

$$C_T = C_L + \frac{W N_s^*}{V} \frac{1}{f} \ln(K_T^* C_L) \tag{1.59}$$

Substituting in eq 1.16 the Temkin relationship (eq 1.58) produces

$$- \frac{V}{W S_s} \frac{dC_T}{dt} = k \frac{1}{f} \ln(K_T^* C_L) \tag{1.60}$$

Taking the derivative of eq 1.59 with respect to time, it yields:

$$\frac{dC_T}{dt} = \left[1 + \frac{W N_s^*}{V} \frac{1}{f} \frac{1}{C_L} \right] \frac{dC_L}{dt} \quad (1.61)$$

Substituting eq 1.61 into the left hand side term of eq 1.60, one obtains:

$$-\frac{V}{W S_s} \left[1 + \frac{W N_s^*}{V} \frac{1}{f} \frac{1}{C_L} \right] \frac{dC_L}{dt} = k \frac{1}{f} \ln (K_T^* C_L) \quad (1.62)$$

and, rearranging and separating the variables, the following differential equation is obtained:

$$-\frac{V}{W S_s} \frac{f}{k \ln (K_T^* C_L)} \frac{dC_L}{dt} - \frac{N_s^*}{S_s} \frac{1}{k} \frac{dC_L}{C_L \ln (K_T^* C_L)} = dt \quad (1.63)$$

Equation 1.63 contains five unknown parameters, K_T^* , N_s^* , k , f and $C_{L,0}$, whose determination may be carried out by a best fitting procedure. As done in the cases previously described, integration of eq 1.63 must be performed with the condition that at $t=0$ the substrate concentration in the liquid phase is that in equilibrium with the initial photoadsorbed amount, $C_{L,0}$; this initial concentration is unknown but it may be determined by the regression analysis carried out with the experimental data obtained after the start of irradiation.

2. EXPERIMENTAL SECTION

2.1. Photocatalyst Preparation

2.1.1. Preparation of Rutile TiO_2 at Moderate Temperature

The precursor solution was obtained by slowly adding drop wise 20 mL of TiCl_4 (Fluka, >98%) in a 2 L beaker containing 1 L water under agitation, since the hydrolysis of TiCl_4 is a highly exothermic reaction producing significant amounts of HCl vapours. The addition had a total duration of 5 min. After magnetic stirring (450 rpm) for 10 minutes, the resulting sol was kept closed in oven for 2 days at 333 K. Then a white suspension was obtained and drying at 333 K by means of a rotary evaporator machine (model Buchi Rotovapor M) working at 50 rpm was performed, eventually obtaining the powdered catalyst which is indicated as HP333. In order to check the influence of the degree of crystallinity, HP333 was calcined at 673 K and 973 K for 6 hours. The obtained samples were coded HP673 and HP973, respectively. Another sample (HP333D) was prepared by dialysing HP333 by means of a Dialysis Tubing Cellulose Membrane Flat with MW 12400 cut off pores (Aldrich), for ca. 3 days, changing every 8 h the distilled water (5 L), until the conductivity value of water was found to be negligible. An amorphous TiO_2 powder (HP298) was also prepared by following the hereafter described procedure. 2.5 mL of TiCl_4 were added drop wise into a 100 mL beaker containing 25 mL of water. During the addition that lasted 5 min, the solution was magnetically stirred at 450 rpm. Upon closing the beaker and mixing the solution for 12 h at room temperature, a clear solution was eventually obtained. Afterwards the so-prepared solution was added to 90 mL of 1 M NaOH (J.T. Baker, >99%) aqueous solution under magnetic agitation. Hence the resulting suspension was filtered and washed until the washing water was found to have a neutral pH and a negligible conductivity. The catalysts are addressed to as “HP” followed by a number, indicating the treatment temperature in Kelvin.

2.1.2. Preparation of Rutile TiO_2 at Room Temperature

The precursor solutions were obtained by adding 20 mL of TiCl_4 to 400, 700, 1000, 1500 or 2000 mL water contained in a volumetric flask; the addition was carried out very slowly without agitation in order to avoid the warming of the sol. At the end of the addition, the resulting sol was mixed for 2 minutes by a magnetic stirrer and then the flask was sealed and maintained at room temperature (ca. 298 K) for 4-9 days. Just after ca. 12 h aging, the sol became almost a transparent solution and then, after waiting a few days, the precipitation process started. The solid powder precipitated at the end of the whole treatment was separated by centrifugation (20 min. at 5000 rpm) and dried at room temperature. The final HP catalysts are hereafter indicated as HP1/20, HP1/35, HP1/50, HP1/75 and HP1/100 where the figures indicate the $\text{TiCl}_4/\text{H}_2\text{O}$ volumetric ratio.

2.1.3. Preparation of Anatase, Anatase-Rutile Mixture and Rutile TiO_2 at 373K

The preparation method has been reported elsewhere (Palmisano et al 2007b). The precursor solution was obtained by adding 5 mL of TiCl_4 drop by drop into a 200 mL beaker containing 50 mL of water. During the addition, that lasted 5 min, the solution was magnetically stirred by a cylindrical bar at 600 rpm. After that the beaker was closed and mixing was prolonged for 12 h at room temperature, eventually obtaining a clear solution. This solution was transferred to a round-bottom flask fitted with a Graham condenser. The flask was heated in boiling water for 0.5, 2, 4, 6 and 8 h, obtaining a white suspension at the end of each treatment. The suspensions were then dried at 323 K by means of a rotary evaporator machine (model Buchi rotary evaporator M) working at 50 rpm, in order to obtain the final powdered catalysts. The HP powders were washed with distilled water and centrifuged several times until the chloride ion concentration in the washing water reached a negligible value, as checked by AgNO_3 (Sigma-Aldrich) test. Hereafter the HP catalysts are referred to as “HPx” in which the x figure indicates the boiling time of the precursor, expressed in hours.

2.1.4. Preparation of TiO₂ Supported on Pyrex Beads

HP TiO₂ catalyst was used in all the experiments. The procedure used to prepare the precursor of catalyst (Addamo et al. 2004; Addamo et al. 2005a) and to immobilize it on the Pyrex beads (Loddo et al. 2007) is summarised in the following. TiCl₄ was slowly added to distilled water (volume ratios: 1:10) at room temperature; after continuous stirring, a resulting clear solution was obtained. Pyrex beads of 2 mm diameter were added to the sol and remained immersed for 30 minutes. After that they were filtered and placed in a Pyrex tube, maintained at 423 K and fed with a nitrogen flow until TiCl₄ was completely hydrolysed to Ti(OH)₄. The beads were subjected to a thermal treatment at 673 K in air in order to obtain a thin layer of anatase phase TiO₂, as confirmed by X-ray diffraction (XRD) analysis. On an aliquot of these beads the procedure was repeated in order to support a second layer of catalyst; by following the previous procedure a third layer was supported. The supported catalysts are hereafter indicated as HP1, HP2 and HP3 in which the figures refer to the number of layers.

2.2. Photocatalyst Characterization Techniques

XRD patterns of the powders were recorded by a Philips diffractometer using the Cu K α radiation and a 2 θ scan rate of 1.28 °/min.

Scanning electron microscope (SEM) images were obtained using an ESEM microscope (Philips, XL30) operating at 25 kV. A thin layer of gold was evaporated on catalysts samples, previously sprayed on the stub and dried at room temperature.

BET specific surface areas were measured by the single-point BET method using a Micromeritics Flow Sorb 2300 apparatus. Before the analysis, the samples were dried 1 h at 100 °C, 2 h at 150 °C and degassed 0.5 h at 150 °C. In addition, a multi point BET method (Quantachrome NovaWin2) used for the samples HP0.5, HP2, HP4, HP6 and HP8 in order to obtain BET specific surface areas, total porosity and average pore radius.

The thickness of the TiO₂ film deposited on the glass beads was estimated by means of a SEM-EDAX (SEM–Energy dispersive X-ray spectroscopy) mapping carried out on samples prepared by embedding the beads in a polystyrene resin before to be smoothed (Philips XL30 ESEM microscope).

Diffuse reflectance spectra of the solids were obtained using an UV–vis spectrophotometer (Shimadzu, U{\GuliverItalicvee}- 2401PC). Samples were spread onto BaSO₄ plates; the background reflectance of BaSO₄ was measured before. Reflectance was converted by the instrument software to F(R_∞) values according to the Kubelka–Munk theory (Kortüm 1969).

Thermogravimetric analyses were performed by using a Netzsch equipment (model STA 409). The heating rate was 10 °C/min in static air and the powder amount, put in open Pt crucible, was 190 mg for all the samples.

Photoelectrochemical measurements were performed by according to the literature (Roy et al. 1995). Fifty mg of catalyst and 10 mg of MV dichloride (Sigma-Aldrich, > %99) were suspended in a 100 mL two necked flask in 50 mL of 0.1 M KNO₃. A platinum flag and Ag/AgCl served as working and reference electrodes, respectively. A pH-meter allowed to follow the proton concentration; HNO₃ (Sigma-Aldrich) (0.1 M) and NaOH were used to adjust the pH value. The suspension was magnetically stirred and flushed with dinitrogen throughout the experiment carried out at room temperature. In general the starting suspension had pH 2.5. In order to check the influence of ethanol on the flat band potential, 5 mL of ethanol (Merck, 99.9%) were added into the suspension and the same procedure was carried out. Irradiation was performed with a 150 W xenon arc lamp (OSRAM XBO, I0 (300–400 nm) = 1.4×10^{-6} Einstein s⁻¹cm⁻²) installed in a light-condensing lamp housing (PTI, A1010S) on an optical train. The flask was mounted at a distance of 30 cm from the lamp.

In Situ ATR-FTIR (Attenuated Total Reflectance - Fourier Transform Infrared Spectroscopy) measurements were performed as following. Infrared spectra of thin films of the photocatalysts were recorded using a Thermo Nicolet Nexus FTIR spectrometer equipped with a liquid nitrogen-cooled MCT detector and a SensIR Technologies DurasamplIR 9-reflection horizontal ATR accessory (4 mm diameter diamond-faced ZnSe prism). Titania samples grounded in an

agate mortar were suspended in Milli-Q deionized water (25 mg solid in 25 mL water) and sonicated for 20 min (Elma Transsonic T470/H ultrasonic cleaning unit). Thin films were prepared by dropping 50 μL of the suspension onto the ATR crystal and then allowing the solvent to evaporate. The procedure was repeated twice to obtain thin films containing ca. 100 μg TiO_2 . A 100 mL volume glass flow cell was attached to the ATR plate through an o-ring sealed connection and the thin film was dried at room temperature for several minutes in a stream of synthetic air (Air Liquide, Alphagaz Air 1). Adsorption of water, ethanol (Panreac, 99.5%) and benzyl alcohol (Sigma–Aldrich, purity >99%) vapours on the dried TiO_2 thin films was carried out at room temperature under static conditions by introducing 0.2 mL of each liquid adsorbate inside the closed glass cell previously purged with synthetic air. After adsorption in the dark for around 1 h, UV irradiation of the photocatalyst films in contact with the water/alcohol-saturated air atmosphere was performed using an 80 W mercury vapour lamp (OSRAM HQL de luxe MBF-U). The light was filtered by passing through a Pyrex vessel containing a 0.1 M CuSO_4 aqueous solution. Time-resolved FTIR spectra in the 4000–900 cm^{-1} wavenumber range, with a resolution of 4 cm^{-1} , were recorded along with the adsorption and irradiation steps at room temperature. Each spectrum was obtained by averaging 10 scans accumulated in 4 s. Happ–Genzel apodization function was applied. The spectra were referenced against the spectrum of the dried TiO_2 thin film.

2.3. Photoreactivity Set Up and Procedure

2.3.1. Photocatalytic Oxidation of Aromatic Alcohols in Batch Reactor

The photoreactivity runs concerning the oxidation of 4-methoxybenzyl alcohol (MBA), benzyl alcohol (BA), 4-methylbenzyl alcohol (MeBA) and 4-nitrobenzyl alcohol (NBA) have been carried out in a cylindrical Pyrex batch photoreactor with immersed lamp, containing 0.5 L of aqueous suspension. All these alcohols were purchased from Sigma-Aldrich with a purity of > 99%. Figure 2.1 shows the photoreactor set up. The photoreactor was provided with ports in its upper section for the inlet and outlet of oxygen and for sampling. A magnetic

stirrer guaranteed a satisfactory suspension of the photocatalyst and the homogeneity of the reacting mixture. A 125 W medium pressure Hg lamp (Helios Italquartz, Italy), axially positioned within the photoreactor, was cooled by water circulating through a Pyrex thimble; the temperature of the suspension was about 300 K. The radiation energy impinging on the suspension had an average value of 10 mW/cm^2 . It was measured at 360 nm by using a radiometer UVX Digital.

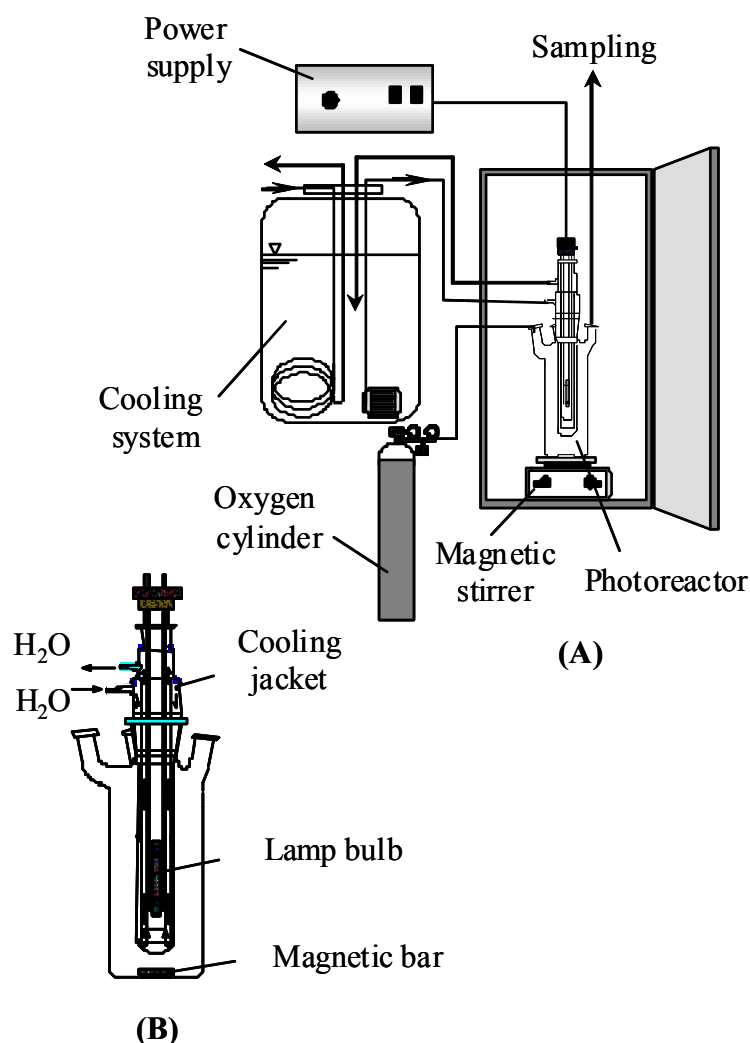


Figure 2.1. (A) Set up of experimental apparatus and (B) photoreactor

The medium-pressure Hg lamp emits mainly at 365 nm even if radiations at 310 nm are also generated (see Fig. 1.2b). The emission at wavelengths lower than 300 nm is cut off by the Pyrex wall of the cooling jacket, whereas radiations

at wavelengths higher than 385 nm are not effective for the activation of the photocatalyst.

The initial concentration used for MBA, BA, MeBA and NBA was 1 mM. As to concern the amount of catalyst contained in the suspension, since the surface area and the agglomerate size of the various photocatalysts were different, it was chosen to carry out the photoreactivity runs at equal irradiation conditions of the suspension, i.e. at equal flow of photons absorbed by the suspensions. For each catalyst the amount chosen for the photocatalytic runs was that for which the resulting suspension was able to absorb 90% of the impinging radiation. This choice also guaranteed that all the catalyst particles were irradiated. Measurements of the transmitted light in the presence of the suspension were carried out by using the radiometer above described. An amount of 0.2 g/L was used for HP1/20, HP1/75 and HP1/100 samples, 0.6 g/L for HP1/35 and HP1/50 samples, while an amount of 0.4 g/L was required for HP298, HP333, HP673, HP973 and commercial TiO₂ samples: Sigma Aldrich (SA), Merck and Degussa (P25). A selected run of MBA photo-oxidation was carried out by using 0.2 g/L of HP1/50. NaOH (Merck) 1M solution was used to adjust the initial pH to 7. Adsorption of the alcohols under dark conditions was always quite low, i.e. less than 5%.

Before switching on the lamp, oxygen was bubbled into the suspension for 30 min. at room temperature to reach the thermodynamic equilibrium.

During the runs samples of reacting suspension were withdrawn at fixed time intervals; they were immediately filtered through a 0.45 µm hydrophilic membrane (HA, Millipore) before being analysed.

2.3.2. Photoadsorption Determination in Batch Reactor

The standardized procedure of the runs was the following one and it was strictly observed; the procedure stages are depicted in Figure 2.2 the photoreactor without the immersed lamp was filled with a fixed volume of substrate aqueous solution of known concentration and pure oxygen (or air for a few runs) was bubbled for 30 minutes under magnetic stirring (bubbling and

stirring were never interrupted in the course of runs); then the desired amount of catalyst was added and samples (5 cm^3) of the suspension were taken at fixed intervals of time until the dark equilibrium conditions were reached (about 30 minutes after catalyst addition). At that time the lamp outside the photoreactor was switched on and time was allowed for reaching steady state conditions of irradiation (about 5 minutes). Once the irradiation did not change, as checked by the radiometer, the lamp was fast immersed into the suspension and that time was taken as the zero time of the photoreactivity run; samples (5 cm^3) for analysis were withdrawn by means of a syringe every 15 minutes in the first 2 hours of the run and then every 0.5 or 1 hour. The samples were immediately filtered by a $0.45\text{ }\mu\text{m}$ hydrophilic membrane on the exit hole of the sampling syringe.

The BA and phenol (Sigma-Aldrich) initial concentrations varied in the 0.5-5.0 and 0.25-4.0 mM ranges, respectively, and the catalyst amounts were in the $0.05\text{-}0.8\text{ g}\cdot\text{L}^{-1}$ range.

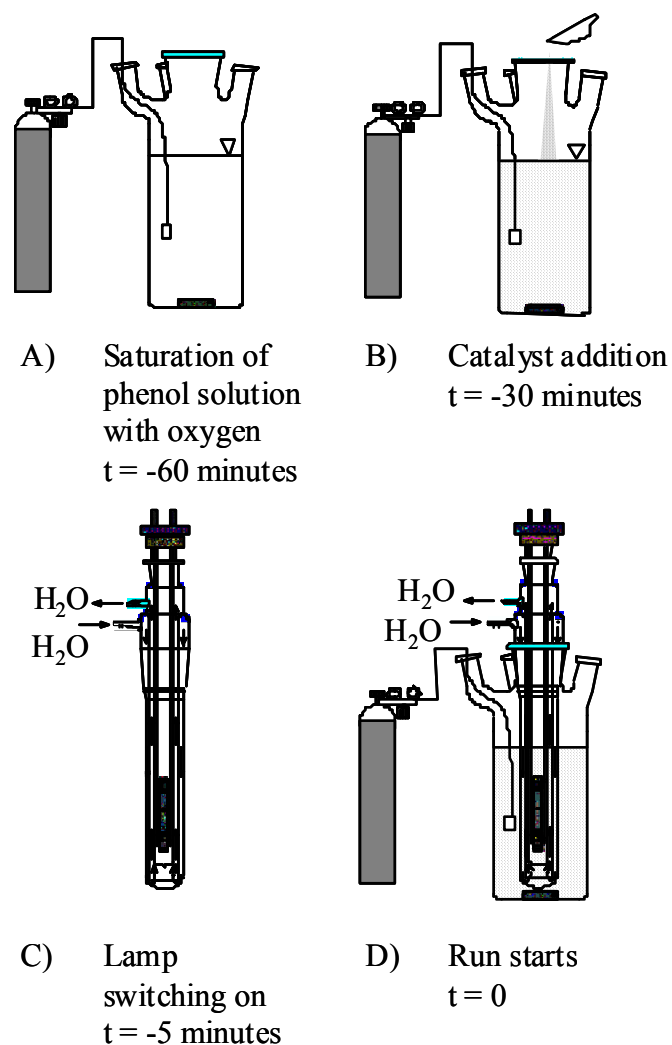


Figure 2.2. Experimental run procedure from A to D for photoadsorption determination

2.3.3. Photocatalytic Oxidation of 4-Methoxybenzyl Alcohol in a Continuous Annular Fixed Bed Photoreactor

A continuous annular Pyrex photoreactor (outer diameter of inner tube, 72 mm; annulus gap, 7 mm) was used for photocatalytic oxidation of MBA. The inner part of the annulus contained a fixed bed (bed height, 186 mm) of the Pyrex beads covered by the catalyst. The void fraction of fixed bed was 0.29; it was determined and checked different times by measuring the volume of distilled water needed for filling the dry bed for its total height. Figure 2.3. shows the scheme of the photoreactor. A reservoir of 10 L was used to feed the photoreactor through a peristaltic pump which allowed to vary the liquid flow rate in the 0.810-

$3.75 \text{ cm}^3 \cdot \text{s}^{-1}$ range. A 500, 700 or 1000 W medium pressure Hg lamp (Helios Italquartz, Italy) was axially positioned inside the reactor; it was cooled by water circulating through a Pyrex thimble. The radiation energy of lamps was measured by using a radiometer UVX Digital, at $\lambda = 360 \text{ nm}$. The measurements of energy incident on the fixed bed were carried out by positioning the radiometer at the outer surface of the annulus with the photoreactor containing only an aqueous solution of MBA; the figures corresponding to the three used lamps are reported in Fig. 2.4. The same procedure was used for measuring the values of radiation energy transmitted by the photoreactor when it contained HP1 or HP2 beads; Figure 2.4. also reports these values for the used lamps. By considering that the annular bed is irradiated from the inner part, the knowledge of incident and transmitted photon flows allows one to calculate the absorbed photon flow from a macroscopic photon balance. With HP2 beads and the 500 W lamp, the bed transmittance was about 2%, indicating that in the less favourable irradiation conditions all of the bed is active for the photoreaction occurrence as the amount of catalyst deposited on all the bed is not able to absorb all the impinging photons. The HP3 bed (data not reported) did not transmit any radiation even with 1000 W lamp, i.e. all the photons were absorbed by the reactor. This finding indicated that the bed was partially irradiated and, consequently, it was decided to investigate only with HP1 and HP2 beds, the optimum catalyst amount being that of HP2.

The experimental runs were carried out in the following way. Before starting the feeding of photoreactor the reservoir solution was saturated with oxygen by bubbling pure oxygen or artificial air (20% oxygen, 80% nitrogen) for 0.5 h. The oxygenated solution was fed to the photoreactor until the outlet MBA concentration values did not change, then the lamp was switched on and samples were withdrawn at fixed intervals of time. The photoreactor reached steady state conditions in ca. 10 minutes. The run was stopped when three consecutive sample analyses gave MBA concentration values differing less than 2% of their averaged value; this generally occurred about 40-60 minutes from the starting of irradiation. The inlet substrate concentration of the solution fed to the photoreactor was varied in the 0.125-5.00 mM range. The pH of the solution was the natural one, i.e. ca. 7. A photoreactivity run was carried out by feeding the reactor with an aqueous

solution of MBAD (1 mM at pH 7, in the presence of 500 W lamp) in order to check the reactivity of this molecule in the used photocatalytic system.

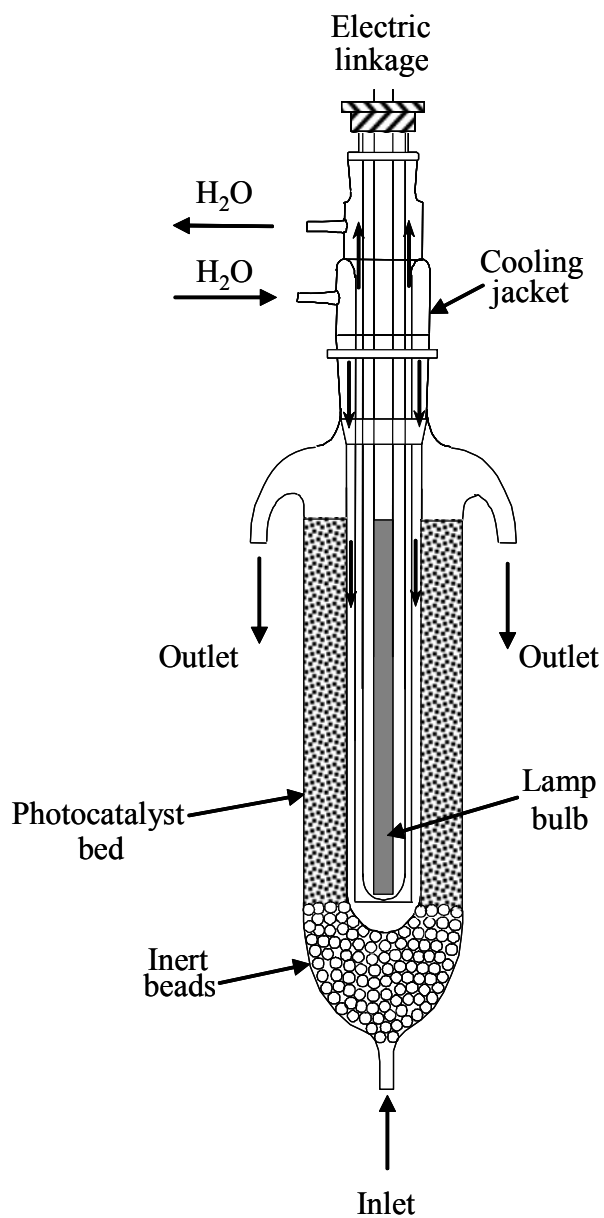


Figure 2.3. Scheme of the continuous fixed bed photoreactor

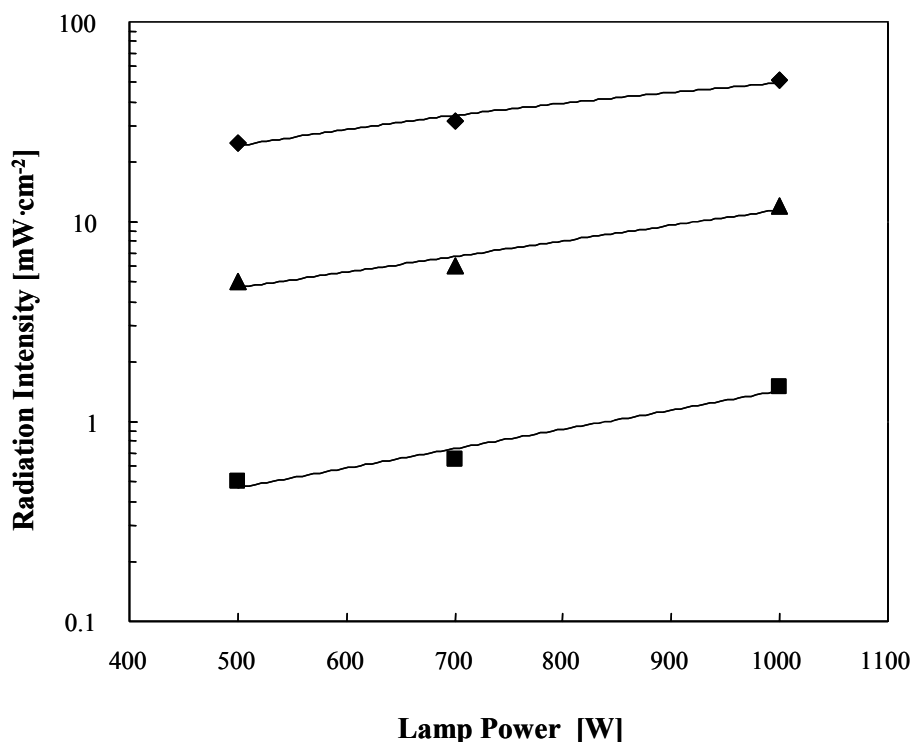


Figure 2.4. Light energy incident on the fixed bed (♦) and transmitted by HP1 (▲) and HP2 (■)

2.4. Analytical Techniques

The quantitative determination and identification of the aromatic alcohols and their derivatives were performed by means of a Beckman Coulter HPLC (System Gold 126 Solvent Module and 168 Diode Array Detector), equipped with a Luna 5 μ Phenyl-Hexyl column (250 mm long $\times$ 2 mm i.d.). The standards of 4-substitute benzyl alcohols, 4-substitute benzaldehydes, hydroxyl benzyl alcohols and acids were purchased from Sigma-Aldrich with a purity of >99%. Retention times and UV spectra of the compounds were compared with those of standards. The eluent consisted of: 17.5% acetonitrile (Fluka, >99.9 %), 17.5% methanol (J. T. Baker, >99.8 %), 65% 40 mM KH₂PO₄ (Sigma, >99.0 %) aqueous solution.

Total organic carbon (TOC) analyses were carried out by using a 5000A Shimadzu TOC analyser; for each sample, six analyses were performed; the mean value was calculated after rejecting the highest and the lowest ones. Since no volatile organic compounds are formed in the MBA oxidation process, these analyses aimed to determine the amount of organic carbon mineralized to CO₂.

Aliphatic alcohol concentration was measured by using a gas chromatograph (GC-17A, Shimadzu) equipped with a methyl siloxane column (30 m $\times$ 320 μ m $\times$ 0.25 μ m, HP-1, Hewlett-Packard) and a flame ionization detector using He as carrier gas. For the methanol analysis a fixed quantity of liquid sample was injected into a gas-tight glass tube through a syringe, kept at constant temperature of 293 K for 20 min. Upon reaching thermodynamic equilibrium, a 500 μ L sample of the headspace vapour was injected in the gas chromatograph. A multi-point calibration curve allowed to calculate the liquid phase concentrations.

Gas chromatography-mass spectrometry (GC-MS) analyses were performed by means of a GC-MS Perkin/Elmer Turbomass and an Autosystem XL chromatograph; a SGE BPX5 (25 m $\times$ 0.22 mm i.d.) capillary column was used. The injected solution was prepared by following the following procedure: 100 mL of the suspension sample were filtered and extraction was carried out by means of 20 mL diethyl ether (Riedel-de Haen > 99.5%); afterwards the organic phase was concentrated 20 times.

^1H -, ^{13}C - NMR (Nuclear magnetic resonance) spectra were obtained by using a Bruker DPX FT NMR (500 MHz) spectrometer. The spectrometer was equipped with a 5 mm PABBO BB-inverse gradient probe. CDCl_3 (Sigma-Aldrich, >99.0 %) was used as solvent. Standard Bruker pulse programs (Bruker program 1D WIN-NMR, release 6.0) was used throughout the experiments.

A long-lasting photocatalytic run was performed in order to characterize the aldehyde produced by MBA partial oxidation. For this run 500 mL of 10 mM MBA solution and 0.6 g/L of HP1/50 catalyst were used; the run lasted 12 h and a 75% conversion of MBA was reached. At the end of the run the whole suspension was filtered by using a paper filter (Whatman) and the catalyst was separated. Then the organic products present in the aqueous phase were extracted with CHCl_3 and concentrated by the rotary evaporator apparatus. MBAD was separated by column chromatography by using a silica support (Silicagel 60, Merck) and a mixture of hexane and ethyl acetate (8:1 v/v) as the mobile phase.

3. RESULTS AND DISCUSSIONS

3.1. Photocatalytic Oxidation of Benzyl Alcohol and 4-Methoxybenzyl Alcohol in Aqueous Suspension of Rutile TiO₂ Prepared at Different Temperatures: Effect of TiO₂ Treatment Temperature to Aldehyde Selectivity

The first part of this Thesis work has been devoted to investigate the influence of treatment temperature of HP rutile TiO₂ catalysts on their ability to perform the partial oxidation of aromatic alcohols to corresponding aldehydes. To reach this goal, the photoreactivity runs have been carried out in batch reactor by using the HP TiO₂ samples at moderate and high temperatures for the oxidation of BA and MBA compounds. For comparison purposes also commercial TiO₂ samples, consisting of rutile (SA), anatase (Merck) or mixtures of the two phases (Degussa P25) were employed.

3.1.1. Photocatalyst Characterization

As previously reported, the HP rutile TiO₂ samples were synthesized by hydrolyzing TiCl₄ at room temperature and by treating the resulting solids at different temperatures, up to 973 K.

Figure 3.1 shows the XRD patterns of all the catalysts, both HP and commercial ones. The patterns of HP298, prepared at room temperature, do not show any crystallinity peaks, probably due to the very small size of particles and to a substantial amorphousness of this sample. HP333, prepared by simply keeping the TiCl₄ sol at 333 K for two days, is made of a badly crystallized rutile phase. Upon calcining HP333, crystallinity increased with the treatment temperature and HP973 diffractogram looks quite similar to that of SA rutile.

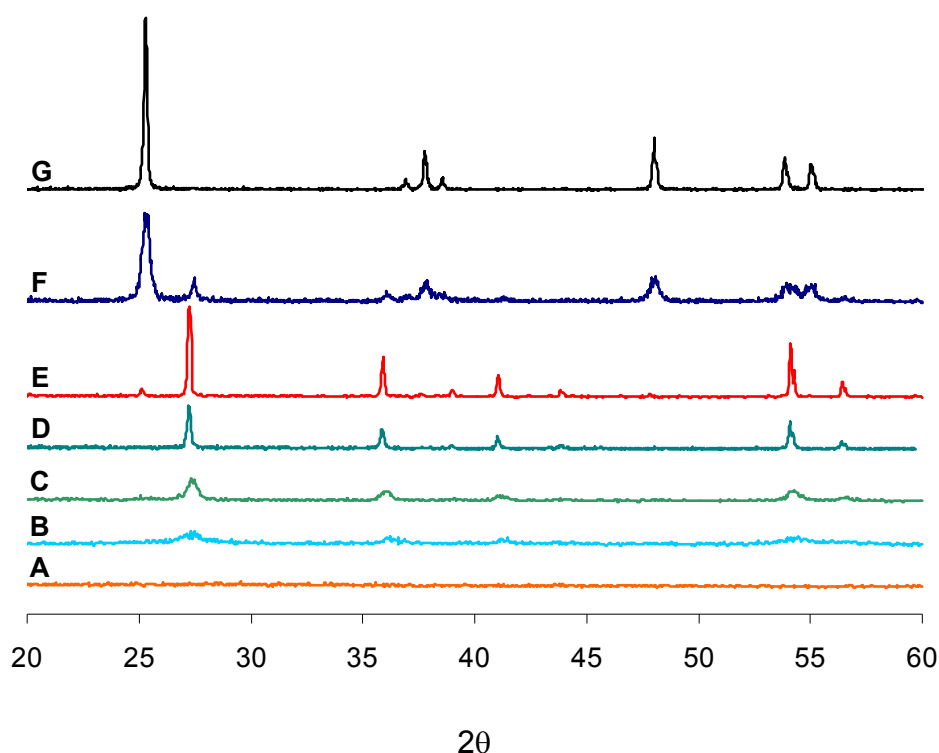


Figure 3.1. XRD patterns of HP and commercial TiO_2 . A) HP298; B) HP333; C) HP673; D) HP973; E) Sigma-Aldrich; F) Degussa P25; G) Merck

Specific surface area (SSA), crystallite and particle agglomerate size strongly change with treatment temperature (see Table 3.1). Values of SSA between 4 and 215 m^2/g were obtained for HP samples, the lowest ones being very close to that of SA sample. Primary crystallite size, determined by using the Scherrer's equation:

$$\tau = K \lambda / \xi \cos \theta \quad (3.1)$$

where τ is the mean crystallite dimension, K is the shape factor, λ is the X-ray wavelength, typically 1.54 Å, β is the line broadening at half the maximum intensity in radians, and θ is the Bragg angle. The dimensionless shape factor has a typical value of about 0.9, shifts from 7 to 41 nm for HP catalysts, whereas commercial samples show sizes ranging from 30 to 60 nm. The highest values were observed for HP973 and for commercial TiO_2 's, i.e. the most crystalline

catalysts. Particle agglomerate sizes, measured by means of SEM images (reported in Fig. 3.2), vary between ca. 50 to 240 nm, increasing with preparation temperature. Specific surface area along with crystallite size depend on the temperature used during the preparation process, drastically decreasing and increasing, respectively, by increasing the temperature.

Table 3.1. Preparation temperature, BET specific surface area, crystallite size and agglomerate size of catalysts and their photocatalytic performance for the oxidation of aromatic alcohols to aldehydes. Catalyst amount: 0.4 g/L

Catalyst	Phase A: anatase R: rutile	SSA [m ² /g]	Crystallite size [nm]	Agglomerate size [nm]
HP298	-	215	—	-
HP333	R	107	7	50
HP333D ^[a]	R	107	7	50
HP673	R	35	13	80
HP973	R	4	41	170
Sigma-Ald.	R	2.5	52	240
Merck	A	10	60	190
Degussa P25	A, R	50	30	80
	t _{irr.} ^[b] BA [h]	Selectivity ^[b] BA [% mol]	t _{irr.} ^[b] MBA [h]	Selectivity ^[b] MBA [% mol]
HP298	22	12.1	—	—
HP333	8.4	38.2	2.36	60.0
HP333D ^[a]	5.3	33.5	2.18	56.2
HP673	6.0	12.2	2.20	50.1
HP973	9.4	9.91	3.81	40.0
Sigma-Ald.	3.8	9.23	2.15	20.9
Merck	2.0	7.94	1.50	15.9
Degussa P25	1.0	7.82	0.72	8.30

[a] HP333D was prepared by dialysing HP333

[b] t_{irr.} (irradiation time) and selectivity (to aldehyde) refer to an alcohol conversion of 50%.
Selectivity = (moles of formed aldehyde)/(moles of converted alcohol)

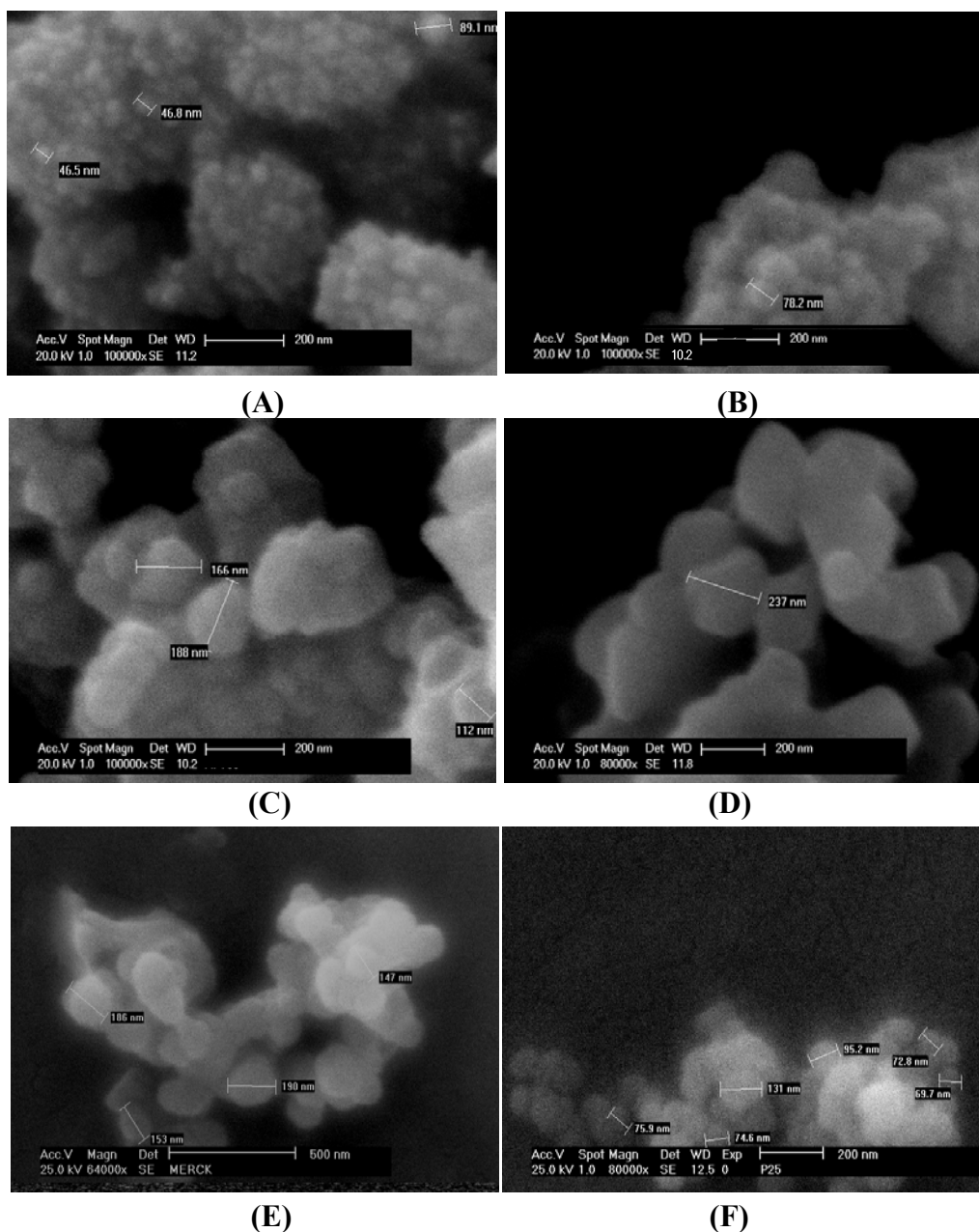


Figure 3.2. SEM micrographs of HP and commercial rutile TiO_2 samples: (A) HP333; (B) HP673; (C) HP973; (D) Sigma-Aldrich; (E) Merck; (F) Degussa P25

3.1.2. Photoreactivity Experiments

Preliminary runs indicated that no conversion of BA and MBA was observed in the dark, both in the absence and in the presence of catalyst, even by continuously bubbling oxygen. Reactivity runs of BA and MBA oxidation were carried out in irradiated aqueous solutions without catalyst under experimental

conditions similar to those used during the heterogeneous experiments. BA and MBA conversion of 50% needed reaction times of 176 and 21 h, respectively. As the 50% conversion was reached in much lower times in photocatalytic runs, it may be assumed that the homogeneous oxidation process plays a negligible role in the heterogeneous systems.

Photocatalytic oxidation runs were carried out with HP333 amounts in the 0.2-0.6 g/L range in order to determine the catalyst amount able of maximizing the selectivity towards aldehyde (calculated as the ratio between the formed aldehyde and the converted alcohol). This study showed that the selectivities are indeed very close each other independently of catalyst amount. Reaction rate values are quite different; they increase for catalyst amount from 0.2 to 0.4 g/L and remain constant for higher amounts of catalyst thus indicating that for those amounts all the emitted photons are absorbed by the suspension. 0.4 g/L of catalyst is also optimum selective and reactivity amount of HP333. Consequently the catalyst amount used in all the BA and MBA oxidation runs was 0.4 g/L. On the grounds of the above reported data, this quantity also determined the lowest irradiation time needed to reach 50% alcohol conversion. All the subsequent runs were performed with this amount of TiO_2 so that the comparison of the reactivity results obtained with HP333 with those of other catalysts has been carried out at equal mass of catalyst in the suspension. It should be underlined that the irradiated surface of the used samples is in some cases very different. Selectivity however was not significantly influenced in any case by the amount of solid present in the reacting medium. For a catalyst amount as low as 0.02 g/L the selectivity was almost the same of that obtained with the other HP catalysts.

In the course of BA and MBA photocatalytic oxidation, CO_2 and the main products formed were determined through TOC and HPLC analysis, respectively. For HP333 the predominant products were the corresponding aldehydes and CO_2 , the other products being present only as traces. On the contrary, when commercial or calcined (HP673 and HP973) catalysts were used, CO_2 and the corresponding aromatic aldehydes together with a lot of other products, such as mono- and di-hydroxylated aldehydes, were detected. During BA oxidation traces of benzoic acid were also found no matter what the used catalyst was.

Figures 3.3 and 3.4 show the trends of reagent and main products (aldehyde and CO₂) during the photocatalytic oxidation of BA and MBA carried out with the commercial SA rutile and with the best performing HP rutile (HP333).

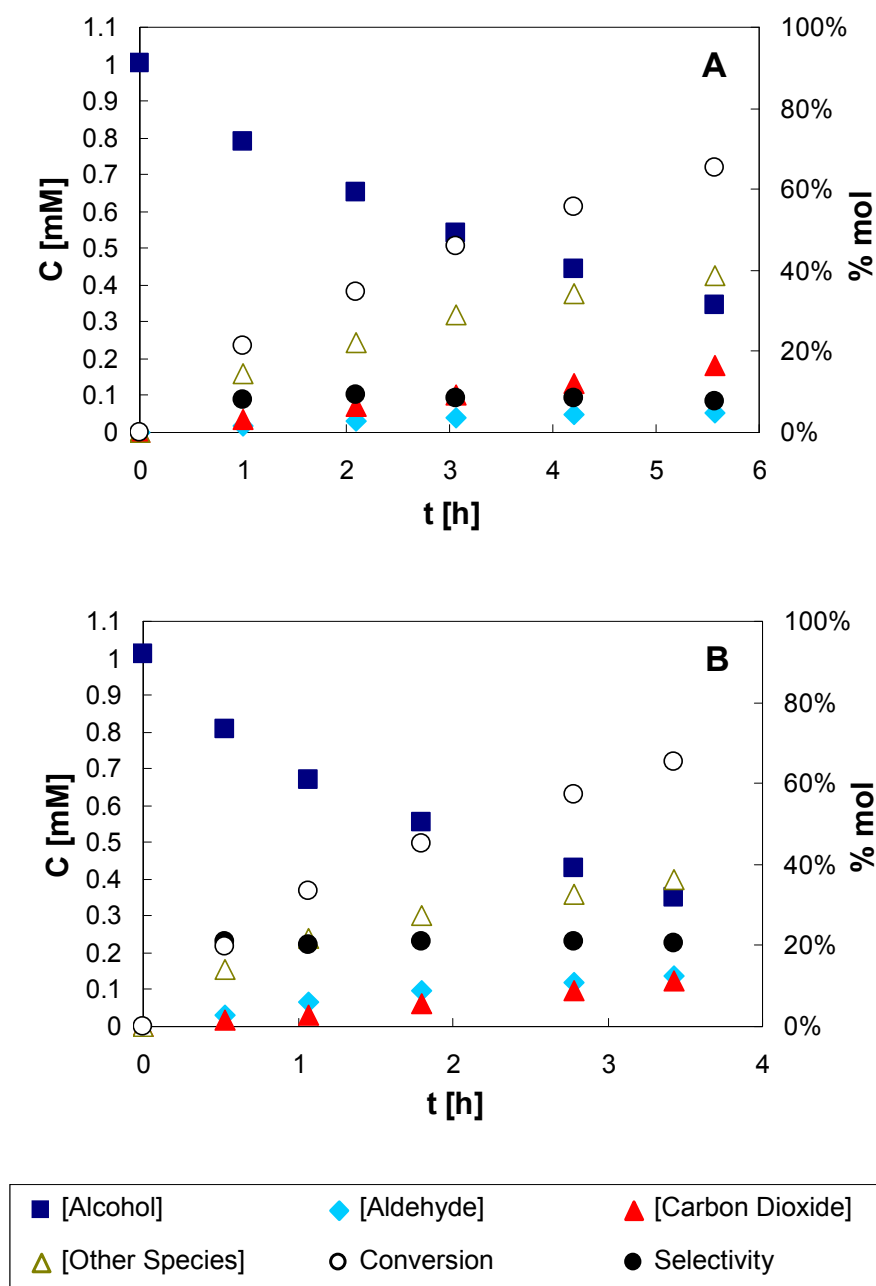


Figure 3.3. Experimental results of a representative oxidation run of BA (A) and MBA (B) with TiO₂ rutile Sigma-Aldrich. Conversion and selectivity are scaled on right side. The CO₂ concentration values were divided by 7 (A) or 8 (B) for normalization purposes

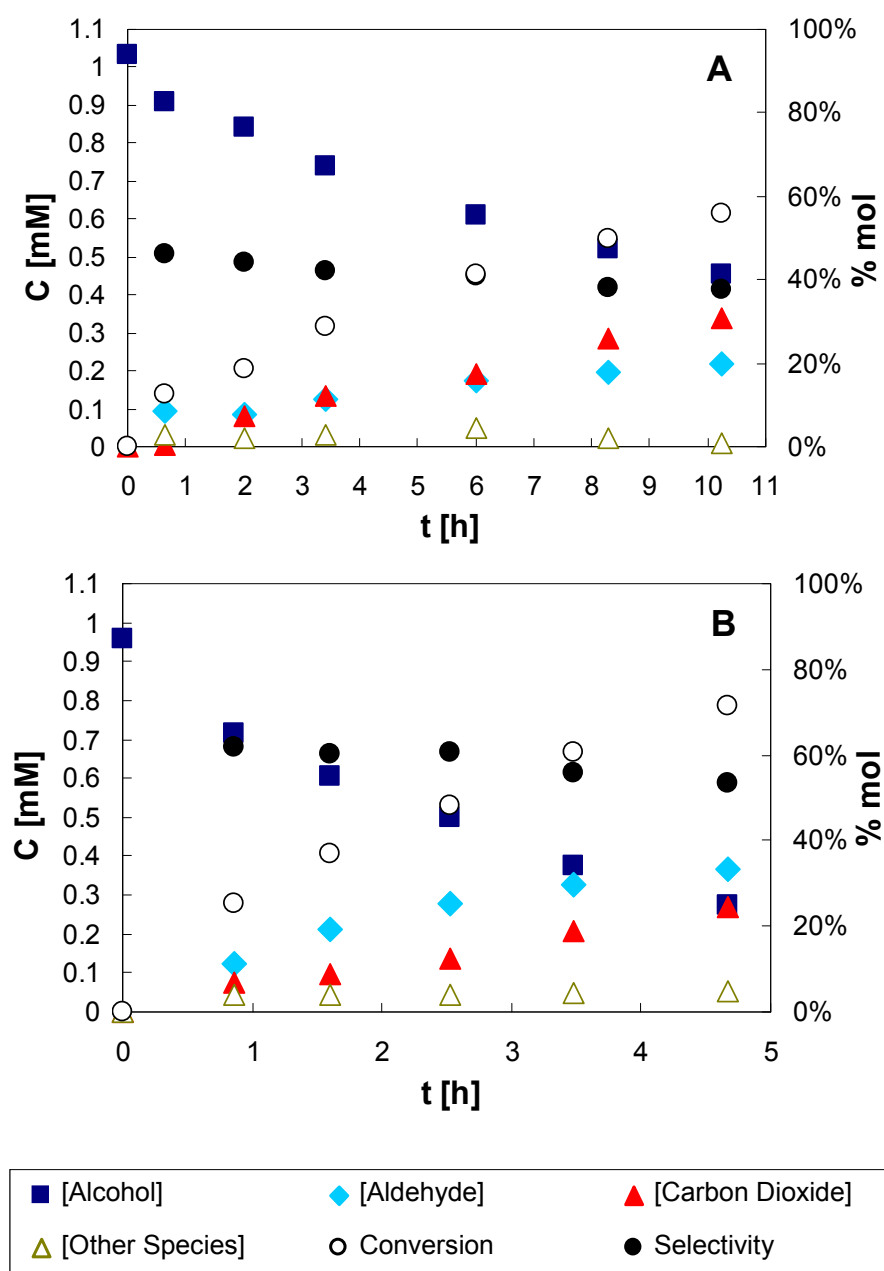


Figure 3.4. Experimental results of a representative oxidation run of BA (A) and MBA (B) with TiO_2 rutile HP333. Conversion and selectivity are scaled on right side. The CO_2 concentration values were divided by 7 (A) or 8 (B) for normalization purposes

The total amount of the organic carbon belonging to identified (but not separately quantified) and unidentified (mainly open-ring products) compounds is also reported. The corresponding values reported in Figure 3.3 and 3.4 were evaluated from the difference between initial TOC and the sum of residual alcohol,

produced aldehyde and CO_2 (quantified from the extent of mineralization, measured by TOC). Figure 3.3 and 3.4 also show conversion and selectivity values *versus* irradiation time. It can be highlighted how selectivity slowly decreases during reaction time.

From the data reported in Figs. 3.3 and 3.4 it may be noted that from the start of irradiation two parallel reaction pathways take place: direct mineralization to CO_2 (occurring through a series of reactions taking place over the catalyst surface and producing intermediates not desorbing to the bulk of solution) and partial oxidation to aldehyde. The importance of each of these pathways depends on the physico-chemical and structural properties of catalyst, but also on the features of the reacting alcohols and produced aldehydes.

The commercial SA, Merck and Degussa P25 samples produced a significant amount of species different from aldehyde and carbon dioxide (Figure 3.3), whereas HP333 did not determine the production of other species (Figure 3.4). This different behaviour can be ascribed to the considerable presence of hydroxylated aromatics and open-ring products (visible in HPLC chromatograms at very low retention times) which appear only when commercial and calcined samples were used.

For the HP rutile and commercial samples, Table 3.1 reports the irradiation time and selectivity values determined for 50 % conversion of BA and MBA. The activity of the HP rutile samples was always much lower than that of commercial catalysts. HP333 needed 8.4 h to reach 50% BA conversion, against 3.8, 2.0 and 1.0 for SA, Merck and Degussa P25, respectively. Interestingly, an increase in crystallinity, obtained by means of thermal treatment, resulted in selectivities further lower than HP333 one.

The most selective rutile sample was HP333 (Table 3.1), and the selectivity values drastically decreased from 38.2 to 9.9% mol (for BA) by increasing the treatment temperature to which this catalyst was subjected. Commercial TiO_2 catalysts gave a selectivity from 4 to 5-fold lower than HP333, the least selective sample being Degussa P25. As far as MBA is concerned, the selectivity decreases from 60% mol for HP333 to 8.3% mol for Degussa P25.

The above reported selectivity clearly shows an opposite trend with respect to catalyst activity, if comparing HP333 with commercial samples. The most active ones (commercial samples), indeed, are also the less selective in the formation of aldehyde. On the other hand, by comparing HP samples, it can be inferred that the increasing of the treatment temperature determines a decreasing of selectivity. The last phenomenon can be ascribed to a drastic depletion of the surface hydroxylation of HP673 and HP973.

HP333 powder was subjected to a dialysis treatment in order to study the influence of chloride ions on selectivity. The samples obtained from TiCl_4 , indeed, can contain not negligible residuals of Cl^- . The results attained with HP333D (the dialyzed sample) highlighted only a small decrease in selectivity (from 38.2 to 33.5% for BA), while a significant increase in activity was evidenced: irradiation time needed to convert 50% of the initial alcohol decreased from 8.4 to 5.3 h. This finding, pointing to a higher mineralization when using the dialyzed sample, can be explained with the well known detrimental effect of Cl^- ions on photocatalytic activity, caused by their good properties of hole-traps (Minero et al. 2000).

Finally the run carried out with the catalyst synthesised at 298 K, by simply adding a NaOH solution to TiCl_4 clear solution, gave worse results than those related to HP333, in terms of both activity and selectivity. The former feature can be due to the absence of crystallinity highlighted by XRD (Figure 3.1). The reaction time needed to reach a 50% conversion was however 22 h, a much lower figure than that found during homogenous reaction (176 h). In any case the catalyst was found active, and this insight could be explained by two different factors: i) the presence of small amounts of crystallites, not detectable through XRD; ii) the occurrence of a photoreaction in adsorbed phase. On the other hand, selectivity was considerably lower than that of HP333, highlighting that lower activity not always results in higher selectivity.

3.1.3. Mechanistic Aspects

The obtained results clearly indicate that while low-temperature HP333 rutile gave rise only to aldehyde and CO_2 in the course of BA and MBA oxidation,

the commercial catalysts and the calcined rutile ones yielded a very unselective reaction, with the formation of hydroxylated aldehydes and open-ring products, besides aldehyde and CO₂.

The results of the oxidation of alcohol to aldehyde in terms of selectivity are surprisingly high (up to 60% for MBA), since the highest value previously reported for MBA was 41%, and it was found by using a HP anatase catalyst (Palmisano et al. 2007b). It should be considered that the reaction takes place in water, without any organic co-solvent. In these conditions, the solvent represents a highly unselective medium, where hydroxyl radicals behaviour is equally unselective. The features of the synthesized catalysts allow, instead, to reach high selectivities even in this environment.

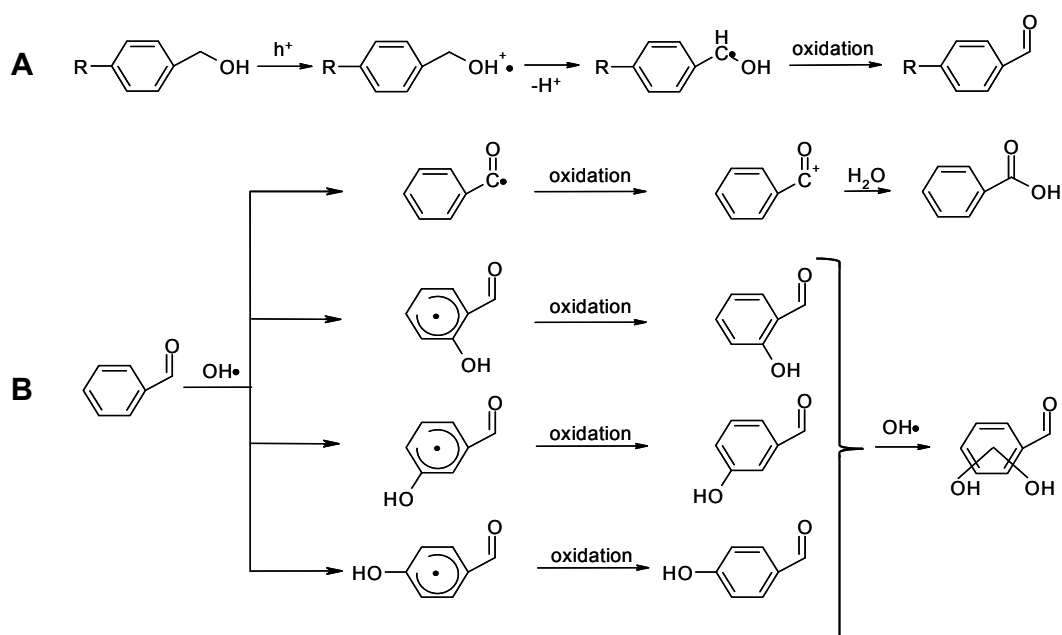
Table 3.1 shows that an increase in crystallinity determines a significant decrease in selectivity, except for the amorphous HP298. This insight could be ascribed not only to the different crystallinity, but also to a drastic reduction of surface hydroxyls and hence hydrophilicity of samples, occurring upon calcination. A FTIR investigation (see section 3.4.4) shows that this feature determines a higher difficulty of the produced aldehyde to desorb from the catalyst surface to the bulk of solution, thus undergoing further oxidation.

Upon using highly crystalline samples, GC-MS analyses have highlighted the presence of the three isomers of hydroxy-benzaldehyde, but no presence of hydroxyl benzyl alcohol was observed. The latter insight should be caused by the easier transformation of an aromatic alcohol into aldehyde rather than into hydroxyl benzyl alcohol isomers. Moreover, 2,5-dihydroxy benzaldehyde was also detected, but the presence of other isomers obtained from the entrance of a hydroxyl radical in the ring position activated by the first OH radical, can be also hypothesized, following a previously reported general behaviour (Palmisano et al. 2006 and 2007c). These recent results showed that the attack of an OH radical into an aromatic ring takes place in *ortho*- and *para*-positions when an electron donor group is present; vice versa, in its absence, all the three isomers are formed.

Previously reported results for anatase (Palmisano et al. 2007b) showed that the primary oxidation step of MBA involves in any case either direct mineralization to CO₂ or formation of aldehyde. However no hydroxylated 4-

methoxybenzaldehyde isomers were detected. These species were detected in trace amounts even when using commercial and highly crystalline HP samples.

Scheme 3.1 reports the hypothesized mechanism for the two alcohols. Both BA and MBA can either undergo directly mineralization to CO₂ (not shown) through adsorbed intermediates (Palmisano et al. 2007b), or be partially oxidized to other aromatic and eventually aliphatic compounds.



Scheme 3.1. Proposed reaction schemes (it should be considered that all the aromatic compounds reported in the scheme can undergo direct mineralization to CO₂). R = H, OCH₃.

The first step (A) for partial oxidation of both BA and MBA to corresponding aldehyde is the abstraction of an electron from OH group by a hole (abstraction from aromatic ring is indeed much more difficult). Once this (likely slow) step has taken place, the subsequent transformations involve the formation of $-CHO$ group, by means of either hole or OH radical. Moreover it is worth noting that O_2^- could play a role producing oxidant species (for instance HO_2 radicals) by reacting with H_2O .

BAD, once formed, can be subjected to a further attack of OH radical on the aromatic ring (B). This is the rate determining step for the production of hydroxylated aromatics through the elimination of a hydrogen by means of either

hole or OH radical. All the mono-hydroxylated isomers are obtained because an electron withdrawing group ($-\text{CHO}$) is present (Palmisano et al. 2006 and 2007c). Analogously the second hydroxylation can take place in the position activated by the first $-\text{OH}$ group.

A different fate of benzaldehyde (BAD) can be the oxidation to benzoic acid, by means of hydrogen abstraction from the aldehydic carbon, with formation of an acyl radical (B). The two following possibilities could be: (i) an electron transfer to acyl cation followed by the attack of a water molecule as depicted in the Scheme 3.1 or (ii) a cross-dimerisation with an OH radical. Considering that the concentration of these two different radicals should be rather low, we have preferred the first hypothesis.

On the contrary, MBAD, once formed, is subjected only to direct mineralization, since neither hydroxylated species nor acid were formed in detectable amounts, when using low-temperature prepared catalysts.

The presence of hydroxylated aldehydes (B), detected only for BA and with the most crystalline catalysts, suggests that the higher oxidising power of these samples can allow the hydroxylation reaction, decreasing the selectivity towards aldehyde. So the mild oxidising power of HP333 gives rise to a high selectivity, due to a higher difficulty of hydroxylating the obtained aldehyde or directly breaking the aromatic ring.

From the data of Table 3.1 it may be noted that the selectivity towards aldehyde, reaction rate and chemical nature of intermediates are very different for BA and MBA. This could be ascribed to the presence of an electron donor group in *para*-position, such as methoxy. The significantly higher reaction rate of MBA can be ascribed to a much easier abstraction of hydrogen by hole due to the presence of a methoxy group, since it increases the delocalization on the ring. This donor group could be effective as hole trap because includes an oxygen atom and can stabilise the aromatic ring, thus increasing the selectivity towards aldehyde. Regarding this transformation, it is worth noting that literature reports that gas phase as well as solution electron transfers occur from the oxygen of the benzylic alcohol and this transfer is easier in the case of MBA compared with BA (McEvoy and Grätzel 1994).

The presence of some amounts of benzoic acid on one hand, and the absence of 4-methoxybenzoic acid (for conversion < 80%) on the other hand, suggest that electron donor groups inhibit the formation of aromatic acid, as previously reported (Bacocchi et al. 2002).

The different amount of the produced CO₂ from BA and MBA could be also attributed to the very different solubility of BAD and 4-methoxybenzaldehyde (MBAD) in water (100 vs. 4290 mg/L at 293K, respectively). Desorption of BAD from the catalyst surface after its formation can be hence prevented by its hydrophobic character, so that either a subsequent hydroxylation or mineralization to CO₂ could be favoured.

3.2. Photocatalytic Oxidation of 4-Substituted Aromatic Alcohols in Aqueous Suspension of Rutile TiO₂ Prepared at Room Temperature

The investigation carried out with rutile TiO₂ prepared at different temperatures (see Section 3.1) clearly indicated that: (i) amorphous catalyst (HP298) shows very poor reactivity and selectivity; (ii) a certain degree of crystallinity is needed for improving reactivity and selectivity; and (iii) an increase of treatment temperature is detrimental for selectivity. On this ground it was decided to test rutile catalysts prepared at room temperature provided that these catalysts have a well recognizable crystalline structure. Contemporarely it was investigated the influence on reactivity and selectivity of different substituent groups on 4-position of aromatic alcohol.

3.2.1. Photocatalyst Characterization

Both the hydrolysis of TiCl₄ and subsequent condensation steps were carried out at room temperature, producing the photocatalysts with the following stoichiometric reactions:



The preparation experimental conditions (the $\text{TiCl}_4/\text{H}_2\text{O}$ v/v ratio, aging time and time needed for the starting of precipitation) and some physical features (BET surface area, crystallite and agglomerate size) of photocatalysts are summarized in Table 3.2. In agreement with literature (Yin et al. 2002; Yang et al. 2003), in strongly acidic solution, only nuclei of thermodynamically stable rutile phase are formed, even if at a very low precipitation rate. It has been found that the only aging of the sol produces rutile crystals and that a decrease of the $\text{TiCl}_4/\text{H}_2\text{O}$ v/v ratio lowers the time needed for crystal precipitation. For instance a catalyst was prepared with $\text{TiCl}_4/\text{H}_2\text{O}$ ratio of 0.1 for which the crystal precipitation started only after 50 days of aging. This time is not practical for a catalyst preparation so that ratios higher than 0.05 (that of HP1/20) have not been used in the present investigation.

Table 3.2. BET specific surface area (SSA), particle size and crystallite size of the photocatalysts

Catalyst	$\text{TiCl}_4/\text{H}_2\text{O}$ ratio [v/v]	Aging time [day]	Time for precipitation starting [day]	SSA [m^2/g]	Crystallite size [nm]	Agglomerate size [nm]
HP1/20	0.05	9	8	129	5.5	286
HP1/35	0.029	6	3	116	5.6	1050
HP1/50	0.02	6	3	118	6.8	719
HP1/75	0.013	4	2	125	7.1	304
HP1/100	0.01	4	2	135	6.1	244
SA	—	—	—	2.5	52	240

XRD patterns of rutile HP samples and of a commercial one (SA) are reported in Figure 3.5. The peaks assignable to rutile are those at $2\theta = 27.5^\circ$, 36.5° , 41° , 54.1° and 56.5° ; it may be noted that the peaks of commercial rutile are well defined while those of all of the HP samples are broad, indicating that their crystallinity is low.

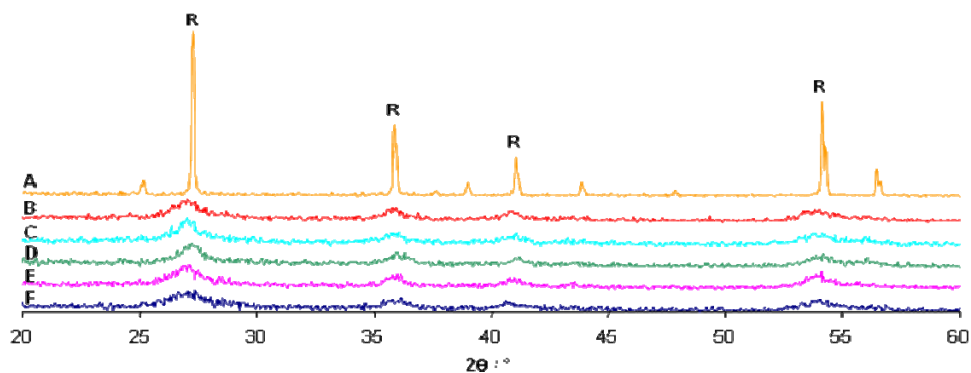


Figure 3.5. XRD patterns of HP and commercial TiO_2 samples; A) SA, B) HP1/100, C) HP1/75, D) HP1/50, E) HP1/35, F) HP1/20. “R”: rutile peaks

Size values of primary crystallites (calculated by Scherrer's equation) resulted quite low (5.5-7.1 nm, see Table 3.2), and very similar to each other. The sizes of the crystallite aggregates were much higher (see Table 3.2), as estimated from SEM observations (reported in Fig. 3.6) and they increased with the increase of the $\text{TiCl}_4/\text{H}_2\text{O}$ ratio, i.e. acidity, and the time needed for the starting of precipitation. The aggregate size values from HP1/35 to HP1/100 decreased, but the situation for HP1/20 was quite different. Due to the high $\text{TiCl}_4/\text{H}_2\text{O}$ ratio, the precipitation started only at the end of 8th day, so that the time allowed for aggregation (1 day) was much lower than those allowed to all the other catalysts. BET specific surface areas of HP samples are significantly higher than that of SA. The former ones increase with the decrease of agglomerate sizes.

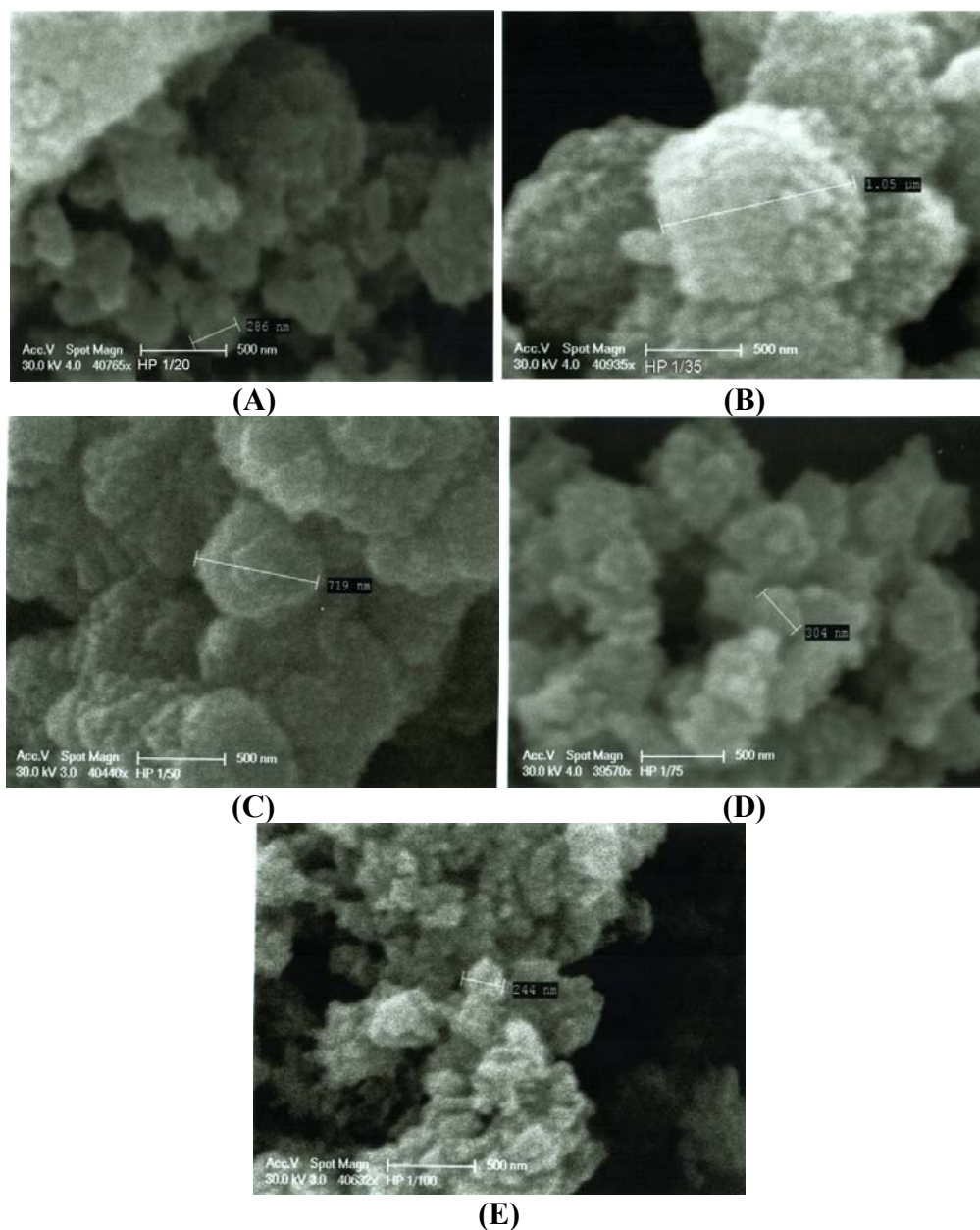


Figure 3.6. SEM micrographs of HP TiO₂ samples: (A) HP1/20; (B) HP1/35; (C) HP1/50; (D) HP1/75; (E) HP1/100

3.2.2. Photoreactivity Experiments

In the initial part of this investigation, the testing of the performance of rutile catalyst prepared at room temperature was carried out by using as “test” reaction the photocatalytic oxidation of MBA; for the sake of comparison also the commercial SA rutile was tested at equal reaction conditions.

No oxidation of MBA was observed in the absence of irradiation and/or catalyst and/or oxygen under the same experimental conditions used for the photoreactivity runs. Irradiation, catalyst and oxygen were all needed for the occurrence of the process.

The photoreactivity experiments confirmed that the MBA oxidation (Palmisano et al. 2007b; Yurdakal et al. 2008) proceeds through two parallel pathways, both effective since the start of irradiation: (i) complete oxidation of MBA to CO_2 and H_2O through intermediates which do not desorb from the catalyst surface; and (ii) partial oxidation of MBA to the corresponding aldehyde, MBAD, which is released to the liquid phase and may compete with MBA for mineralization. Equation 3.4 describes the MBA oxidation process.



Selectivity values depend on the competition between the two pathways; surface physico-chemical and structural properties of the photocatalysts (see Section 3.4) are the most important factors influencing that competition, although other parameters like the structure of the starting aromatic molecule and its initial concentration can not be neglected.

For a representative run carried out by using the HP1/50 sample, Figure 3.7 reports the concentration values of MBA, MBAD and CO_2 versus irradiation time. Carbon balance, overall conversion of MBA and selectivity to aldehyde are also reported. A carbon balance has been performed by summing the MBA and MBAD concentrations to that of CO_2 concentration, by dividing for 8 the value obtained by TOC determination.

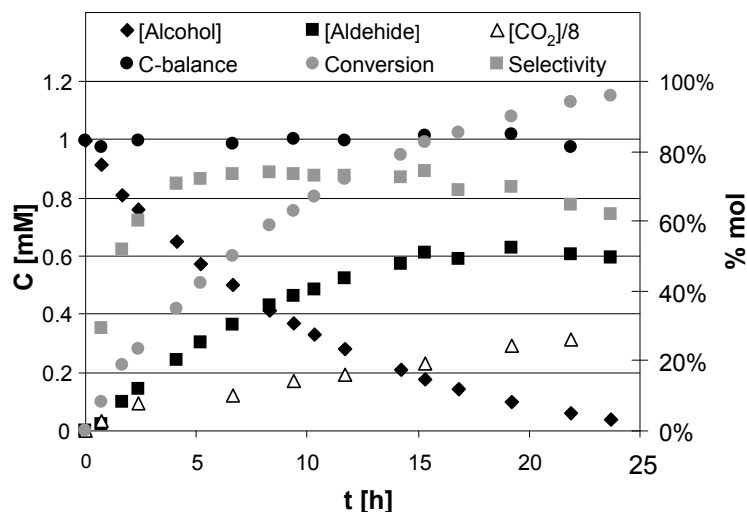


Figure 3.7. Experimental results of photocatalytic oxidation of MBA using the HP1/50 (0.2 g/L) sample. Conversion and selectivity are scaled on the right side. The CO_2 concentration values were divided by 8 for normalization purposes

It is worth noting that the selectivity values plateaued at the highest value in the conversion range of 20-80%. From 0 to 20% conversion, the selectivity increases probably because of the occurrence of transient phenomena on the catalyst surface (Yurdakal et al. 2009a); it must be underlined that the TOC and MBAD quantitative determinations at low MBA conversion may be strongly affected by experimental errors. For conversions higher than 80% the selectivity decreases along with the MBAD concentration in the liquid phase (see Figure 3.7). In this condition the produced aldehyde molecules favourably compete with remaining alcohol molecules for adsorption and (photo)oxidation onto the surface sites. On the basis of this finding the comparison of catalyst performances has been done by determining the selectivity and the time needed for achieving a MBA conversion of 50%.

The photoreactivity results obtained with the HP and commercial (SA) catalysts are summarized in Table 3.3. This Table reports the reaction time needed for 50% MBA conversion, $t_{1/2}$, the corresponding selectivity to MBAD and the carbon balance percentage. It can be noticed that all the HP catalysts result much more selective (ca. 2-4 fold) than SA, but HP1/50 sample showed the highest selectivity (74%) towards MBAD production. To the best of our knowledge this value is the highest one ever reported in the literature for heterogeneous

photocatalytic oxidation of alcohol to aldehyde in water. The HP1/35, HP1/75 and HP1/100 samples showed a similar selectivity, i.e. ca. 60%, while the HP1/20 sample the lowest one, i.e. 45%. The commercial catalyst, SA, which exhibits a selectivity far lower than those of HP samples, however, gives rise to a similar reactivity, i.e. $t_{1/2}$.

Table 3.3. Photocatalysts performance for MBA photo-oxidation to MBAD for 50% conversion

Catalyst	Catalyst amount [g/L]	$t_{1/2}$ [h]	Selectivity [% mol]	C balance [%]^a
HP1/20	0.2	2.3	45	91
HP1/35	0.6	3.6	60	96
HP1/50	0.2	6.65	74	99
HP1/50	0.6	2.6	72	98
HP1/75	0.2	2.95	55	94
HP1/100	0.2	3.3	61	96
SA	0.4	2.15	21	70

^a C balance was obtained as sum of MBA, MBAD and CO₂ concentration.

The carbon balance, verified by taking into account only the unreacted alcohol, the produced aldehyde and CO₂, was quite satisfied by the HP samples of higher selectivity (HP1/35 and HP1/50). It may be noted from the data in Table 3.3 that the failure on carbon balance increases with the decrease of the sample selectivity, the highest one being for the commercial sample (i.e. the one with the lowest selectivity). In the course of the photocatalytic runs, in addition to the main products of MBA oxidation, i.e. aldehyde and CO₂ (see eq 3.4), hydroxylated aromatics, benzoic acids and open-ring products were also found. The amounts of these last products depended on the used photocatalyst; for the most selective HP samples only traces of them were found while for the others HP and the commercial sample the amounts were higher. It is likely that these products arise from the subsequent oxidation of produced aldehyde, being this pathway more relevant for the less selective, and therefore more oxidizing, samples.

By comparing the results obtained from runs carried out with different amounts of HP1/50 (see Table 3.3), it may be noted that the use of lower amount

of photocatalyst (0.2 instead of 0.6 g/L, three times less) gives rise to a small increase of the selectivity while the $t_{1/2}$ increases about three times. By considering that the suspension with 0.2 g of catalyst absorbs about half of the photons absorbed with 0.6 g but that the photons absorbed per unit mass of catalyst increase of about 150%, it can be concluded that the photoprocess is quite insensitive to the irradiation conditions, at least under the used experimental conditions.

In order to check the potentiality of this process as a green synthetic one, produced MBAD and residual MBA were separated, analysed and purified according to the procedure described in Experimental section. MBAD was isolated with a yield of ca. 48%. ^1H -NMR and ^{13}C -NMR analyses (not shown for the sake of brevity) confirmed that the obtained MBAD has a high purity (>99%).

In the last part of this study the effect of different substituent groups on the photoprocess performance was investigated with the aim of checking if the selectivity to the corresponding aldehyde is a feature of the photocatalyst or it is affected by the chemical nature of aromatic alcohol. The most selective sample, HP1/50, and the commercial one, SA, were used to carry out the photo-oxidation of BA, MeBA and NBA. The photoreactivity results obtained with the 4-substituted alcohols are summarized in Table 3.4.

Table 3.4. Results of photocatalytic oxidation of BA, MBA, MeBA, NBA, using HP1/50 (0.6 g/L) and SA samples (0.4 g/L). The selectivity to aldehyde was determined for 50% conversion of alcohol

	MBA		MeBA		BA		NBA	
Catalyst	HP1/50	SA	HP1/50	SA	HP1/50	SA	HP1/50	SA
$t_{1/2}$ [h]	2.6	2.2	4.2	4.2	6.5	3.8	9.8	6.7
Selectivity [mol%]	72	20.9	47	9.5	42	9.2	5.3	3.3
C Balance [mol%]	98	70	96	68	95	66	90	65
k_D [h^{-1}]	0.267	0.266	0.165	0.265	0.107	0.182	0.07	0.073

A thorough investigation of the intermediates produced in the course of photocatalytic degradation was not the aim of this paper. As found with MBA, the

oxidation of MeBA, BA, and NBA mainly produced the corresponding aldehydes and CO₂, this finding suggesting that the mineralization of adsorbed alcohol molecules occurs by means of subsequent oxidative steps producing species which do not desorb from the photocatalyst surface to the solution. Small amounts of hydroxylated derivatives and open ring products were detected for NBA tested with HP1/50; their amounts were much higher when SA was used.

By taking as reference the unsubstituted benzyl alcohol, the data of Table 3.4 indicate that the presence of electron donor groups (-OCH₃ and -CH₃) positively affects the selectivity for both photocatalysts, although the commercial sample (SA) shows in all cases the worst performance. On the contrary the electron withdrawing group (-NO₂) was detrimental and a very scarce selectivity was observed. It can hence be stated that the presence of an electron withdrawing group such as NO₂ favours the reaction pathway leading to the breakage of the aromatic ring with formation of overoxidised species and eventually CO₂. The same behaviour was observed in the hydroxylation of various aromatic species (Palmisano et al. 2006). In that case it has been reported (Augugliaro et al. 2008a; Palmisano et al. 2006; Baciocchi et al. 2002) that the presence of an electron donor group, due to its inductive and delocalization effects, hinders oxidant attacks towards the aromatic ring.

As to concern the degradation rate, the data of Table 3.4 indicate that reaction times needed to achieve 50% conversion of alcohol decrease in the order: BA > MeBA > MBA while time was longer from BA to NBA. This order indicates that the reaction rate is enhanced by electron-donating substituents and retarded by electron-withdrawing substituents. By considering that no correlation was found between reactivity and the water-octanol partition coefficients of aromatic alcohols (or aldehydes), it may be assumed that the electronic properties of substituent groups play a more significant role than the relative solubility in water of reagents and products. On this ground the influence of the substituent group on the rate of partial oxidation of aromatic alcohols can be interpreted in terms of Hammett's relationship (Hammett 1937).

The basic Hammett equation is:

$$\log \left(\frac{k_{1,PO}}{k_{1,PO}^0} \right) = \rho \sigma \quad (3.5)$$

in which $k_{1,PO}$ is the kinetic constant of the partial oxidation reaction of the substituted reactant, $k_{1,PO}^0$ that of the unsubstituted reactant, σ the substituent constant which is related to the electron orientation effect of the specific substituent R and ρ the reaction constant which depends only on the type of reaction but not on the substituent used. The reaction constant, or sensitivity constant, ρ , describes the susceptibility of the reaction to substituents. A plot of $(\log k_{1,PO})$ versus σ for a given reaction with many differently substituted reactants gives a straight line with slope equal to ρ .

In the present case the rates of overall degradation of alcohol and of partial oxidation to aldehyde are well described by a first order kinetics with respect to alcohol concentration:

$$-\frac{dC_{AA}}{dt} = k_D C_{AA} = (k_{Min} + k_{1,PO}) C_{AA} \quad (3.6)$$

$$\frac{dC_{ALD}}{dt} = k_{1,PO} C_{AA} \quad (3.7)$$

in which C_{AA} and C_{ALD} are the concentration of aromatic alcohol and aldehyde, respectively, t the irradiation time, k_D the first order kinetic constant of overall degradation reaction and $k_{1,MIN}$ that of mineralization reaction. Dividing eq 3.7 by eq 3.6 produces:

$$-\frac{dC_{ALD}}{dC_{AA}} = \frac{k_{1,PO}}{k_{Min} + k_{1,PO}} \quad (3.8)$$

Integration of eq 3.8 with the condition that at the start of irradiation, i.e. for $C_{AA} = C_{AA,0}$, $C_{ALD} = 0$ gives:

$$\frac{C_{\text{ALD}}}{C_{\text{AA},0} - C_{\text{AA}}} = \frac{k_{1,\text{PO}}}{k_{\text{Min}} + k_{1,\text{PO}}} \quad (3.9)$$

The left hand side term of eq 3.9 represents the reaction selectivity towards aldehyde, S , and the $(k_{1,\text{MIN}}+k_{1,\text{PO}})$ term is equal to k_{D} . The values of k_{D} may be determined by a best fitting procedure applied to the experimental data of alcohol concentration versus time once integration of eq 3.6 is performed. In this way the $k_{1,\text{PO}}$ values can be calculated as:

$$k_{1,\text{PO}} = S k_{\text{D}} \quad (3.10)$$

Table 3.4 reports the values of k_{D} obtained by a least-squares best fitting procedure applied to all the photoreactivity runs. By using eq 3.10 the values of $k_{1,\text{PO}}$ have been calculated. Figure 3.8 reports in a semilogarithmic plot the values of $k_{1,\text{PO}}$ versus the Hammett constant of each substituent group of the aromatic alcohol for both used catalysts. The solid straight lines through the data represent the Hammett relationship (eq 3.5) best fitted to HP1/50 data ($R^2>0.99$) and SA ones ($R^2>0.94$). The ρ values obtained by the best fitting procedure are -3.32 and -2.75 for HP1/50 and SA, respectively. The very good proportional relationship shown in Figure 3.8 confirms the influence of the electrophilic nature of the substituent on the photocatalytic partial oxidation of aromatic alcohols to aldehydes.

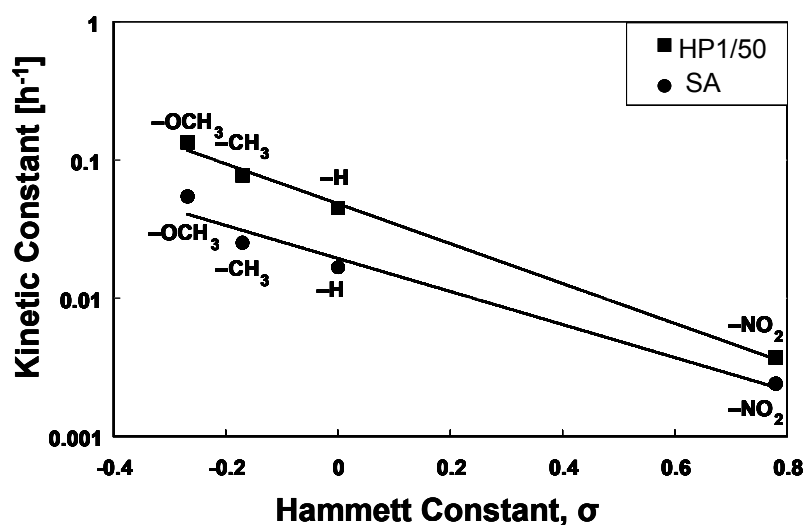


Figure 3.8. Correlation between kinetic constant of partial oxidation reaction, $k_{l,PO}$, and Hammett constant

3.3. Kinetics of 4-Methoxybenzyl Alcohol Oxidation in Aqueous Solution in a Fixed Bed Photocatalytic Reactor

In the present investigation the photocatalytic oxidation of MBA in water was performed in a fixed bed continuous annular reactor by using a HP TiO_2 catalyst supported on Pyrex glass beads. In order to improve the efficiency of the reactor, the catalyst amount supported on the beads was optimised and the influence of light intensity on reactivity was also studied. The aim of the present investigation is to model the kinetics of the photoprocess with emphasis on determining the dependence of MBA oxidation rate on reactants concentration and on absorbed photons. On this ground the influence of liquid flow rate, inlet concentrations of alcohol and oxygen, catalyst amount and irradiation power on the photoreactivity was studied.

3.3.1. Photocatalyst Characterization

The supported catalyst is anatase phase of TiO_2 confirmed by XRD analysis (not shown for the sake of brevity). Figure 3.9 shows a micrograph and an EDAX mapping of HP2 where the TiO_2 layer supported on a glass bead can be easily

distinguished; the thickness of the film was 0.5 μm for HP1, 1 μm for HP2, and 1.6 μm for HP3. The total amount of catalyst present in the fixed bed containing HP1 beads was ca. 60 mg; for HP2 and HP3 beads the catalyst amounts were 125 and 185 mg, respectively. These amounts were determined by measuring the weight decrease of a certain amount of HP1, HP2 or HP3 beads after that the beads were ultrasonicated in water for thirty hours. BET specific surface area of the TiO_2 layer was about $58 \text{ m}^2\cdot\text{g}^{-1}$; it was measured by using the single-point BET method.

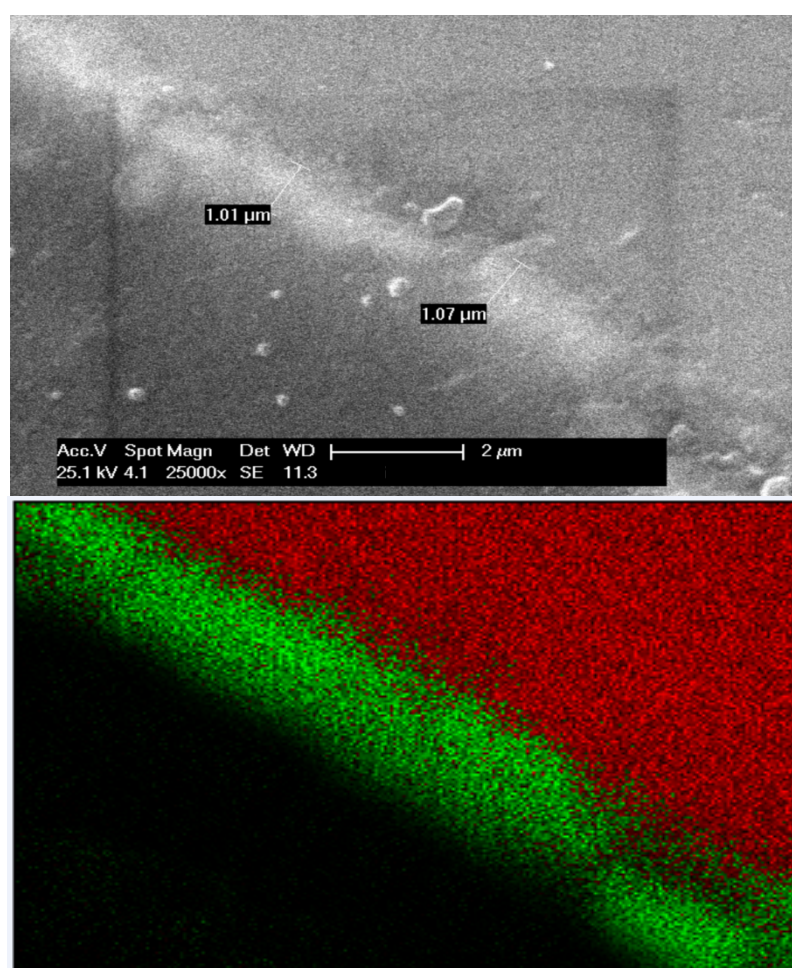


Figure 3.9. Cross-section micrograph (up) and EDAX (down) mapping of a layer of TiO_2 supported on a glass beads

3.3.2. Photoreactivity Experiments

Preliminary runs were carried out in order to determine the influence of the liquid flow rate on the MBA oxidation rate, $(-r)$, calculated with the following relationship:

$$(-r) = Q(C_{\text{MBA,I}} - C_{\text{MBA,O}}) \quad (3.11)$$

in which Q is the volumetric liquid flow rate and $C_{\text{MBA,I}}$ and $C_{\text{MBA,O}}$ the molar concentrations of MBA at the inlet and outlet of the photoreactor, respectively. Figure 3.10 reports the results obtained by experiments carried out with HP2 photocatalyst. It may be noted that the same reaction rates are obtained for flow rates higher than $2 \text{ cm}^3 \cdot \text{s}^{-1}$ indicating that in these conditions the liquid-solid mass transfer resistance plays a negligible role on the photoprocess kinetics. On the basis of this finding all the photoreactivity results have been carried out at a constant flow rate of $2.6 \text{ cm}^3 \cdot \text{s}^{-1}$. For this flow rate circulating in the packed bed the corresponding Reynolds number (Reynolds 1883) has a value of about 5, indicating that the fluid-dynamic regime is the laminar one.

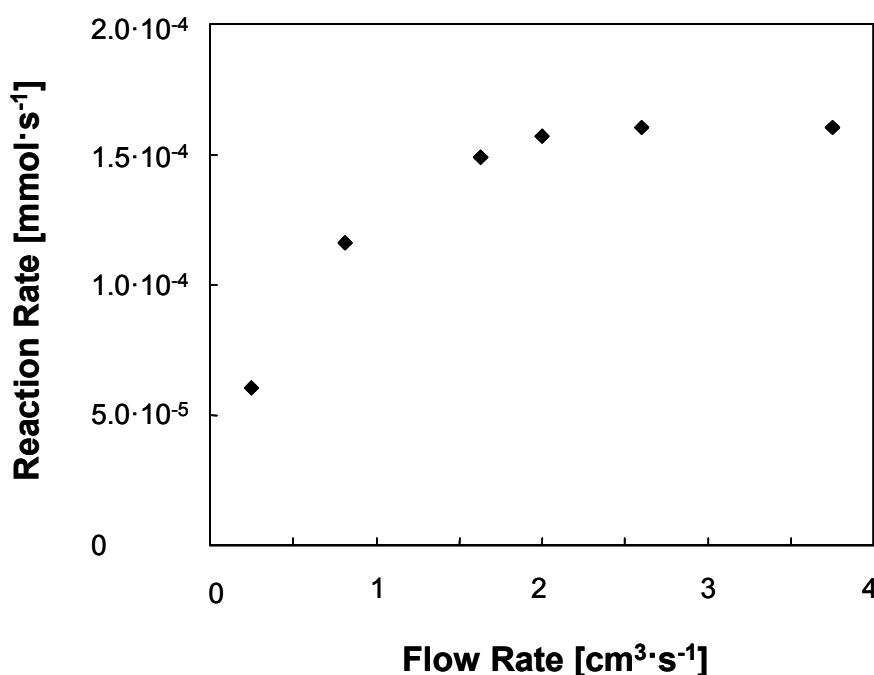


Figure 3.10. Influence of liquid flow rate on the MBA oxidation rate with HP2 bed

No oxidation of MBA was observed in runs performed in the absence of oxygen and/or light. The contemporary presence of photocatalyst, oxygen and light determined the MBA oxidation, CO₂ and MBAD being the main degradation products detected in the liquid phase. Owing to the fact that no volatile organic compounds are formed (Palmisano et al. 2007b; Addamo et al. 2008), the decrease of TOC concentration is ascribed only to CO₂ production. It is worth noting that the values of the mineralized carbon concentration were obtained dividing by 8 the measured TOC values in order to be comparable with the concentrations of the oxidised compound that contains 8 carbon atoms. For each run the mass balance on carbon contained in the outlet stream was verified by adding the unreacted MBA and MBAD concentrations to that of produced CO₂ and it was always accomplished for more than 99%.

At very high conversion values of MBA and only when the 1000 W lamp was used, trace amounts of 4-methoxybenzoic acid were also detected. In order to check the formation pathway of this compound, a photoreactivity run was carried out by feeding the photoreactor with an aqueous solution containing only MBAD. 4-Methoxybenzoic acid was the only stable intermediate detected in this run together with CO₂ and so it may be concluded that this compound derives from MBAD partial oxidation.

Figure 3.11 reports the values of reaction rate obtained with HP1 and HP2 beads at different inlet MBA concentrations and lamp power; the abscissa of this Figure is the inlet MBA concentration. Figure 3.12 reports the conversion and selectivity values for the same experimental runs shown in Fig. 3.11. The conversion, X , and the selectivity, Y , are defined as:

$$X \equiv \frac{C_{\text{MBA,I}} - C_{\text{MBA,O}}}{C_{\text{MBA,I}}} \quad (3.12)$$

$$Y \equiv \frac{C_{\text{MBAD,O}}}{C_{\text{MBA,I}} - C_{\text{MBA,O}}} \quad (3.13)$$

in which $C_{\text{MBAD,O}}$ is the molar concentrations of MBAD at the outlet of photoreactor. The data of Fig. 3.11 indicate that the reaction rate increases by

increasing both the MBA concentration and the irradiation power. At equal reaction conditions, the HP2 catalyst exhibits reaction rates higher than those of HP1. The data of Fig. 3.12 indicate for both HP1 and HP2 catalysts that the selectivity towards MBAD improves with an increase in MBA concentration but decreases by increasing the irradiation power. The selectivity values are almost the same for both catalysts, being the data obtained with HP2 less scattered than those with HP1.

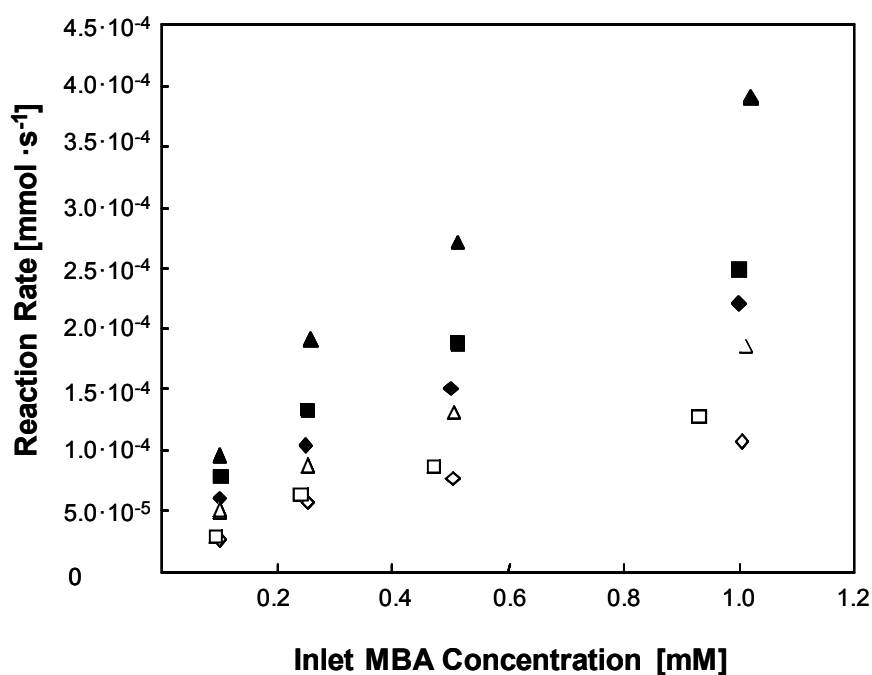


Figure 3.11. Data of MBA oxidation rate vs. inlet MBA concentration for runs carried out with different lamp powers. HP1: (◇) 500 W, (□) 700 W, (△) 1000 W. HP2: (◆) 500 W, (■) 700W, (▲) 1000 W

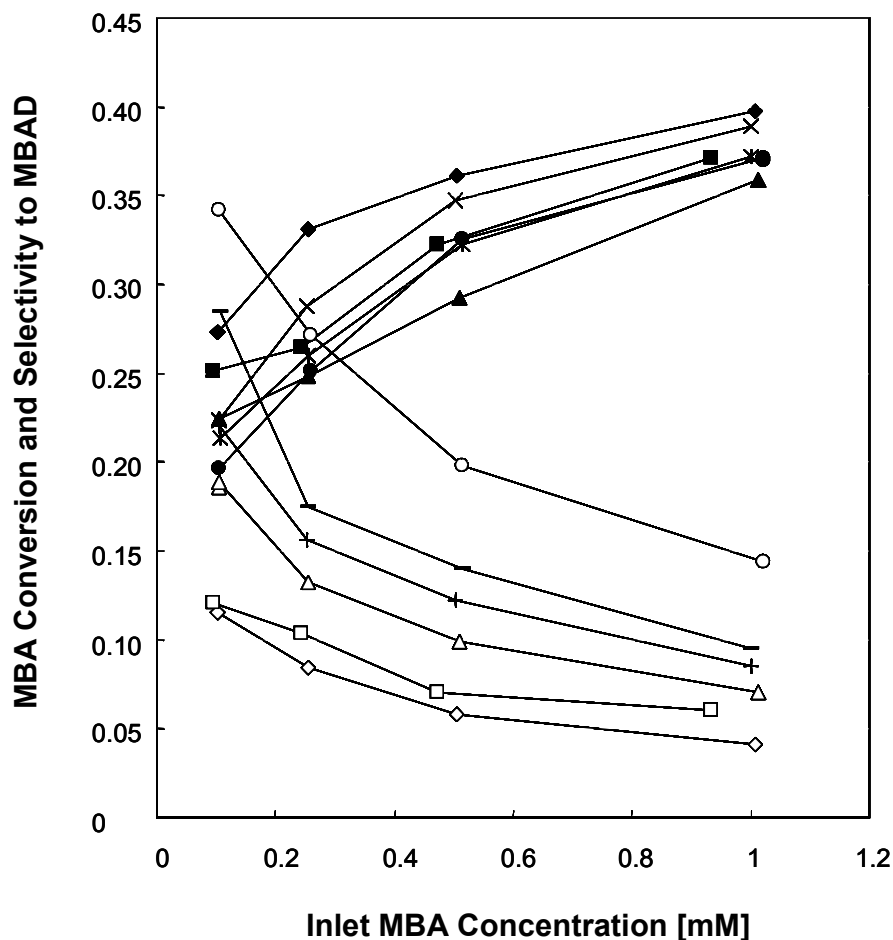


Figure 3.12. MBA conversion, X, and selectivity to MBAD, Y, corresponding to the runs reported in Fig. 3.11. HP1 conversion data: (◇) 500 W, (□) 700 W, (Δ) 1000 W and HP1 selectivity data: (◆) 500 W, (■) 700W, (▲) 1000 W. HP2 conversion data: (+) 500 W, (-) 700 W, (○) 1000 W and HP2 selectivity data: (x) 500 W, (*) 700W, (●) 1000 W

Figure 3.13 reports the values of reaction rate obtained with HP2 beads at different inlet MBA concentrations and oxygen concentration in the liquid phase; Figure 3.14 shows the corresponding values of conversion and selectivity. From the observation of data reported in these Figures, it may be noted that the reaction rate increases by increasing the concentration of oxygen dissolved in the liquid phase; the percentage of this increase is quite independent of the inlet MBA concentration and ranges between 7 and 11%. On the contrary an increase in oxygen concentration has a detrimental effect on selectivity to MBAD.

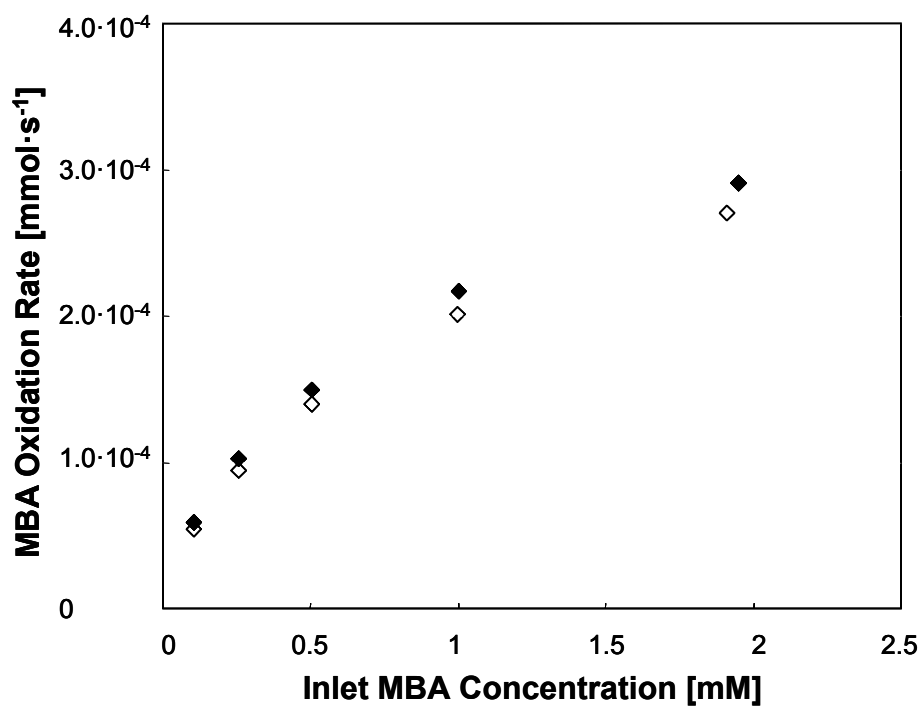


Figure 3.13. Influence of oxygen concentration on the MBA degradation rate with HP2 bed. Data obtained by bubbling pure oxygen (◆) or air (◇)

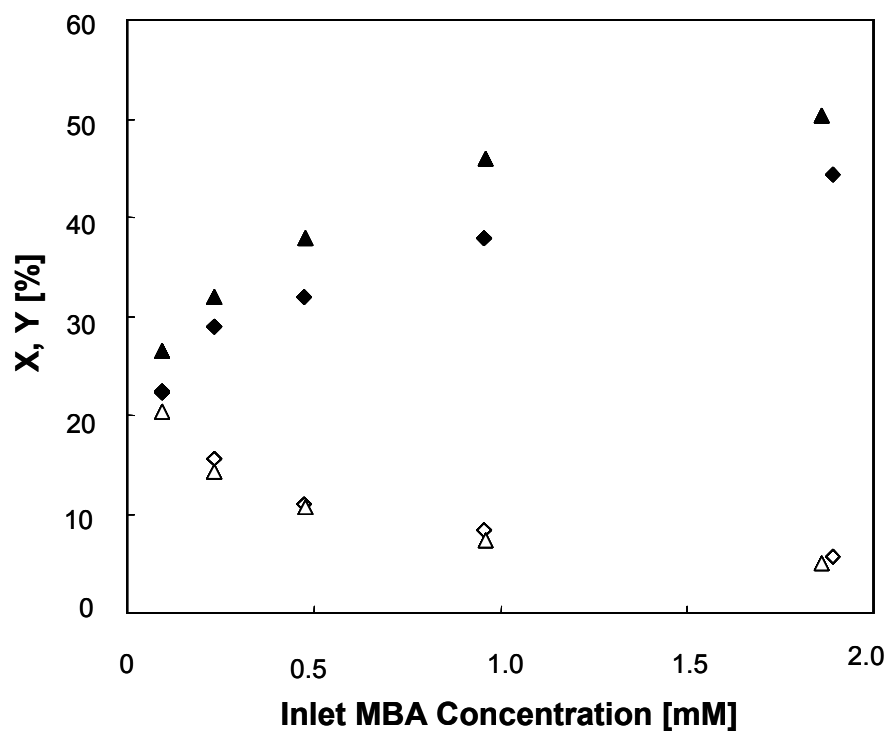


Figure 3.14. Influence of oxygen concentration on the MBA conversion, X, and selectivity to MBAD, Y (runs reported in Fig. 3.13), with HP2 bed at different inlet MBA concentrations. S: (◆) pure oxygen, (▲) air. X: (◇) pure oxygen, (Δ) air

The stability of the catalyst was checked by performing a reactivity run with duration of 24 hours. During this run, neither modification of the reactivity nor macroscopic alterations of catalyst were observed.

3.3.3. Kinetic Modelling

The main feature of heterogeneous photocatalysis is that it involves the photoactivation of the semiconductor catalyst. When the semiconductor oxide is irradiated with light of band gap (or higher) energy, the primary event is light absorption; the absorbed light produces equivalent bulk concentrations of charge carriers, electrons and holes:



After the light absorption, the charge carriers may recombine in bulk by producing heat or migrate to the catalyst surface where they can recombine on surface traps or be trapped; then, they can determine redox transformations of species adsorbed onto the catalytic surface according to thermodynamic constraints. It is generally assumed that surface hydroxyl groups act as hole traps producing OH radicals:



Adsorbed oxygen acts as electron trap according to the following equations:



Thermal recombination of charge carriers at the semiconductor surface is possible and in competition with the reactions involving dissolved molecules; the bulk and superficial thermal recombinations of electrons and holes limit the

quantum yield for the photocatalytic process and produces the warming of catalytic particle.

As shown by reaction 3.14, the generation of electron-hole pairs needs both photons and TiO_2 . The photoreactivity results obtained with HP1 and HP2 catalytic beads show that the thickness of the TiO_2 layer deposited on the beads positively affects the reaction rate; this finding is a clear indication that the path length of radiation absorbed by the TiO_2 layer is higher (or equal) than the thickness of the two layers film (about 1 μm).

Analysis of photocatalytic kinetics over semiconductor catalysts is frequently performed with the application of LH rate expression (Salaices et al. 2004; Ibrahim and de Lasa 2004; Addamo et al. 2005b; Murzin and Salmi 2005; Gora et al. 2006) on the basis that the oxidation rate of substrate is unquestionably proportional to the surface concentration of the substrate. The LH model hypothesizes that the rate is given by the actual amount of adsorbed species that can react with surface generated active species. The amount of species adsorbed on the catalyst surface is related to the species concentration in the fluid phase by the Langmuir adsorption isotherm. In the simplest form the LH approach assumes one relatively rapid adsorption step achieving equilibrium followed by a single, slow surface reaction step. The LH model parameters are the rate constant and the equilibrium adsorption constant.

Even if the LH model shows the advantage of justifying the plateauing behaviour of the rate versus the substrate concentration, it has been widely recognized (Okamoto et al. 1985; Turchi and Ollis 1990; Davis and Huang 1993; Gerischer 1993; Serpone et al. 2000; Emeline et al. 2000) since the starting of its application that this formulation is a convenient, but not mechanistic, description of the photocatalytic process. The LH kinetic model is not able to explain the experimentally observed dependence of the rate parameters on light intensity. In fact, it does not give explicitly the dependence of rate on the absorbed photon intensity (Xu and Langford 2000); this dependence is masked in the rate constant which varies depending on absorbed light intensity, I , as I^γ , where γ is typically between 0.5 and 1. Moreover the value of adsorption equilibrium constant derived from dark adsorption experiments is different from that obtained from

photoreactivity experiments modelled by using the LH equation (Cunningham and Al-Sayyed 1990; Minero 1995; Cunningham and Sedlack 1996; Minero et al. 1996; Cunningham et al. 1999).

Having in mind the LH discrepancies, Minero (1995) developed a rigorous kinetic model by taking into account the complex reaction pathways of photocatalytic degradations. In the case in which only reactions 3.14, 3.15 and 3.17 are considered, by assuming that the rate of recombination is negligible with respect to the rate of electron scavenging, a rate equation similar to the LH one is obtained in an analytical form. This function has the correct limiting behaviour and is linear for small values of substrate concentrations; however, the rate parameters no longer have any physical significance.

The recent discussion on the flaws of the conventional LH treatment (Emeline et al. 2005; Ollis 2005a; Ollis 2005b) for photocatalytic systems where adsorption-desorption is not equilibrated evidenced that the slow step approximation cannot be applied. In this case, the pseudo-steady state (PSS) approach (Ollis 2005b; Murzin 2006; Serrano et al. 2007) has been proposed by assuming that the surface concentrations of reacting species are in steady state. The difference of the PSS model with the LH approach is that the reactivity is considered dependent on the actual concentration of the photogenerated reactive species, which is generally not constant as a function of the experimental conditions. According to Ollis (2005a), the PSS model should be applied for virtually all photocatalyzed reactions, where adsorption-desorption equilibrium cannot be achieved. The PSS results in the dependence of both constants on intensity. It must be outlined that both the PSS and slow-step approximations yield the same global rate form, like to the LH equation, but only the PSS analysis provides explanation of the intensity influence on the rate equation parameters. Such dependence (Ollis 2005a; Ollis 2005b) on I can only be possible when the assumption of adsorption-desorption equilibrium is relaxed.

It is useful to report that the simple rate form of the LH approach may have origins which take into account different photoreaction mechanisms (Demeestere et al. 2004; Krýsa et al. 2006; Minero and Vione 2006). Recently, it has been obtained (Murzin 2006) by extending the procedure for derivation of reaction rates

in case of multi-step single-route catalytic reactions to kinetics of photocatalytic processes.

Having in mind all the limitations of LH model, in the present investigation, the LH approach is used for modelling the MBA oxidation kinetics. The modelling does not describe the mechanisms of MBA oxidation in details; its main scope is that of fitting the experimental data well and providing operational constants useful for the engineering of the photooxidation process. In any case, if the results of the modelling procedure would demonstrate that the assumptions of LH model do not hold in the present case, the used relationships should continue to be valid but the fitted parameters should lose their physical meanings.

The dependence of reaction rate on the MBA concentrations, shown by the experimental data of Fig. 3.11, is of Langmuir type thus indicating that the adsorption kinetics of MBA onto the catalyst surface plays an important role in the overall rate of the process. The modelling of the photoreactivity results is performed by assuming that all the elementary reactions of MBA oxidation, both partial and total, occur on the catalyst surface and involve adsorbed species, which can interact with hydroxyl groups. Owing to the fact that the reaction rate values observed in this work are not affected by external mass transfer resistance nor by diffusion inside pores as the diffusion path (the film thickness) is of the same order of the irradiation wavelength (Chen et al. 2001), the rate-determining step of the process is hypothesised to be the second order reaction between OH radical and the aromatic molecule adsorbed onto the catalyst surface. This simple model is commonly used to analyse the kinetics of photocatalytic reactions, and it generally provides a satisfactory prediction of the progress of species concentration in liquid phase (Turchi and Ollis 1989; Gora et al. 2006).

The reactivity results indicate that oxygen is needed for the photoreaction to proceed; moreover, an increase of oxygen concentration increases the reaction rate. The occurrence of two parallel pathways, i.e. partial oxidation and mineralization, suggests that the adsorption sites, responsible for these pathways, have different features (Suda 1988; Nagao and Suda 1989; Muggli et al. 1996; Nimlos et al. 1996; Muggli and Falconer 1998; Muggli et al. 1998a; Muggli et al. 1998b; Lewandowski and Ollis 2003). On these grounds, the kinetic modelling of

photoreactivity results is made by assuming that three different types of site exist on the catalyst surface. The first type is able to adsorb oxygen so that the OH radical concentration depends on the fractional sites coverage by O₂ (as the adsorbed oxygen acts as an electron trap thus hindering the e⁻-h⁺ recombination), the second one adsorbs the organic molecules by producing their partial oxidation, and the third one adsorbs the organic molecules by eventually producing their mineralization. These last two types compete for adsorbing organic molecules present in the solution, while the partial oxidation sites release to the solution the partially oxidised molecule, the mineralization sites only release the final oxidation products, in our case CO₂ and H₂O.

Under these hypotheses, the MBA partial oxidation rate, r_{PO} , and the MBA mineralization rate, r_{MIN} , per unit surface area are modelled as second order reactions:

$$r_{PO} = \frac{1}{S_{PO}} \frac{dn_{PO}}{dt} = k_{2,PO} \theta_{Ox} \theta_{PO} \quad (3.18)$$

$$r_{MIN} = \frac{1}{S_{MIN}} \frac{dn_{MIN}}{dt} = k_{2,MIN} \theta_{Ox} \theta_{MIN} \quad (3.19)$$

in which n_{PO} indicates the MBA moles partially oxidised to MBAD, n_{MIN} indicates the MBA moles oxidised to CO₂, S_{PO} and S_{MIN} the catalyst surface area on which partial oxidation and mineralization occur, $k_{2,PO}$ and $k_{2,MIN}$ are the second order rate constants for partial oxidation and mineralization, θ_{Ox} is the fractional site coverage of oxygen, and θ_{PO} and θ_{MIN} the fractional coverages of MBA on sites determining its partial oxidation to MBAD or its mineralization to CO₂, respectively. The MBA molar balance between the photoreactor inlet (for which $n_{MBA} = n_{MBA,I}$) and a generic section may be expressed in the following way:

$$n_{MBA,I} = n_{MBA} + n_{PO} + n_{MIN} = n_{MBA} + n_{MBAD} + n_{MIN} \quad (3.20)$$

in which n_{MBAD} is the moles of produced MBAD ($n_{\text{PO}}=n_{\text{MBAD}}$). Dividing the terms of eq 3.20 by the liquid volume V produces the following relationship:

$$C_{\text{MBA,I}} = C_{\text{MBA}} + C_{\text{PO}} + C_{\text{MIN}} \quad (3.21)$$

The photoreactivity run carried out by feeding a MBAD solution to the photoreactor showed that MBAD may participate both to partial oxidation reaction producing 4-methoxybenzoic acid and to mineralization reaction producing CO_2 . This finding suggests that, in the course of MBA oxidation, the produced MBAD may compete with MBA for adsorption both on the partial oxidising and mineralising sites. As previously reported, 4-methoxybenzoic acid was also detected; its very low concentration values may be explained by considering that as soon as the acid is obtained, it is converted very easily to CO_2 , because its acidic group hinders its desorption from the TiO_2 surface. On this ground the fractional site coverages of eqns. 3.18 and 3.19 may be written in terms of the Langmuir relationship as:

$$\theta_{\text{Ox}} = \frac{K_{\text{Ox}} C_{\text{Ox}}}{1 + K_{\text{Ox}} C_{\text{Ox}}} \quad (3.22)$$

$$\theta_{\text{PO}} = \frac{K_{\text{PO}} C_{\text{MBA}}}{1 + K_{\text{PO}} (C_{\text{MBA}} + C_{\text{MBAD}})} \quad (3.23)$$

$$\theta_{\text{MIN}} = \frac{K_{\text{MIN}} C_{\text{MBA}}}{1 + K_{\text{MIN}} (C_{\text{MBA}} + C_{\text{MBAD}})} \quad (3.24)$$

where C_{Ox} , C_{MBA} and C_{MBAD} are the oxygen, MBA and MBAD concentrations in the aqueous phase, whereas K_{Ox} is the equilibrium adsorption constant of oxygen and K_{PO} and K_{MIN} those of MBA and MBAD on partial oxidising and mineralising sites, respectively. Equations 3.23 and 3.24 are written under the hypothesis that the equilibrium adsorption constants of MBA and MBAD on those sites are similar (Turchi and Ollis 1989; Palmisano et al. 2007a).

The photoreactivity runs carried out with lamps having different power show conversions up to 35% (see Figures 3.12 and 3.14). Under these conditions the photoreactor cannot be considered differential. By considering that the thickness of the catalytic bed is small (7 mm) as also the size of catalyst bead (2 mm), the assumption is here made that the concentration gradient in radial direction may be neglected. By taking into account a differential volume of the reactor, molar balances on partially oxidised and mineralized MBA produce the following equations:

$$Q dC_{PO} = (r_{PO}) dS_{PO} = k_{2,PO} \theta_{Ox} \theta_{PO} dS_{PO} \quad (3.25)$$

$$Q dC_{MIN} = (r_{MIN}) dS_{MIN} = k_{2,MIN} \theta_{Ox} \theta_{MIN} dS_{MIN} \quad (3.26)$$

in which dS_{PO} and dS_{MIN} are the irradiated surface areas of the photocatalyst in the control volume. By defining the parameter α as the fraction of the total surface area of catalyst, S , on which partial oxidation reaction occurs, the following equalities may be written.

$$S_{PO} = \alpha S \quad S_{MIN} = (1 - \alpha) S \quad (3.27)$$

By differentiating eqs 3.21 and 3.27, one obtains the following:

$$dC_{MIN} = -dC_{MBA} - dC_{PO} \quad (3.28)$$

$$dS_{PO} = \alpha dS \quad dS_{MIN} = (1 - \alpha) dS \quad (3.29)$$

By substituting eq 3.28 into eq 3.26, the resulting equation may be divided by eq 3.25 and one obtains:

$$\frac{-dC_{MBA} - dC_{MBAD}}{dC_{MBAD}} = \frac{k_{2,MIN} \theta_{MIN} dS_{MIN}}{k_{2,PO} \theta_{PO} dS_{PO}} \quad (3.30)$$

in which the $dC_{PO}=dC_{MBAD}$ equality has been substituted. By introducing eqs 3.23, 3.24 and 3.29 into eq 3.30 and rearranging, the following differential equation is obtained:

$$-\frac{dy}{dx} = \frac{A + A K_{PO}(y + x)}{1 + K_{MIN}(y + x)} + 1 \quad (3.31)$$

in which

$$y = C_{MBA} \quad x = C_{MBAD} \quad \text{and} \quad A = \frac{S_{MIN} k_{2,MIN} K_{MIN}}{S_{PO} k_{2,PO} K_{PO}} \quad (3.32)$$

Equation 3.31 may be transformed in a differential equation with separable variables by defining a new variable, z , as

$$z = K_{MIN}(y + x) \quad (3.33)$$

and a new parameter, β , as

$$\beta = \frac{AK_{PO} + K_{MIN}}{K_{MIN}} \quad (3.34)$$

By taking the derivative of z with respect to x and by substituting eq 3.31 in that derivative, the following equation is obtained.

$$\frac{dz}{dx} = \frac{K_{MIN}(z + 1) - K_{MIN}(\beta z + A + 1)}{z + 1} \quad (3.35)$$

The integration of eq 3.35 with the following limit conditions

$$\begin{aligned} z = z_I = K_{MIN} C_{MBA,I} & \quad \text{for} \quad x = x_I = 0 & \quad (\text{photoreactor inlet}) \\ z = z_O = K_{MIN} (C_{MBA,O} + C_{MBAD,O}) & \quad \text{for} \quad x = x_O = C_{MBAD,O} & \quad (\text{photoreactor outlet}) \end{aligned}$$

gives the relationship among the MBA and MBAD concentrations at the outlet and inlet of photoreactor:

$$\frac{S_{PO}k_{2,PO}}{S_{MIN}k_{2,MIN}} \left[\frac{(C_{MBA,I} - C_{MBA,O} - C_{MBAD,O})}{\left(\frac{1}{K_{MIN}} - \frac{1}{K_{PO}} \right) \ln \frac{K_{PO}C_{MBA,I} + 1}{K_{PO}(C_{MBA,O} + C_{MBAD,O}) + 1}} \right] = C_{MBAD,O} \quad (3.36)$$

By substituting in eq 3.36 the experimental values of $C_{MBA,I}$, $C_{MBA,O}$ and $C_{MBAD,O}$ obtained from each run and by applying a least-squares best fitting procedure, the values of $(S_{PO} \cdot k_{2,PO})/(S_{MIN} \cdot k_{2,MIN})$, K_{PO} and K_{MIN} have been obtained ($R^2 > 0.96$). This non linear fit was carried out by using the curve-fitting function available in Mathematica version 4 (Wolfram Media). The results of the fitting procedure applied to the runs carried out with HP1 and HP2 catalysts at different lamp powers are reported in Figs. 3.15. The abscissa of these Figures is the experimental value of $C_{MBAD,O}$, and the ordinate is the $C_{MBAD,O}$ value furnished by eq 3.36 with the best fitted $(S_{PO} \cdot k_{2,PO})/(S_{MIN} \cdot k_{2,MIN})$, K_{PO} and K_{MIN} values. The main diagonal represents the theoretical relationship between the x-y variables and a satisfactory fitting may be noted. Figure 3.16 reports the values of $(S_{PO} \cdot k_{2,PO})/(S_{MIN} \cdot k_{2,MIN})$, K_{PO} and K_{MIN} as a function of energy absorbed by the reacting system.

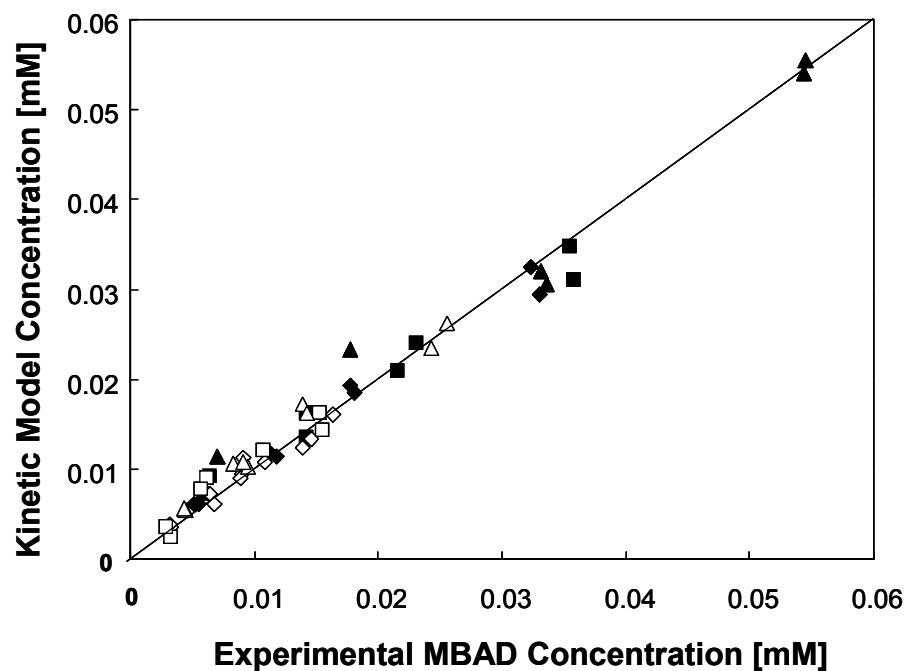


Figure 3.15. MBAD concentration values obtained by means of kinetic modelling (eq 3.36) versus experimental ones. HP1 catalyst: ($\diamond$) 500 W, ($\square$) 700W, (Δ) 1000 W. HP2 catalyst: ($\blacklozenge$) 500 W, ($\blacksquare$) 700W, ($\blacktriangle$) 1000 W

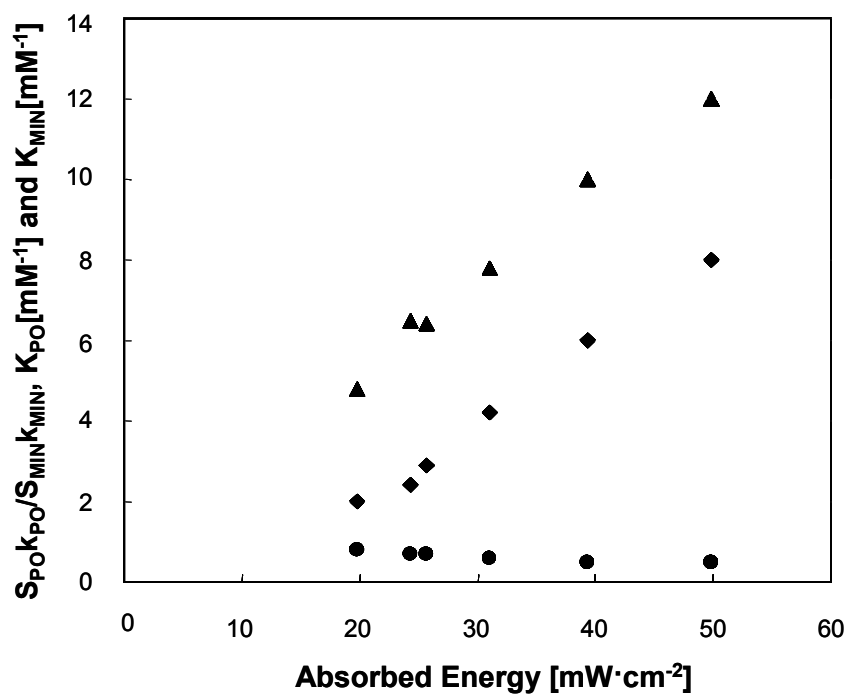


Figure 3.16. Values of $S_{PO}k_{PO}/S_{MIN}k_{MIN}$ ratio (●) and of equilibrium adsorption constant for partial oxidation (◆) and mineralization (▲) versus the energy absorbed by the catalytic bed

The data reported in Figure 3.13 indicate that an increase of oxygen coverage positively affects the MBA degradation rate, this increase being independent on the inlet MBA concentration. By assuming that for the runs with low conversion the fractional coverages by MBA and oxygen do not appreciably change from the inlet to the outlet of the photoreactor, the ratio between the disappearance rate of MBA in the presence of pure oxygen, $(r_{PO}+r_{MIN})_{OX}$, and that in the presence of air, $(r_{PO}+r_{MIN})_{AIR}$, may be written in the following way (see eqns. 3.18, 3.19 and 3.22):

$$\frac{(r_{PO} + r_{MIN})_{OX}}{(r_{PO} + r_{MIN})_{AIR}} = \frac{(\theta_{OX})_{OX}}{(\theta_{OX})_{AIR}} = \frac{K_{OX} (C_{OX})_{OX}}{1 + K_{OX} (C_{OX})_{OX}} \frac{1 + K_{OX} (C_{OX})_{AIR}}{K_{OX} (C_{OX})_{AIR}} \quad (3.37)$$

in which $(\theta_{OX})_{OX}$ and $(C_{OX})_{OX}$ and $(\theta_{OX})_{AIR}$ and $(C_{OX})_{AIR}$ indicate the oxygen fractional coverage and the oxygen saturation concentration obtained by bubbling pure oxygen or air in water, respectively. The introduction in eq 3.37 of the values of 1.076 for $(r_{PO}+r_{MIN})_{OX}/(r_{PO}+r_{MIN})_{AIR}$, 1.27 mM for $(C_{OX})_{OX}$ and 0.254 mM for $(C_{OX})_{AIR}$ gives the value of 41.3 mM⁻¹ for K_{OX} . The values of $(\theta_{OX})_{OX}$ and $(\theta_{OX})_{AIR}$ are 0.98 and 0.92, respectively, indicating that oxygen is not a rate determining reactant under the used experimental conditions. A five times decrease of oxygen concentration in the liquid phase indeed determines only a 6% decrease in the catalyst coverage.

The kinetic modelling expressed by eq 3.36 is able to furnish values of the $(S_{PO} \cdot k_{1,PO})/(S_{MIN} \cdot k_{2,MIN})$ group, but it can not separately give the values of the $(S_{PO} \cdot k_{2,PO})$ and $(S_{MIN} \cdot k_{2,MIN})$ constants. In order to have an approximate determination of these values the following procedure has been developed. By considering that for some runs the MBA conversion was lower than 10%, the assumption is here made that for those runs the photoreactor behaves as a differential one. On this ground by substituting eq 3.23 in eq 3.25 and by introducing the MBA and MBAD concentration values averaged between the inlet and outlet of the photoreactor, the following relationship is obtained after some arrangements:

$$S_{PO}k_{2,PO} = \frac{Q C_{MBAD,O}}{\theta_{Ox}} \left(\frac{2}{K_{PO}} \frac{1}{C_{MBA,I} + C_{MBA,O}} + \frac{C_{MBAD,O}}{C_{MBA,I} + C_{MBA,O}} + 1 \right) \quad (3.38)$$

By substituting in eq 3.38 the experimental values of $C_{MBA,I}$, $C_{MBA,O}$ and $C_{MBAD,O}$ obtained from low-conversion runs, the values of $S_{PO} \cdot k_{2,PO}$ have been obtained. The $S_{PO} \cdot k_{2,PO}$ values are reported in Fig. 3.17 together with the $S_{MIN} \cdot k_{2,MIN}$ values as a function of the energy absorbed by the reacting system.

By considering that S_{PO} and S_{MIN} (the aliquots of TiO_2 surface area dedicated to partial oxidation or mineralization, respectively) do not depend on absorbed photon flux, it may be observed, from the results reported in Figs. 3.16 and 3.17, that all parameters of the kinetic model, i.e. $k_{2,PO}$, $k_{2,MIN}$, K_{PO} and K_{MIN} , increase by increasing the energy absorbed by the catalyst. The K_{PO} and K_{MIN} values show a similar dependence on the absorbed photons; on the contrary, while the $k_{2,MIN}$ parameter is strongly dependent on the absorbed energy, the $k_{2,PO}$ parameter seems quite insensitive to that parameter.

The finding that all the parameters depend on absorbed photons clearly indicates that the LH model is inadequate to describe the present system; therefore, the model parameters have no physical significance and it would be better to call them “apparent kinetic constant” and “apparent adsorption equilibrium constant”. However the good fitting of the used relationships to the experimental data suggests that the equations arising from the LH model continue to be valid for describing the photoprocess kinetics, even if only from an engineering point of view. The dependence of model parameters on absorbed photons could include a dependence on the system temperature. In fact, by considering that the photocatalytic reactions show a low quantum yield, i.e. that the aliquot of absorbed photons useful for reaction events is low, most pairs generated by absorbed photons recombine by determining a bulk and superficial heating of the catalyst particle. Higher values of photon absorption may determine higher values of particle temperature which eventually may affect the model parameters. All the reactivity results indicate that the partial oxidation pathway is favoured by low flux of absorbed photons and by low oxygen coverage on the TiO_2 surface; opposite conditions favour the mineralization pathway.

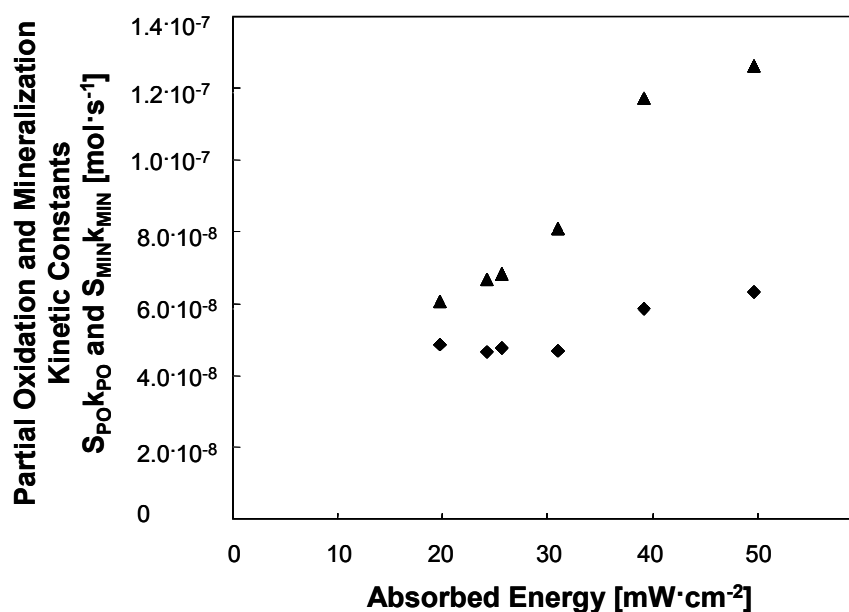


Figure 3.17. Values of kinetic constant $S_{PO}k_{PO}$ and $S_{MIN}k_{MIN}$ for partial oxidation (♦) and mineralization (▲) versus the energy absorbed by the catalytic bed

3.4. Photocatalytic Oxidation of Aromatic Alcohols to Aldehydes in Aqueous Suspension of Home Prepared Titanium Dioxide: Selectivity Enhancement by Aliphatic Alcohols with Intrinsic and Surface Features of Catalysts

This chapter has been devoted to study the selective oxidation of BA to BAD and MBA to MBAD in water by using irradiated TiO_2 catalysts. The photoreactivity runs were carried out with aqueous suspensions of different HP TiO_2 specimens and of a commercial TiO_2 catalyst (Degussa P25). The performances of catalysts were compared in terms of BA and MBA oxidation rate and selectivity towards BAD and MBAD production. The HP catalysts exhibited reaction rates always lower than that of the commercial one but selectivity values about four times higher. With the aim of affecting the photoprocess selectivity, an aliphatic alcohol (methanol, ethanol, 2-propanol or tert-butanol) was added to the reacting system in small amounts with respect to water. These species are frequently used in heterogeneous photocatalytic systems due to their capability to work as strong hole traps (Bickley and Jayanty 1974; Tamaki et al. 2006;

Schindler and Kunst 1990; Brezová et al. 2003; Yamashita et al. 2002); here, however, the aliphatic alcohols are exploited to influence the performance of complex oxidation processes. The addition to the HP catalyst suspension of aliphatic alcohols decreases the overall oxidation rate of BA and MBA but it determines a significant improvement of the photoprocess selectivity towards aldehydes. The selectivity enhancement by ethanol seems to be specific of HP catalysts, this effect being negligible with Degussa P25. The textural characterization of HP catalysts was carried out with XRD, SEM observations, BET surface area and porosity measurements. The other aim of this investigation was that of finding likely explanations for the different photoactivity and selectivity shown by HP and commercial catalysts. In order to reach this goal, bulk and surface properties have been investigated. For the first ones some intrinsic electronic features of catalysts were investigated by diffuse reflectance spectroscopy and quasi-Fermi level measurements; for the second ones in situ ATR-FTIR spectroscopy has been used. The ATR-FTIR study has been focused on the comparison of the HP catalyst showing the highest selectivity and the Degussa P25 TiO₂ sample, which exhibits the highest activity for the BA photocatalytic oxidation. The features of the interaction of BA with the catalyst surface, the identification of the species adsorbed on catalyst upon photo-oxidation of BA and the effect of water and ethanol on the overall process were investigated. The water adsorption capability of both catalysts was also investigated by thermogravimetric analysis.

3.4.1. Photocatalyst Characterization

All the information obtained by the textural characterisation of catalysts is summarised in Table 3.5.

Table 3.5. Photocatalysts textural properties

Catalyst	Phase A, anatase R, rutile	SSA [m ² g ⁻¹]	Total porosity [mm ³ g ⁻¹]	Average pore radius [Å]
Degussa P25	A, R	50	–	–
Merck	A	10	–	–
HP0.5	A	235	351	26
HP2	A	226	325	29
HP4	A, R	220	318	28
HP6	A, R	206	292	28
HP8	R	108	205	38

XRD patterns of the HP catalysts indicated the presence of only anatase phase up to boiling times of 2 h. For boiling times of 4 and 6 h the rutile phase also appears being the anatase the predominant one; and at 8 h almost only rutile is present. The crystallite sizes, as obtained from Scherrer's equation, were in the 5-9 nm range. In the literature (Sclafani et al. 1990; Addamo et al. 2004) preparation of rutile is generally carried out at very high temperature (ca. 1000 K) but in very acidic medium anatase phase may transform to rutile at low temperature (Nag et al. 2007; Li et al. 2006; Chen et al. 1999) giving rise to anatase-rutile mixtures whose ratio depends on the treatment duration.

BET specific surface areas were found to be ca. 220 m²·g⁻¹ for all the HP catalysts except for HP8 which exhibited a much lower value (108 m² g⁻¹), probably due to the anatase to rutile transformation occurring for this long boiling time. All the values are however considerably higher than those of commercial TiO₂ samples used due to the lesser crystallinity of HP catalysts. The HP samples showed to be mesoporous and the total porosity decreased with boiling time. Figure 3.18 reports SEM images of the HP0.5 and HP8 samples showing that the catalysts consist of agglomerates. The average diameter of the agglomerates was ca. 25 nm and it was independent of boiling time.

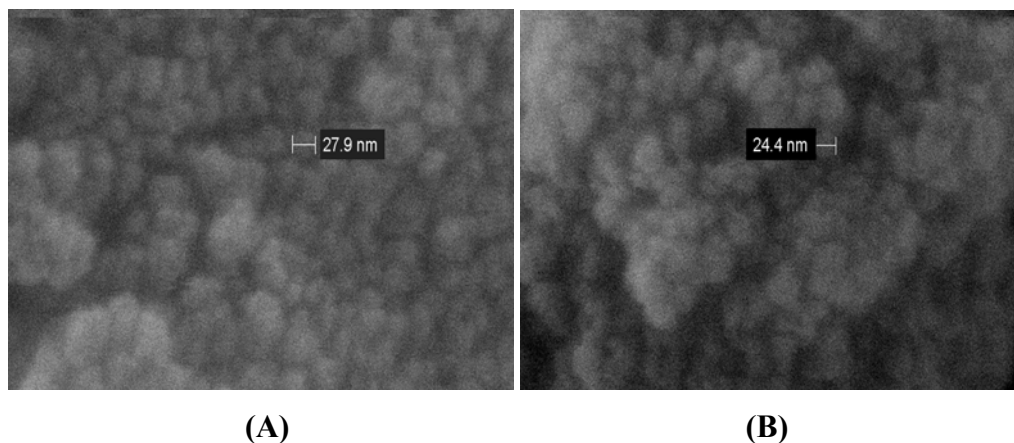


Figure 3.18. SEM images of (A) HP0.5 and (B) HP8

3.4.2. Photoreactivity Experiments

Preliminary oxidation runs of BA and MBA were carried out in the 3-11 pH range and with different amounts of catalyst, being the optimality criterion that of maximising the selectivity. The highest selectivity to aldehyde was observed at pH = 7. Even if the oxidation rates increase with the catalyst amount, the highest selectivity was reached for HP catalysts with amounts of $0.4 \text{ g}\cdot\text{L}^{-1}$ for BA and of $0.2 \text{ g}\cdot\text{L}^{-1}$ for MBA. All the photoreactivity runs were therefore carried out with those catalyst amounts and at neutral pH. For commercial catalysts the reaction rate increased and the selectivity sharply decreased at increasing catalyst amount; on this basis it was decided to use a powder amount of $0.02 \text{ g}\cdot\text{L}^{-1}$ for both aromatic alcohols as for this amount there was a high selectivity at a measurable reaction rate.

The main intermediate products detected in the course of BA and MBA photocatalytic oxidation were the corresponding aldehydes, CO_2 being the other oxidation product. For BA in the presence of commercial TiO_2 benzoic acid, hydroxylated derivatives and aliphatic compounds were observed while in the presence of HP catalysts the previous compounds were present in traces being hydroxylated derivatives absent. For MBA all the used catalysts did not produce any other intermediates except 4-methoxybenzoic acid that was detectable only for long lasting runs when the conversions were higher than 80%. All the reactivity runs indicated that the rates of formation of aromatic aldehydes and CO_2

had values different from zero from the starting of irradiation thus suggesting that their formation started contemporarily once the irradiation was turned on.

For all the used catalysts Table 3.6 reports the values of the irradiation time, $t_{irr.}$, needed for achieving a BA conversion of 50% together with the corresponding values of overall selectivity to aldehyde; these values are relative to $t_{irr.}$ and have been calculated as the ratio between the produced moles of aldehyde and the reacted moles of aromatic alcohol. During irradiation indeed the overall and the instantaneous selectivities had almost the same value. For the sake of comparison Table 3.6 also reports the data obtained for MBA oxidation (Palmisano et al. 2007b) at a 65 % conversion. The previous values of conversion were chosen as for them the aldehyde concentration reached the optimum value.

Table 3.6. Irradiation time and selectivity for aromatic alcohols oxidation to aldehydes

Catalyst	BA			MBA		
	Catalyst amount [g L ⁻¹]	$t_{irr.}$ [h]	Selectivity [% mol]	Catalyst amount [g L ⁻¹]	$t_{irr.}$ [h]	Selectivity [% mol]
Degussa P25	0.02	3.9	8	0.02	5.6	11
Merck	0.02	17.6	9	0.02	13.8	14
HP0.5	0.4	6.1	28	0.2	7.7	41
HP2	0.4	6.0	26	0.2	4.7	37
HP4	0.4	5.7	26	0.2	3.9	36
HP6	0.4	4.3	24	0.2	2.8	31
HP8	0.4	5.3	17	0.2	3.2	32

$t_{irr.}$ and selectivity refer to a BA and MBA conversion of 50% and 65%, respectively.
Selectivity is determined as (moles of formed aldehyde)/(moles of converted alcohol).
Alcohol initial concentration: 1 mM

For HP0.5, the most selective photocatalyst, a specific study has been carried out to determine the influence of aliphatic alcohols (methanol, ethanol, 2-propanol, and tert-butanol) on reaction rate and selectivity. Preliminary photocatalytic runs were carried out with each aliphatic alcohol in the absence of aromatic alcohol and indicated that the HP0.5 was able to oxidize them. Figure 3.19 reports the concentration values of methanol versus the irradiation time for representative runs carried out without aromatic alcohol and in the presence of MBA. In this case the typical intermediates of methanol oxidation, such as formaldehyde and formic acid, were not detected in the slurries of HP0.5 catalyst and CO₂ was the only product detected (Chen et al. 1999). This finding has been

also confirmed by the fact that carbon balance was satisfied in the course of the runs by only methanol and CO_2 . On the contrary, the photocatalytic degradation of ethanol, 2-propanol, and tert-butanol produced a lot of stable intermediate compounds, that eventually were mineralized. On this ground all the data obtained in the course of BA and MBA degradation runs in the presence of methanol are representative of the methanol influence on the degradation process. For the runs carried out with the other aliphatic alcohols, only the data at low aliphatic alcohol conversion should be taken into account since at high conversion also the stable intermediates deriving from aliphatic alcohol degradation may affect the process.

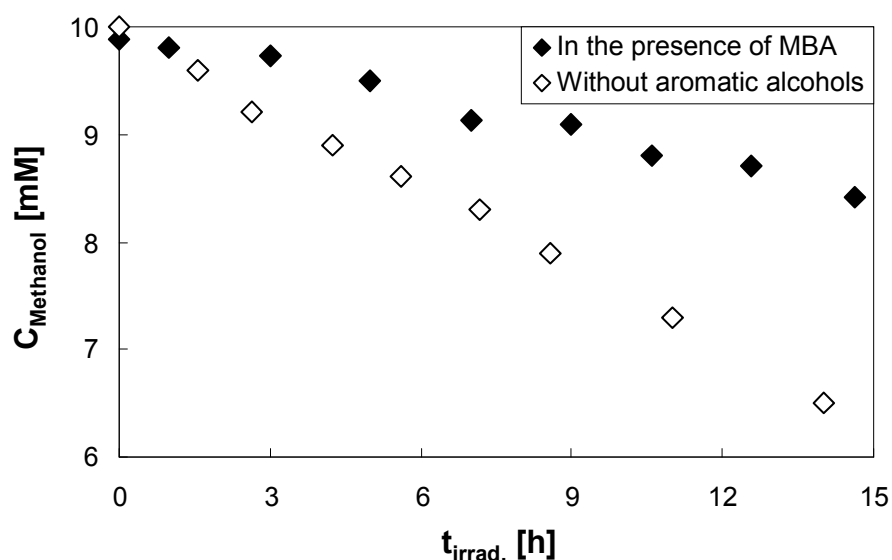


Figure 3.19. Concentration of methanol in the presence or absence of MBA 1 mM. The catalyst: HP0.5

The reactivity results obtained from representative runs of BA and MBA oxidation in the presence of methanol are reported in Figs. 3.20 and 3.21, respectively.

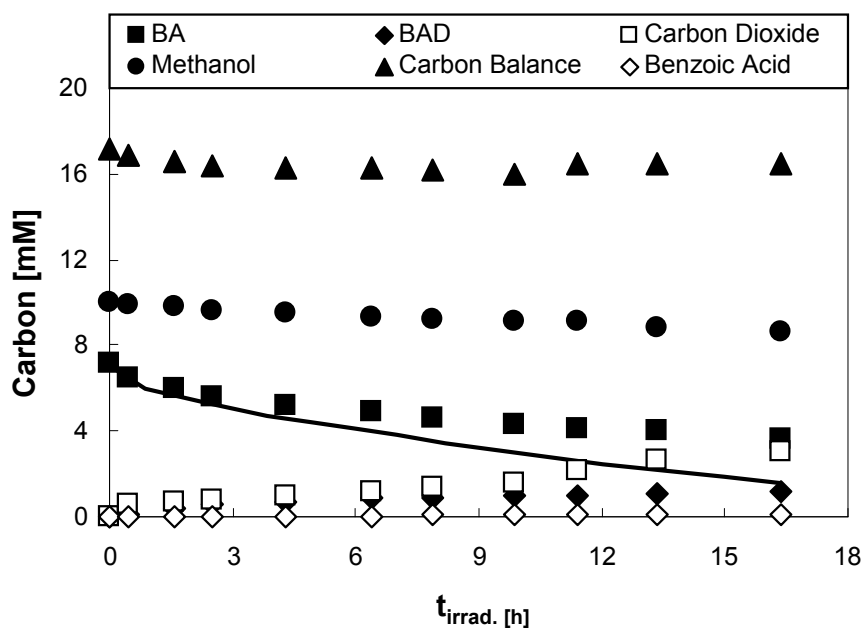


Figure 3.20. BA photocatalytic oxidation to BAD in the presence of 10 mM methanol. The continuous line refers to BA concentration values obtained in a run without methanol. The concentrations are referred to carbon. The catalyst: HP0.5

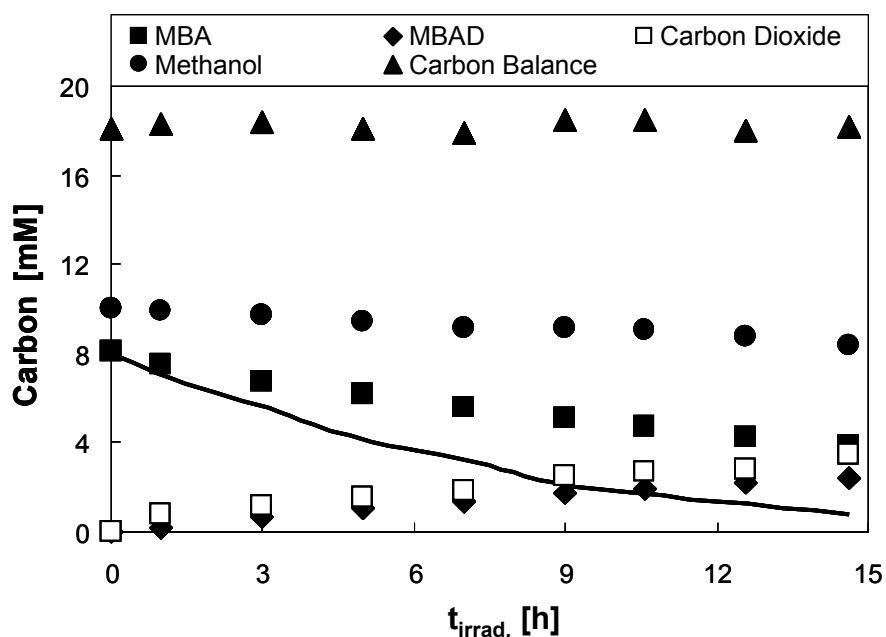


Figure 3.21. MBA photocatalytic oxidation to MBAD in the presence of 10 mM methanol. The continuous line refers to MBA concentration values obtained in a run without methanol. The concentrations are referred to carbon. The catalyst: HP0.5

From these Figures it may be noted that the data of aromatic aldehyde and CO₂ production show a slope different from zero from the starting of irradiation thus suggesting that aldehyde and CO₂ are contemporarily produced, as also observed for runs without alcohol. HPLC analyses revealed that the same chemical intermediates were formed from the aromatic alcohols also in the presence of methanol. Moreover, no volatile organic compounds were detected in the gaseous stream leaving the photoreactor, except negligible amounts of methanol desorbed from the aqueous solution. In Figs. 3.20 and 3.21, to clearly illustrate the contribution of different species to the carbon balance, the species concentrations have been normalized to carbon, thus multiplying the concentration of BA, BAD and benzoic acid by 7 (Figure 3.20) and that of MBA and MBAD by 8 (Figure 3.21). Since no intermediates of methanol oxidation were detected, it was assumed that the entire reacted methanol was transformed into CO₂. The total amount of CO₂, produced by the aliphatic and aromatic alcohol mineralization, was calculated as the difference between the starting carbon content and the TOC measurement. The carbon balance, performed by summing the carbon amounts of aromatic alcohol, aliphatic alcohol, aldehyde, aromatic acid and CO₂, was satisfactorily attained for all the runs, as Figures 3.20 and 3.21 show. In these Figures the continuous lines show the BA and MBA decrease with irradiation time for runs carried out without aliphatic alcohol; it may be noted that the oxidation of BA and MBA proceeds faster in the absence of aliphatic alcohol. The aromatic alcohol plays the same role on the oxidation rate of the aliphatic one; the data reported in Fig. 3.19 show that the methanol degradation rate in the presence of MBA is quite lower than in its absence.

Table 3.7 reports the selectivity and t_{irr} values for BA and MBA oxidation in the presence of HP0.5 at different initial concentrations of methanol, ethanol, 2-propanol and tert-butanol. These values refer to a BA conversion of 50% and a MBA conversion of 65%. This Table also reports selectivity and t_{irr} values obtained for BA oxidation in the presence of ethanol with Degussa P25. For some representative runs Figures 3.22 and 3.23 report the concentration values of BAD and MBAD, respectively, versus the irradiation time for runs carried out at increasing initial concentrations of aliphatic alcohols. It must be outlined that the

MBAD data of Fig. 3.23 are the initial ones, i.e. those for which the stable intermediates deriving from 2-propanol degradation do not affect the MBA oxidation process.

Table 3.7. Selectivity values and irradiation times for BA and MBA in the presence of aliphatic alcohols at different initial concentrations

		BA		
		Selectivity for 10% conversion [% mol]	Selectivity for 50% conversion [% mol]	t _{irr} for 50% conversion [h]
Without aliphatic alcohol		30	28	7.7
		9*	8*	3.9*
Methanol	1 mM	34	30	8.2
	10 mM	40	34	16.3
	38 mM	43	38	23.7
Ethanol	1 mM	36	30	8.0
	10 mM	45	37	14.2
		10*	9*	4.1*
2-Propanol	38 mM	52	42	21.0
	1 mM	32	30	8.3
	10 mM	40	34	12.3
Tert-butanol	38 mM	44	36	24.2
	1 mM	31	29	9.1
	10 mM	41	32	11.9
	38 mM	38	34	16.8
		MBA		
		Selectivity for 10% conversion [% mol]	Selectivity for 65% conversion [% mol]	t _{irr} for 65% conversion [h]
Without aliphatic alcohol		44	41	7.7
Methanol	1 mM	55	50	9.0
	10 mM	64	58	13.5
	38 mM	68	62	17.2
Ethanol	1 mM	60	54	8.9
	10 mM	58	56	9.4
	38 mM	62	61	14.3
2-Propanol	1 mM	55	47	8.0
	10 mM	57	52	10.2
	38 mM	61	60	17.8
Tert-butanol	1 mM	59	51	9.9
	10 mM	56	54	10.5
	38 mM	64	58	12.2

Selectivity is determined as (moles of formed aldehyde)/(moles of converted alcohol). Initial concentration of aromatic alcohol: 1 mM. The catalyst: HP0.5, amount: 0.2 g L⁻¹. The data with (*) have been obtained with Degussa P25, 0.02 g L⁻¹.

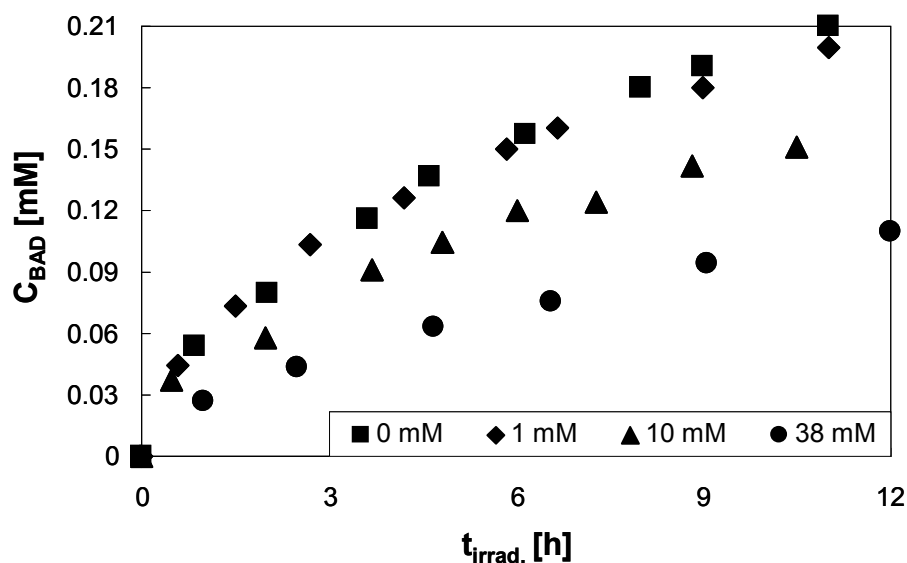


Figure 3.22. Concentration of BAD versus irradiation time in the presence of different initial concentrations of methanol. Initial BA concentration: 1 mM. The catalyst: HP0.5

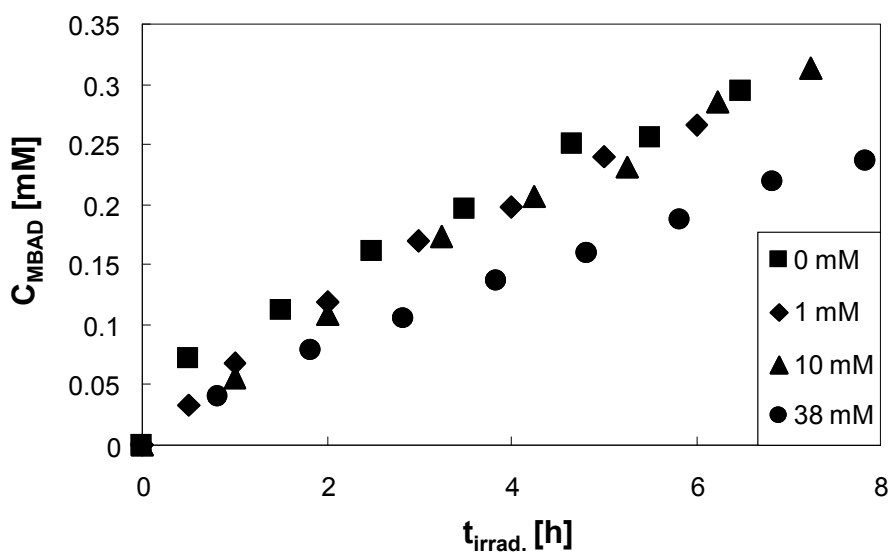


Figure 3.23. Concentration of MBAD versus irradiation time in the presence of different initial concentrations of 2-propanol. Initial MBA concentration: 1 mM. The catalyst: HP0.5

All the reactivity results indicate that the aromatic alcohol disappearance occurs through two parallel reactions: partial oxidation to the corresponding aldehyde and total oxidation to CO₂. The occurrence of two parallel pathways for BA and MBA suggests that the aromatic alcohol molecules may interact with the

TiO₂ surface in two different ways that eventually determine their partial oxidation or mineralization. This is in agreement with Palmisano et al. (2006 and 2007a) who have recently modeled the oxidation kinetics of aromatic molecules in water onto TiO₂ surface by invoking the existence of two types of sites which are specific for the occurrence of mineralization or partial oxidation. In the mineralizing sites the aromatic alcohols molecules adsorb and produce CO₂; it is likely that the mineralisation does not occur in a single step but it proceeds through a series of intermediates that do not desorb to the bulk of solution. In the partially oxidizing sites they adsorb and produce the aldehyde stable intermediates able to desorb to the bulk of solution. Once in the solution the fate of aldehyde molecules is the same of alcohol ones.

The structural results reported in Table 3.5 indicate that the cristallinity increases with the boiling time which also favours the crystal phase change from anatase to rutile (Palmisano et al. 2007b). Reactivity results reported in Table 3.6 indicate that both for BA and MBA oxidation carried out with HP catalysts the reaction rates increase by increasing the cristallinity being the contemporary presence of anatase and rutile favourable, as also shown by P25 TiO₂ which exhibits the highest reactivity even if at very low amount. Selectivities decrease with increasing cristallinity except for HP8, probably due to the predominant presence of the rutile structure. HP0.5 exhibits the lowest reaction rate among the HP catalysts, but the highest selectivity for both aldehydes among all the used catalysts. The irradiation times needed to reach the selected BA and MBA conversions are similar each other but higher than those showed by Degussa P25. It is worth reporting that modifying irradiation time and/or decreasing catalyst amount of commercial samples did not result in selectivities comparable with that of HP0.5.

The attained selectivities point to a quite different behaviour of the two aromatic alcohols. The selectivity of BA to BAD is quite lower than that of MBA to MBAD. A likely explanation is that the MBA's methoxy group (an electron donating one) increases the hydrophilicity of aromatic ring; in other words it increases the desorption capacity from the TiO₂ surface (Palmisano et al. 2006) thus reducing the possibility of direct mineralization to CO₂. It was recently

reported for hydroxylation reactions by heterogeneous photocatalysis (Palmisano et al. 2006; Palmisano et al. 2007a) that the partial oxidation route is preferred when the aromatic ring contains an electron donor group whereas mineralization is favoured by an electron withdrawing substituent. This general rule, verified for many compounds in hydroxylation reactions, seems to hold also in the partial oxidation of an aromatic alcohol to aldehyde in water.

As to concern the influence of aliphatic alcohol, from the data reported in Table 3.7 it is evident that methanol and ethanol determine the highest increase in the selectivity values, being this positive effect directly linked to the aliphatic alcohol concentration. The selectivity improvement is higher for MBA than BA. It can be seen that in the case of MBA a selectivity improvement by 1.5-fold is reached with methanol concentration of 38 mM while for BA the selectivity increase is 1.25-fold at the same methanol concentration. These findings suggest that the aliphatic alcohol can more successfully compete with MBA for the mineralizing pathway than with BA. This could be again ascribed to the presence of an electron donor group in MBA, responsible of supporting the partial oxidation route instead of mineralization. The t_{irr} values obtained in the presence of aliphatic alcohols are all higher than those obtained without them, thus indicating that the alcohols and their stable intermediates negatively affect the overall oxidation rate of aromatic alcohol.

The increasingly better performance of aliphatic alcohols with the decrease of molecular weight can be probably ascribed to a more significant extent of photoadsorption for methanol and ethanol, due to a low steric hindrance. This effect is not evident for the highest aliphatic alcohol concentration used in this work, owing to a saturation effect of TiO_2 surface.

The values of BAD concentration (see Fig. 3.22) do not change by the addition of 1 mM methanol thus indicating that the production rate of BAD is not affected by the aliphatic alcohol at this concentration. At higher methanol concentrations the concentration values of BAD decrease and as a consequence also its production rate. The same qualitative behaviour is observed for the MBAD concentration values with the difference that they were insensitive to alcohol concentration until a 10 mM value (see Fig. 3.23). At high concentrations

of aliphatic alcohol, even if the selectivity to aldehydes shows a small increase (see Table 3.7), the aldehyde production rate appreciably decreases (see Figs. 3.22 and 3.23) thus suggesting that for high concentrations the aliphatic alcohol also competes for the partially oxidizing pathway. These findings indicate not only that the interaction between the catalyst surface and the two aromatic substrates is different but also that there is a probable stronger competition of the aliphatic alcohol for the partially oxidizing pathway in the case of BA oxidation. BA was more easily mineralized than MBA in the presence of HP0.5 and it could interact less with the catalyst surface where partial oxidation occurs, so that for BA this pathway worsens in favour of the aliphatic alcohol.

In conclusion aliphatic alcohols appreciably raise the aldehyde selectivity owing to the fact that these compounds, being highly reducing species, favourably compete with the aromatic alcohols for the mineralizing pathway then lowering their overall disappearance rate. The occurrence of competition between aliphatic and aromatic alcohol molecules is also evidenced by the results reported in Fig. 3.19; in the presence of MBA methanol mineralization is about 2.5 times slower than in its absence. The favourable effect of aliphatic alcohol on selectivity seems to be specific of HP catalysts; in fact, when Degussa P25 was used with ethanol (see Table 3.3), the selectivity showed a negligible increase being also negligible the decrease of the overall oxidation rate. Likely explanations of the different behaviour of used catalysts are presented in Sections 3.4.3 and 3.4.4.

In order to quantitatively characterize the influence of alcohol presence on the partial oxidation and mineralization processes, a rate equation has been fitted to the experimental data of BA, BAD, MBA and MBAD concentrations. A first order kinetic equation, which has only a phenomenological meaning, satisfactorily ($R^2 > 0.98$) fits the data. The disappearance rate of aromatic alcohol ($-r_{AA}$) and the appearance rates of aldehyde, r_{PO} , and carbon dioxide, r_{MIN} , are expressed as:

$$(-r_{AA}) = -\frac{dC_{AA}}{dt} = (k_{1,PO} + k_{1,MIN}) C_{AA} \quad (3.39)$$

$$r_{PO} = \frac{dC_{ALD}}{dt} = k_{1,PO} C_{AA} \quad (3.40)$$

$$r_{\text{MIN}} = \frac{dC_{\text{CD}}}{dt} = k_{1,\text{MIN}} C_{\text{AA}} \quad (3.41)$$

in which t is the time, $k_{1,\text{PO}}$ and $k_{1,\text{MIN}}$ the first order rate constants for partial oxidation and mineralization, respectively, and C_{AA} , C_{ALD} , and C_{CD} the aromatic alcohol, aromatic aldehyde and carbon dioxide concentrations. Integration of eq 3.39 produces an exponential relationship between C_{AA} and t from which the value of $(k_{1,\text{PO}} + k_{1,\text{MIN}})$ may be obtained by a least squares best fitting procedure. For determining the values of $k_{1,\text{PO}}$ and $k_{1,\text{MIN}}$, division of the members of eq 3.40 by the corresponding members of eq 3.41 yields:

$$\frac{dC_{\text{ALD}}}{dC_{\text{CD}}} = \frac{k_{1,\text{PO}}}{k_{1,\text{MIN}}} \quad (3.42)$$

Then by integration of eq 3.42 it is found that:

$$C_{\text{ALD}} = \frac{k_{1,\text{PO}}}{k_{1,\text{MIN}}} C_{\text{CD}} \quad (3.43)$$

since $C_{\text{ALD}} = C_{\text{CD}} = 0$ at $t = 0$.

Figure 3.24 shows the values of first order rate constants corresponding to partial oxidation and mineralization of aromatic alcohols, obtained by regression made with experimental points of the first 4 hours of irradiation. Increasing the concentration of methanol produces a decreasing of both the rate constants, but the effect is much more evident for the mineralization constant thus confirming that methanol preferentially competes with the aromatic alcohols for the mineralizing pathway.

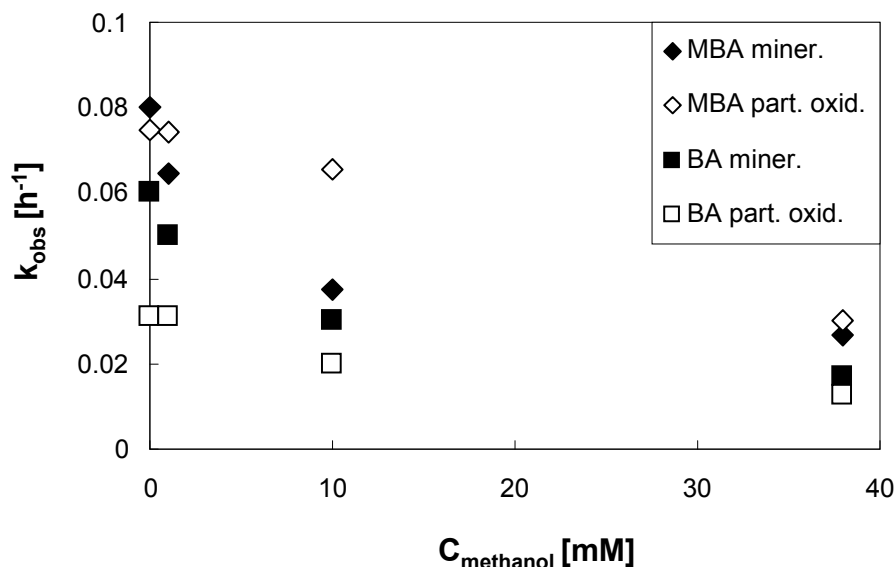


Figure 3.24. First order rate constants of mineralization and partial oxidation reactions of BA and MBA in the presence of different initial concentrations of methanol. Initial concentration of BA and MBA: 1 mM. The catalyst: HP0.5

3.4.3. Photoelectrochemical Measurements

Figure 3.25 exhibits the transformed diffuse reflectance spectra of two HP catalysts, i.e. HP0.5 and HP8; the plots report the values of $[F(R_{\infty}) \cdot E]^{0.5}$, the modified Kubelka-Munk function, versus E , the energy of exciting light. The weak low-energy shoulder may correspond to the presence of rutile phase; its intensity, proportional to the rutile amount, increases by increasing the boiling time. The corresponding band gap energies of all the used HP and commercial catalysts were obtained from plots like those reported in Fig. 3.25, assuming that the solids are indirect crystalline semiconductors (Tauc et al. 1996). The band gap values are reported in Table 3.8; these values are quite similar for predominantly anatase phase catalysts.

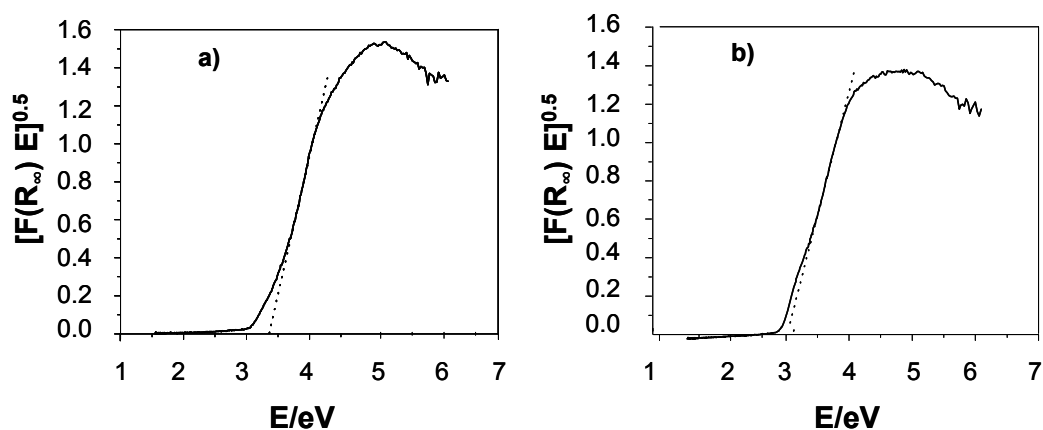


Figure 3.25. Transformed diffuse reflectance spectra of (a) HP0.5 and (b) HP8

Table 3.8. Photoelectrochemical properties of the catalysts

Catalyst	Band gap [eV]	E_{fb} (pH=7) [V]	VB edge [V]
Degussa P25	3.26	– 0.55 – 0.64 ^a	2.71
Merck	3.22	– 0.43	2.79
HP0.5	3.36	– 0.52 – 0.58 ^a	2.84
HP2	3.36	– 0.52	2.84
HP4	3.36	– 0.52	2.84
HP6	3.26	– 0.52	2.74
HP8	3.11	– 0.37	2.74

^a values obtained in the presence of ethanol

The quasi-Fermi level of electrons, E_{fb} , was determined according to literature (Roy et al. 1995) by measuring the photovoltage in the presence of methyl viologen (MV) as a function of pH value. Figure 3.26 reports the measurements obtained with all HP catalysts.

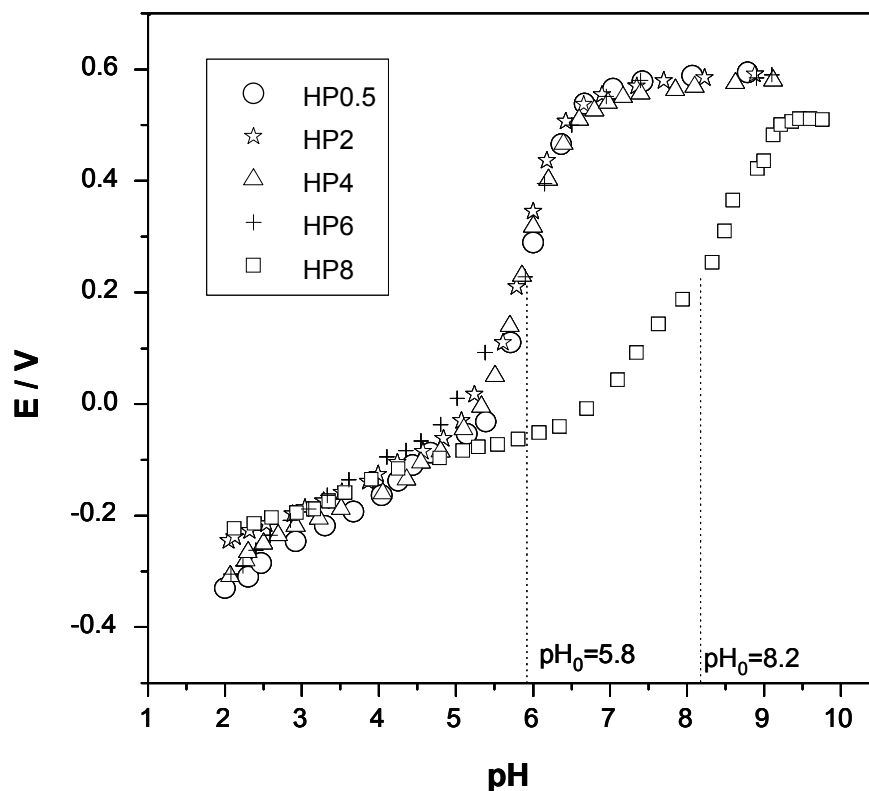


Figure 3.26. Variation of photovoltage with pH value. 50 mg of catalyst with 10 mg of MV dichloride are suspended in 50 mL of 0.1 M KNO₃ aqueous solution at room temperature. Pt, working electrode and Ag/AgCl, reference electrode

Upon increasing the pH value, a blue color is developed when approaching the inflection point, pH₀, due to formation of the MV radical cation. A lower pH₀ value corresponds to a more negative quasi-Fermi level. From pH₀ value of the corresponding titration curve (see Fig. 3.26), the quasi-Fermi level at pH 7 can be calculated via eq 3.44:

$$E_{fb} = E_{MV^{2+}/MV^{+\bullet}}^0 + k_1 (pH_0 - pH) \quad (3.44)$$

where $E_{MV^{2+}/MV^{+\bullet}}^0$ is the redox potential of the MV²⁺/MV^{+\bullet} couple and k_1 is assumed equal to 0.059 V. The E_{fb} values of all catalysts are reported in Table 3.4; it may be noted that the position of the quasi Fermi level for Degussa P25 and HP0.5 to HP6 samples is about the same (-0.55 and -0.52 V, respectively) indicating that interfacial electron transfer to MV proceeds from the anatase conduction band. However, in the case of HP8 this value is -0.37 V, which is

characteristic for rutile type TiO_2 and indicates that reduction of MV occurs via electrons trapped at the rutile conduction band. By assuming that the difference between the quasi-Fermi level potential and conduction band edge is negligible, the valence band edge values can be obtained by addition of the band gap energy. HP0.5, HP2, and HP4 band edge is located at 2.84 V, whereas it is shifted to 2.74 V for HP6, which contains a significant amount of rutile, and for HP8, nearly pure rutile.

These results indicate that the photoelectrochemical features of anatase and anatase-rutile catalysts are very similar. On this basis it is likely that these properties play a minor role in determining the differences of reactivity and selectivity shown by these samples.

In the presence of 10% (v/v) of ethanol the flatband potential of HP0.5 was shifted cathodically by about 0.06 V (see Fig. 3.27) while the shift was about 0.09V in the case of P25. Similar shifts had been reported in the literature (Redmond and Fitzmaurice 1993) when the flatband potential of titania was measured in non-diluted methanol. From these results one can conclude that in aqueous ethanol solution the reductive power of the reactive electron in anatase powders is much higher than in pure water.

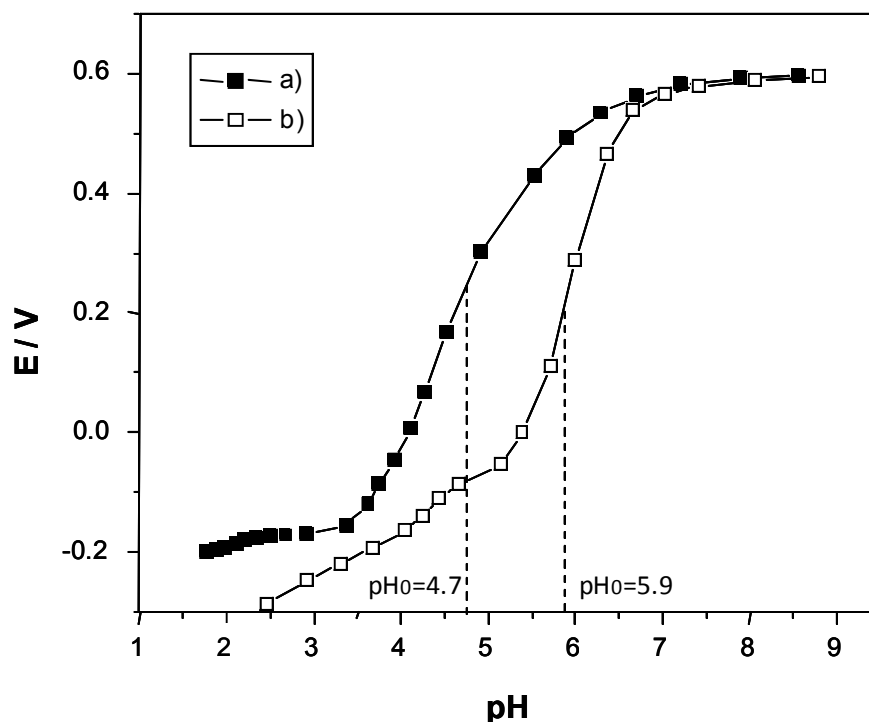


Figure 3.27. Variation of photovoltage with pH value for HP0.5 catalyst in the presence (a) and in the absence (b) of ethanol. 50 mg of catalyst with 10 mg of MV dichloride are suspended in 50 mL of 0.1 M KNO_3 aqueous solution at room temperature. Pt, working electrode and Ag/AgCl, reference electrode. For (a) case 5 ml of ethanol have been added to suspension

3.4.4. Thermogravimetric Analysis

Thermogravimetric and time derivative curves of Degussa P25 and HP0.5 samples are shown and compared in Fig. 3.28. Degussa P25 is stable up to 800 °C and it shows only 1% weight change due to the occurrence of a release of adsorbed moisture below 100 °C. For HP0.5 sample the thermogravimetric curve shows that it contains a significant amount of physically adsorbed water, about 10% weight; in fact the evaporation of bound water becomes significant at about 80 °C, and the highest rate of mass losses is reached at around 140 °C. It is remarkable that the loss of water continues up to 350 °C thus indicating that the energy of interaction between water molecules and HP0.5 surface covers a wide range.

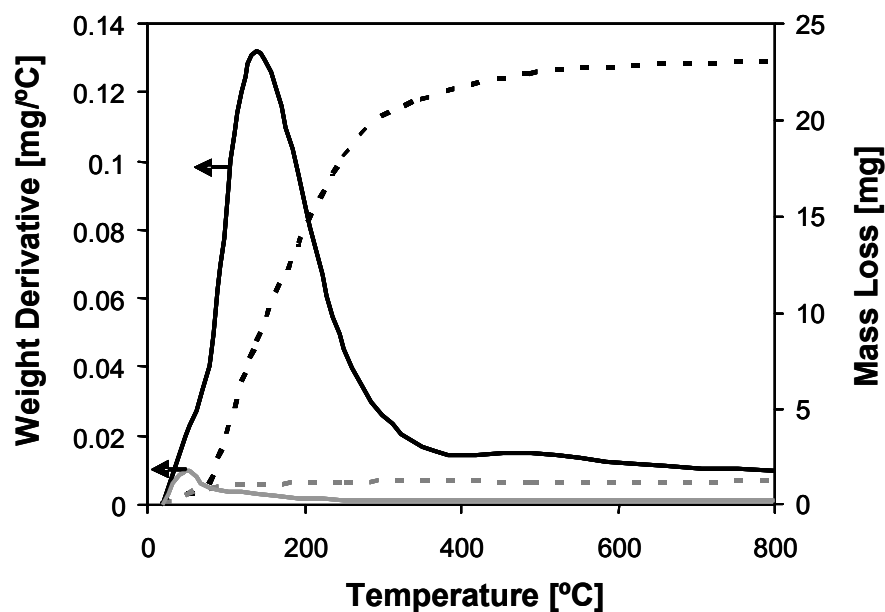


Figure 3.28. Thermogravimetric (dotted lines) and time derivative (continuous lines) curves in air of HP0.5 (—) and Degussa P25 (—)

3.4.5. ATR-FTIR Analysis

3.4.5.1. Adsorption of Water and Benzyl Alcohol on HP0.5

Figure 3.29 displays the in situ ATR-FTIR spectra acquired when exposing HP0.5 in an atmosphere of synthetic air saturated with BA and water. The great enhancement over time in the intensity of the absorption band centred at 1640 cm^{-1} due to the bending vibration mode of adsorbed molecular water indicates a remarkable hydrophilicity of the HP0.5 surface. The clear tailing of the $\delta(\text{HOH})$ vibration band towards low frequencies may be indicative of different adsorption sites for molecular water.

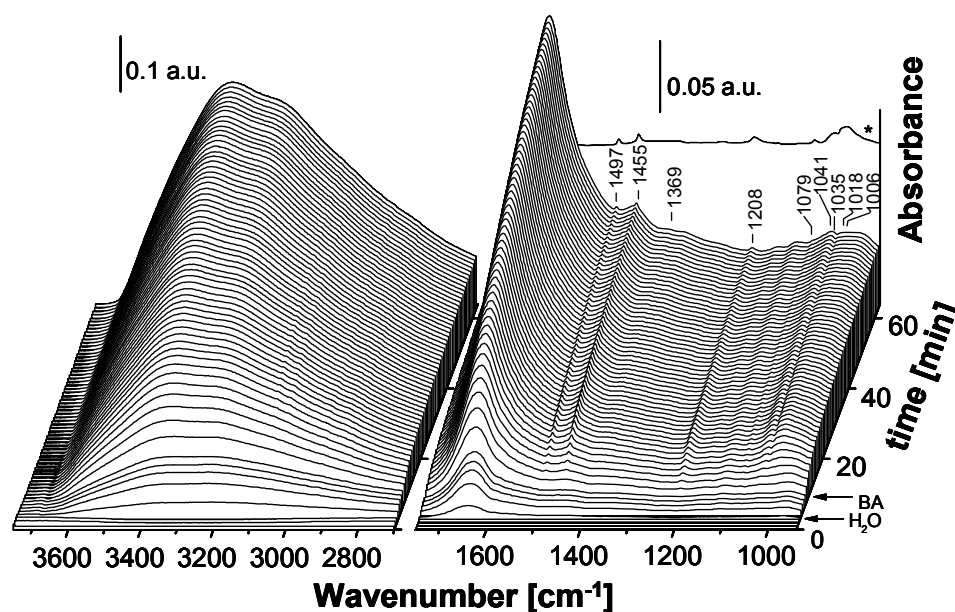


Figure 3.29. Time-resolved ATR-FTIR spectra of HP0.5 thin film recorded during adsorption of water and benzyl alcohol (BA) vapours at room temperature. The arrows indicate the time when each adsorbate was introduced in the cell. The spectrum of neat benzyl alcohol (*) multiplied by a factor 0.01 has been included for comparison

Bands growing in at 1497, 1455, 1369, 1208, 1079, 1035, 1018 and 1006 cm^{-1} are mainly the same as those in pure BA (see Fig. 3.29). At high frequencies, a broad and strong absorption showing two maxima at ca. 3400 cm^{-1} and 3240 cm^{-1} is detected indicating the presence of hydrogen-bonded perturbed OH groups and water. Two weak bands superimposed to this broad absorption appear at 3066 and 3033 cm^{-1} , which are ascribed to the C-H stretching vibrations of the aromatic ring of the alcohol. The bands at 1497 and 1455 cm^{-1} can be readily assigned to skeletal vibrations of the aromatic ring and the band centred at 1208 cm^{-1} to the C-C stretching vibration. The band centred at 1369 cm^{-1} can be attributed to the O-H in-plane deformation mode of the alcohol (Keresszegi et al. 2005). The presence of this band is indicative of non-dissociative adsorption of BA on the HP0.5 surface. According to these FTIR spectra, molecularly adsorbed BA appears to be the predominant surface organic species formed.

It is usually reported that adsorption of alcohols on metal oxide surfaces leads to the formation of alcoholate species. However, in the present study, the

identification of adsorbed benzolate on HP0.5 sample is not straightforward. To the best of our knowledge, infrared spectra of benzolate species on hydroxylated titania have not been reported up-to-date. Moreover, the close wavenumber values usually observed for the different vibration bands of alcohols and their corresponding alcoholate species hinders an unequivocal assignment. In the present case, a clear indication of benzolate formation could be obtained from the analysis of the evolution of the C-C and C-O stretching modes region (bands at 1035, 1018 and 1006 cm^{-1}), as formation of alcoholate species should be accompanied by a significant blue shift of the alcohol C-O stretching band. As adsorption of BA progresses, a band centred at 1041 cm^{-1} grows superimposed to the band located at 1035 cm^{-1} . This shift does not seem to be large enough to definitively justify the formation of benzyl alcoholate species but in any case it is indicative of the existence of different adsorption sites on the HP0.5 surface or different ways of interaction between BA and the sample surface.

Figure 3.30 displays the time evolution of the amounts of water and BA adsorbed on HP0.5; those amounts are plotted as the integrated absorbance of selected IR bands. It can be observed that in the first 10 minutes the amounts of both adsorbed water and BA continuously increase. However, the quantity of adsorbed alcohol reaches a maximum and then it monotonously decreases with time, while the amount of adsorbed water continuously increases, thus indicating that water favourably competes with BA for adsorption determining a partial displacement of BA from the TiO_2 surface.

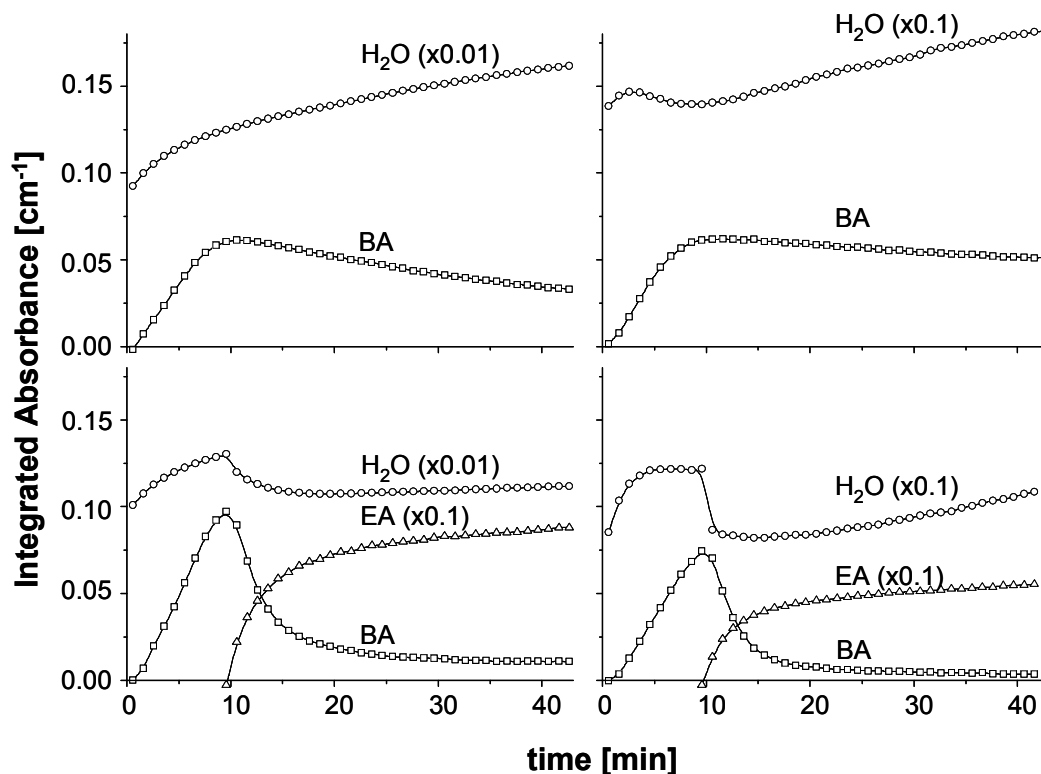


Figure 3.30. Time evolution of the integrated absorbance of IR bands at 1640 cm^{-1} (water), 1208 cm^{-1} (benzyl alcohol: BA) and 2975 cm^{-1} (ethanol: EA) determined from ATR-FTIR spectra recorded during adsorption of water and benzyl alcohol (top) and water, benzyl alcohol and ethanol (bottom) on HP0.5 (left) and Degussa P25 (right) samples. Zero time corresponds to introduction of BA into the cell. EA was introduced in the cell 10 min. after BA

3.4.5.2. Adsorption of Water and Benzyl Alcohol on Commercial TiO_2

The adsorption of BA and water on Degussa P25, following a similar experimental procedure, gives rise to spectra that show remarkable differences with respect to HP0.5 sample (see Fig. 3.31). It is worth to note that the intensity of the absorption band centred at 1645 cm^{-1} due to the $\delta(\text{HOH})$ vibration of molecularly adsorbed water appears for Degussa P25 with much lesser intensity than for HP0.5 sample (note that the integrated absorbance scale for water in Fig. 3.30 is 10 times larger for this sample), thus indicating the substantially lower hydrophilicity of the Degussa P25 surface. This finding is also in accord with thermogravimetric measurements (see Fig. 3.28). Adsorption of BA molecules with scarce modifications is demonstrated by the presence of absorption bands at

1498, 1454, 1372, 1208, 1078 and 1037 cm^{-1} . The time evolution of the integrated absorbance of IR bands at 1208 and 1640 cm^{-1} (see Fig. 3.30) shows that the amounts of BA adsorbed on HP0.5 and Degussa P25 are comparable; however the BA amount per unit surface area is ca. 5 times higher in Degussa P25 than in HP0.5. Figure 3.30 also shows that water is able to displace part of adsorbed BA but, owing to the much lesser amount of water adsorbed on Degussa P25, the displacement of the alcohol is slower than in HP0.5 sample.

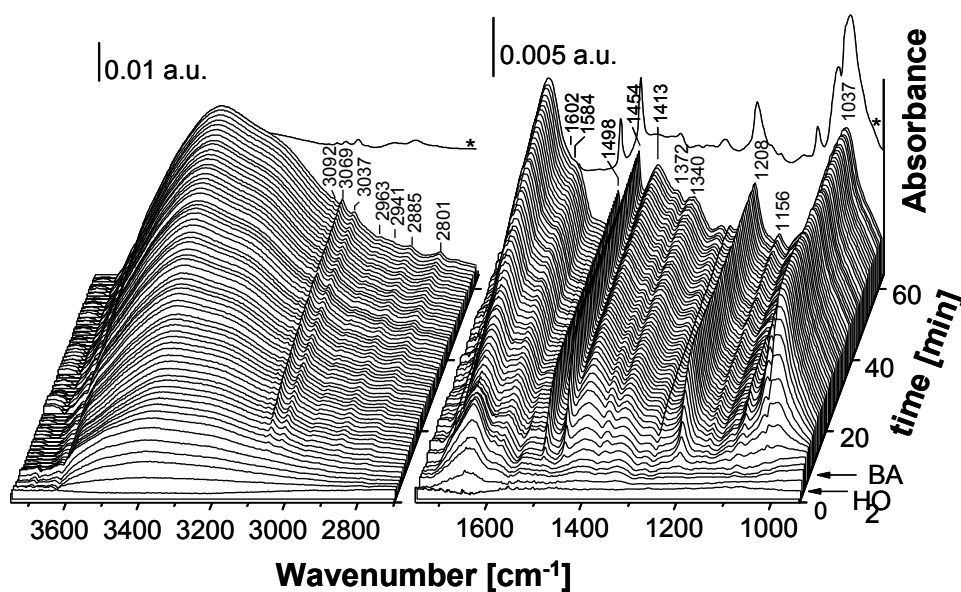


Figure 3.31. Time-resolved ATR-FTIR spectra of Degussa P25 thin film recorded during adsorption of water and benzyl alcohol (BA) vapours at room temperature. The arrows indicate the time when each adsorbate was introduced in the cell. The spectrum of neat benzyl alcohol (*) multiplied by a factor 0.01 has been included for comparison

Besides the above mentioned bands ascribable to the adsorbed alcohol, a group of absorptions (not observed with HP0.5 sample) at 1413, 1340 and 1156 cm^{-1} are also detected in the spectra displayed in Fig. 3.31. The band centred at 1156 cm^{-1} might be ascribed to a C-O stretching vibration; its blue shift with respect to the molecular alcohol is, in contrast with that previously discussed for HP0.5, large enough to indicate the formation of adsorbed benzoate species. On this basis, it may be hypothesized the presence of two distinct adsorption sites for BA on the Degussa P25 surface. Additionally, weak features are initially formed

at 1705, 1602 and 1584 cm^{-1} , although as adsorption progresses they are obscured by the strong water absorption at 1645 cm^{-1} . The frequency value of 1705 cm^{-1} points out to the presence of carbonyl group. In the high-frequency region, besides the broad features centred at ca. 3400 cm^{-1} and 3240 cm^{-1} due to hydrogen-bonded hydroxyl groups, bands at 3092, 3069, 3037, 2963, 2941, 2885 and 2801 cm^{-1} appear upon contact of BA and water with the catalyst. As shown in Fig. 3.31, the bands in the 3100-2880 cm^{-1} range match the C-H stretching bands of BA. However, the band at 2801 cm^{-1} cannot be ascribed to this species. A plausible assignment for this low frequency band would be the C-H stretching mode of an aldehyde group, what would be in agreement with an assignment to the C=O stretching of an aldehyde group for the band centred at 1705 cm^{-1} . Moreover, the bands at 1602 and 1584 cm^{-1} would agree with the presence of BAD (Keresszegi et al. 2005). As BAD is not expected to be formed upon adsorption at room temperature of BA on a hydroxylated titania surface, analysis of the benzyl alcohol purity was performed by HPLC. It was confirmed the presence of traces of BAD, which explains the origin of the corresponding signals in the infrared spectra. It is worthy to note that, even though the amount of adsorbed BA is similar on both titania, infrared bands due to adsorbed BAD are detected only in Degussa P25. This reveals a quite dissimilar ability of both titania samples to adsorb BAD, which is strongly retained on the Degussa P25 surface but hardly hold by HP0.5. This feature should be taken into account to explain the higher selectivity to partial oxidation of HP0.5 with respect to Degussa P25.

3.4.5.3. Influence of Irradiation on HP0.5

After exposure to the water and BA-saturated air atmosphere for around 1 h in the dark, HP0.5 sample was irradiated, which led to the decrease in intensity of the bands derived from the alcohol adsorption together with the further enhancement of the band at 1640 cm^{-1} , and the appearance of new overlapped bands in the 1500-1400 cm^{-1} range and at ca. 1275 cm^{-1} (see Fig. 3.32). It should be stressed that the intensity of the $\delta(\text{HOH})$ vibration band of adsorbed water continuously increased during irradiation but this growth stopped as soon as the

lamp was switched off. This result indicates either that irradiation promotes an effective photoadsorption of water on the HP0.5 surface or that water is formed as a product of the photocatalytic degradation of the aromatic alcohol. Nevertheless, the steep increase of the band suggests that the photoadsorption phenomenon is the predominant one, as the increase of water vapour pressure from the photoreaction cannot be so fast.

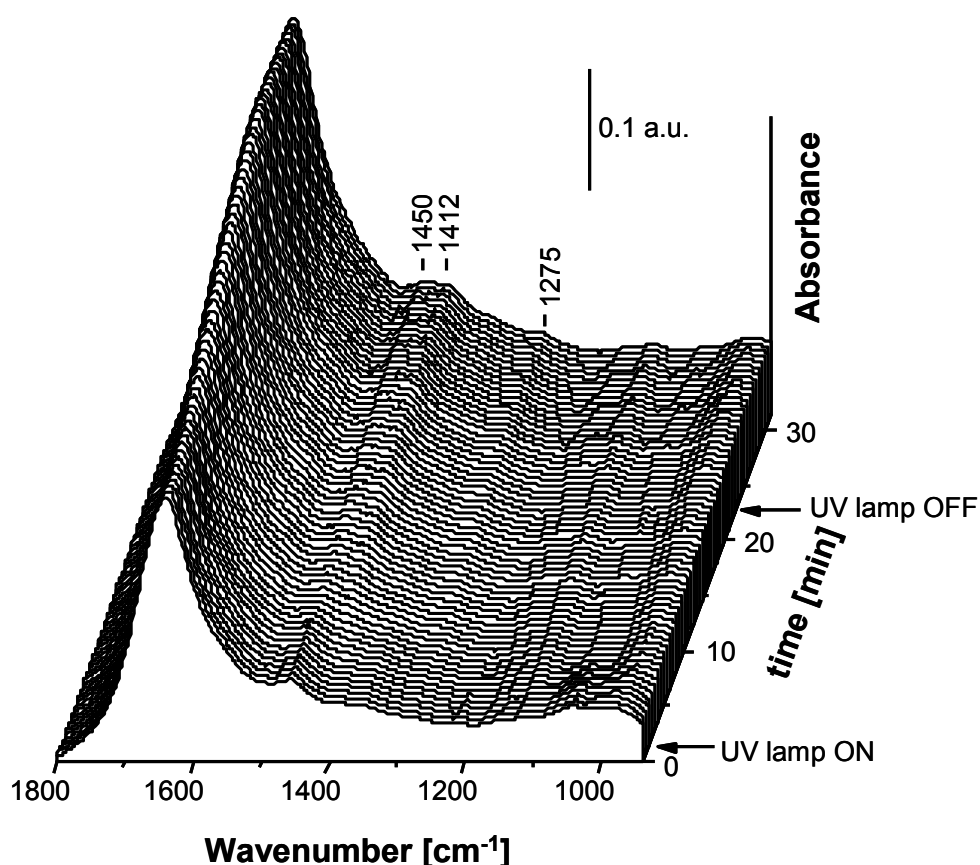


Figure 3.32. Time-resolved ATR-FTIR spectra recorded during irradiation of HP0.5 thin film in an atmosphere of synthetic air saturated with water and benzyl alcohol. The arrows indicate the time when UV lamp was switched on (it took around 2 min to reach full power) and off

The intensity and broadness of the band centred at 1640 cm^{-1} hinders the detection of other oxidation products that might be formed during irradiation such as BAD or benzoic acid, as it overlaps the carbonyl stretching region. On the other side, bands in the 1400 to 1500 cm^{-1} range and the band at 1275 cm^{-1} cannot be unequivocally assigned to specific species, but according to their wavenumber

values they might be indicative of the formation of dicarboxylic acids following the breakage of the aromatic structure. For instance, values of 1271, 1424, 1686 and 1711 cm^{-1} have been previously reported for oxalate adsorbed on TiO_2 (Dobson and McQuillan 1999). In the same study, absorption maxima centred at 1275, 1352, 1430 and 1597 cm^{-1} were found in the infrared spectra of malonic acid adsorbed on TiO_2 .

3.4.5.4. Influence of Irradiation on Commercial TiO_2

In the case of Degussa P25 sample, irradiation produces a remarkable decrease in intensity of the bands associated to adsorbed BA (see Fig. 3.33). However, in contrast with HP0.5 sample, the resulting spectra show a complexity of features, whose intensity increases with the irradiation time.

Besides the water bending band at 1645 cm^{-1} , the most prominent bands are peaked at 1711, 1686, 1603, 1530, 1496, 1451, 1415, 1403 (sh), 1274 and 1246 cm^{-1} . The assignment given to the bands in accordance to previous studies points out to the formation of BAD and benzoic acid as main oxidation products adsorbed on the Degussa P25 surface. The band centred at 1711 cm^{-1} can be ascribed to the C=O stretching vibration of the carbonyl group of BAD (Lampert et al. 1997) whereas the bands at 1603, 1530, 1496, 1451, 1415 and 1403 cm^{-1} would be indicative of the adsorption of benzoic acid as benzoate (Johnson et al. 2007; Finnie et al. 1998). Johnson et al. (2007) observed in the IR spectrum of a dried TiO_2 -benzoic acid aqueous dispersion features centred at 1602 and 1451 cm^{-1} , assigned to the aromatic ring C=C vibrations, a strong band at 1415 cm^{-1} assigned to the COO^- symmetric stretching vibration and a broad band centred at 1538 cm^{-1} , attributed to the COO^- asymmetric vibration.

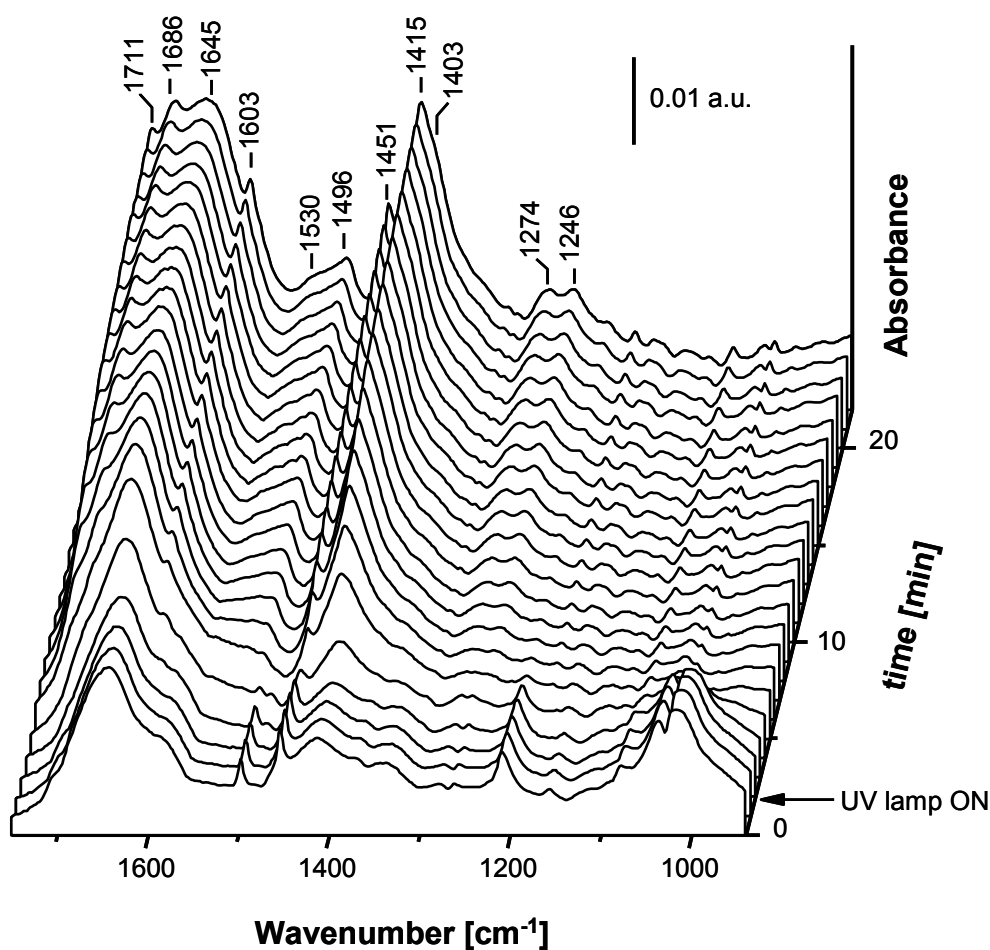


Figure 3.33. Time-resolved ATR-FTIR spectra recorded during irradiation of Degussa P25 thin film in an atmosphere of synthetic air saturated with water and benzyl alcohol. The arrows indicate the time when UV lamp was switched on (it took around 2 min to reach full power)

Upon adsorption of benzoic acid on TiO_2 , Finnie et al. (Finnie et al. 1998) observed bands at 1535 and 1505 cm^{-1} that were assigned to the $\nu_{\text{as}}(\text{COO})$ mode and bands at 1418 and 1405 cm^{-1} , ascribed to the $\nu_{\text{s}}(\text{COO})$ vibration. Splitting of the bands was ascribed to the presence of two different coordination sites on the titania surface. In both studies, the difference between the frequencies of asymmetric and symmetric COO^- group vibrations ($\Delta\nu = \nu_{\text{as}} - \nu_{\text{s}}$) was observed to be higher than that of the benzoate anion, which led to the conclusion that benzoic acid was adsorbed on TiO_2 as a bidentate complex, either chelating or bridging. On this basis, in the present study the bands centred at 1603 and 1451 cm^{-1} are assigned to skeletal vibrations of the aromatic ring in adsorbed benzoic acid,

whereas bands centred at 1530 and 1496 cm^{-1} are ascribed to COO^- asymmetric stretching vibration and the bands at 1415 and 1403 cm^{-1} to symmetric stretching. Accordingly, the largest value for the difference between the frequencies of asymmetric and symmetric COO^- group stretching vibrations would be $\Delta\nu = 1530 - 1415 = 127 \text{ cm}^{-1}$, value which is in agreement with a bidentate chelate or bridging coordination of benzoate on the titania surface (Johnson et al. 2007; Tunesi and Anderson 1992). As for the band centred at 1686 cm^{-1} , it might be ascribed to the $\text{C}=\text{O}$ stretching vibration of undissociated benzoic acid (Boczar et al. 2004) which could be attached to the TiO_2 surface through either unidentate coordination or hydrogen bonding. Finally, the bands centred at 1274 and 1246 cm^{-1} must be indicative of further oxidized compounds, most likely oxalate according to the wavenumber values reported for these species (Dobson and McQuillan 1999). In fact, it has been previously shown that oxalate hardly desorbs from the Degussa P25 surface (Dolamic and Bürgi 2006) so it might be expected on the titania surface if formed during the mineralization of the aromatic alcohol.

3.4.5.5. Influence of Ethanol Co-Adsorption on Concentration of Adsorbed Species

Aiming at giving likely explanations on the influence of aliphatic alcohols on selectivity of BA oxidation, experiments were performed exposing samples to an atmosphere of synthetic air saturated with BA, ethanol and water to obtain further information on the effect of ethanol co-adsorption on the interaction of BA with titania surfaces. The experiments were carried out by exposing the catalyst for 10 min. to BA and water and then ethanol was introduced in the cell. Figure 3.34 shows ATR-FTIR spectra recorded during the adsorption experiment. For HP0.5 and Degussa P25 catalysts, upon ethanol admission in the cell, bands centred at 1480, 1450, 1380, 1326, 1275, 1088 and 1046 cm^{-1} appear in the spectra. These features are identical to the absorptions observed in the spectrum of neat ethanol (spectra not shown) thus indicating that ethanol is adsorbed on the catalyst surface mostly as molecular species. It is worth to note that for HP0.5 the adsorption of ethanol decreased the amount of adsorbed molecular water as

indicated by the much lower intensity of the $\delta(\text{HOH})$ vibration band compared to the spectra shown in Fig. 3.29. Moreover, this band shifted toward higher wavenumber values (1654 cm^{-1}) in both titania surfaces, thus indicating an interaction between adsorbed water and ethanol species most likely through hydrogen bonding. Similar effect was observed upon ethanol adsorption in the absence of BA.

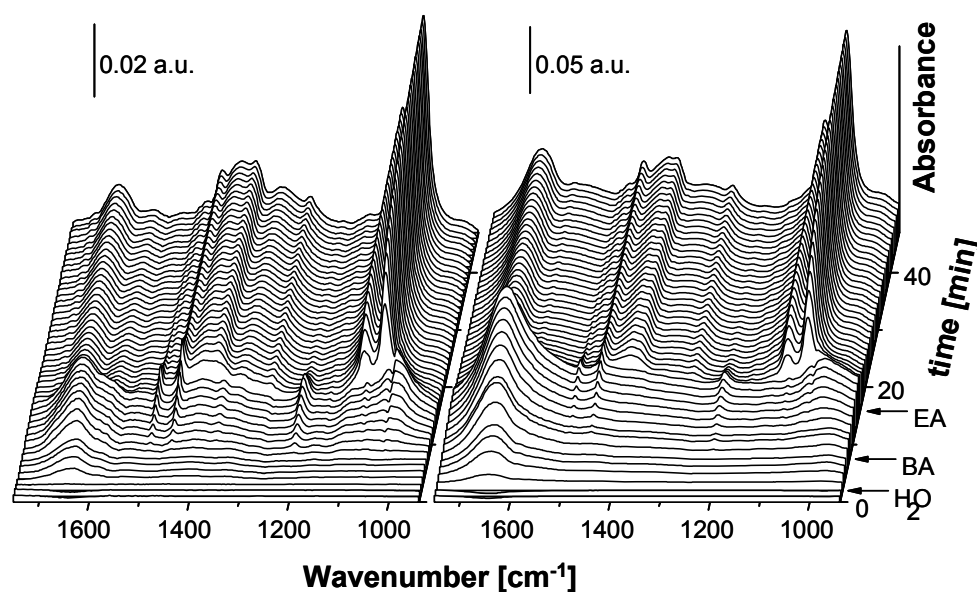


Figure 3.34. Time-resolved ATR-FTIR spectra of Degussa P25 (left) and HP0.5 (right) thin films recorded during adsorption of water, benzyl alcohol and ethanol vapours at room temperature. The arrows indicate the time when each adsorbate was introduced in the cell

From the concentration profiles reported in Fig. 3.30 it may be noted that the presence of ethanol has different effects on HP0.5 and Degussa P25. For both catalysts the amount of BA adsorbed on titania surfaces diminishes to a great extent as ethanol is introduced in the cell. Nevertheless, after 30 min of contact with ethanol vapour, weak bands corresponding to adsorbed benzyl alcohol at 1497 and 1208 cm^{-1} could still be clearly observed in the spectra of both samples (see Fig. 3.34). Exposure to ethanol vapour also produced a significant decrease of the amount of adsorbed water in both samples. However, after the initial sharp decrease, the amount of water adsorbed on Degussa P25 slowly increased with

time, while on HP0.5 sample it reached a nearly constant level, which indicates that ethanol competes more strongly with water for adsorption on HP0.5 sample than on the commercial titania.

3.4.5.6. Influence of Ethanol Co-adsorption on Photooxidation Products

Subsequent irradiation of HP0.5 sample results in the appearance of broad overlapping bands at ca. 1565 and 1522 cm^{-1} , that can be assigned to carboxylate species derived from ethanol photo-oxidation (Kozlov et al. 2000) and the growing in of bands centred at 1407 and 1350 cm^{-1} (see Fig. 3.35). Note particularly that, in contrast with results obtained in the absence of ethanol, the carbonyl stretching region is not hidden by the $\delta(\text{HOH})$ band due to the lower adsorbed water content that induces the co-adsorption of ethanol. Therefore, it can be now clearly observed that no characteristic bands of BAD are formed.

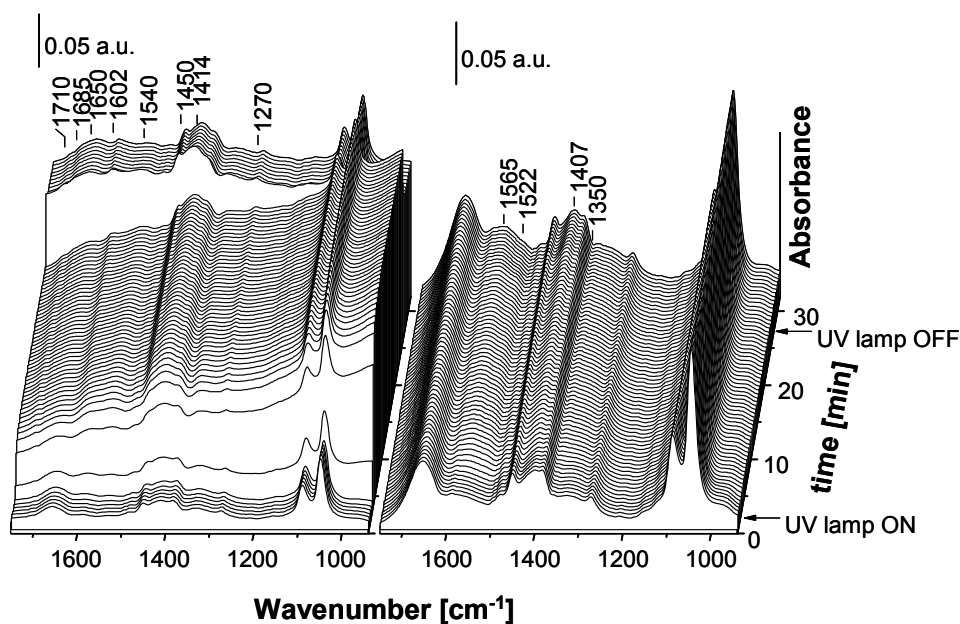


Figure 3.35. Time-resolved ATR-FTIR spectra recorded during irradiation of Degussa P25 (left) and HP0.5 (right) thin film in an atmosphere of synthetic air saturated with water, benzyl alcohol and ethanol. The arrows indicate the time when UV lamp was switched on (it took around 2 min to reach full power) and off. Spectra of Degussa P25 sample recorded after switching off the lamp have been shifted upwards by 0.12 absorbance units for clarity

In the case of Degussa P25, UV irradiation gives rise to a large increase of the spectra baseline at wavenumbers below 2000 cm^{-1} that peak at ca. 900 cm^{-1} . This phenomenon was reproducible and was observed only when ethanol was adsorbed on Degussa P25, either in the presence or absence of co-adsorbed BA. This UV-induced infrared absorption has been already reported for dry Degussa P25 and it has been attributed to excitation of shallow trap electrons to the conduction band (Warren and McQuillan 2004). UV light also produces the development of bands centred at 1710, 1685, 1650, 1602, 1540, 1450, 1414 and 1270 cm^{-1} indicative of the presence on the Degussa P25 surface of products derived from the oxidation of both alcohols. The finding that the bands of BA oxidation products appear also in the presence of ethanol seems to indicate that ethanol does not affect the BA oxidation pathways but it only decreases BA concentration on catalyst surface.

3.5. Determination of Photoadsorption Capacity of Polychrystalline TiO_2 Catalyst in Irradiated Slurry

This chapter of the thesis work presents a quantitative method able to determine the amount of substrate photoadsorbed onto the catalyst surface in liquid-solid systems under reaction conditions. The method is applied to the following photocatalytic processes carried out in aqueous suspensions: (i) oxidation of phenol in the presence of a commercial TiO_2 catalyst (Degussa P25); and (ii) oxidation of benzyl alcohol in the presence of a HP TiO_2 (HP0.5) catalyst. The influence of substrate concentration, catalyst amount and irradiation power on photoadsorption is investigated. The equilibrium data of photoadsorption capacity is fitted versus the liquid-phase substrate concentration by using the following adsorption isotherms: Langmuir, Freundlich, and Redlich-Peterson. By taking into account the photoadsorption phenomena, the kinetic modelling of the photooxidation processes are carried out for each of adsorption isotherms and the parameters of the models are determined. In the case of benzyl alcohol the results indicate that the Langmuir adsorption isotherm best fits the photoadsorption phenomenon while for phenol the Freundlich adsorption isotherm gives a better fit.

In both cases all the parameters of kinetic model are favourably affected by an increase of the photon flow absorbed per unit mass of catalyst.

3.5.1. Photoreactivity Experiments

As expected, no photodegradation of benzyl alcohol or phenol was observed in oxygenated solution under irradiation but without catalyst. In the presence of catalyst but without irradiation no oxidation of benzyl alcohol or phenol was detected but a small adsorption of benzyl alcohol was measured while for phenol it was negligible.

The photoreactivity runs carried out by bubbling pure oxygen or air gave the same results so that it may be concluded that the oxygen concentration is not limiting the substrate degradation rate at the used experimental conditions.

Figures 3.36 and 3.37 report the photoreactivity results obtained from representative runs carried out at different initial benzyl alcohol concentrations and two lamp powers; for all of these runs the same amount of catalyst was used.

In Figures 3.36-3.38 the concentration values reported for the zero time correspond to those of the starting solution, i.e. without catalyst and irradiation. It must be reported that at the end of dark period (lasting 30 minutes) the benzyl alcohol concentration in the suspension is a little lesser than that of the starting solution. The calculations of photoadsorbed amount, however, have been performed by hypothesizing that all the molecules present on the catalyst surface participate to the photoprocess and therefore the concentration of the starting solution has been taken into account.

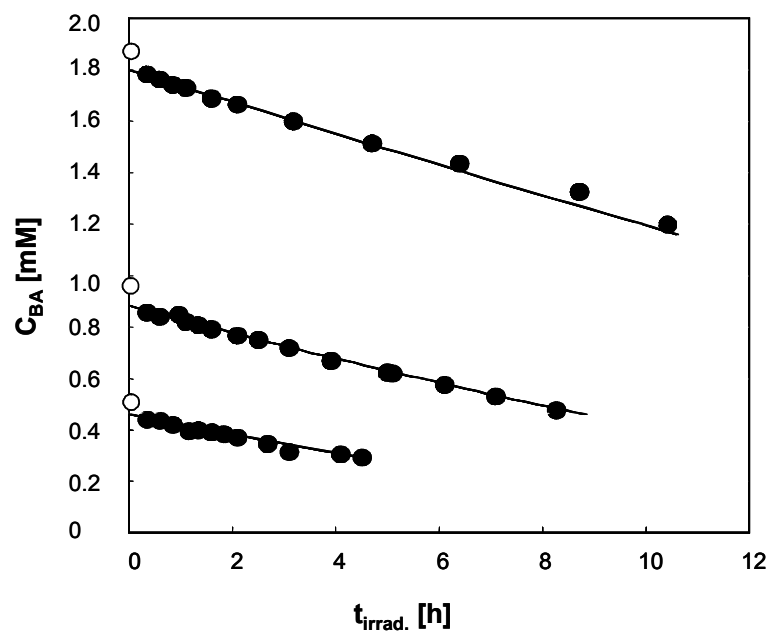


Figure 3.36. Experimental values of benzyl alcohol concentration vs. irradiation time. HP0.5 amount: 0.4 g/L, lamp power, 125 W. The empty symbols indicate the concentration of starting solution. The solid lines represent the Langmuir photoadsorption model (eq 1.24)

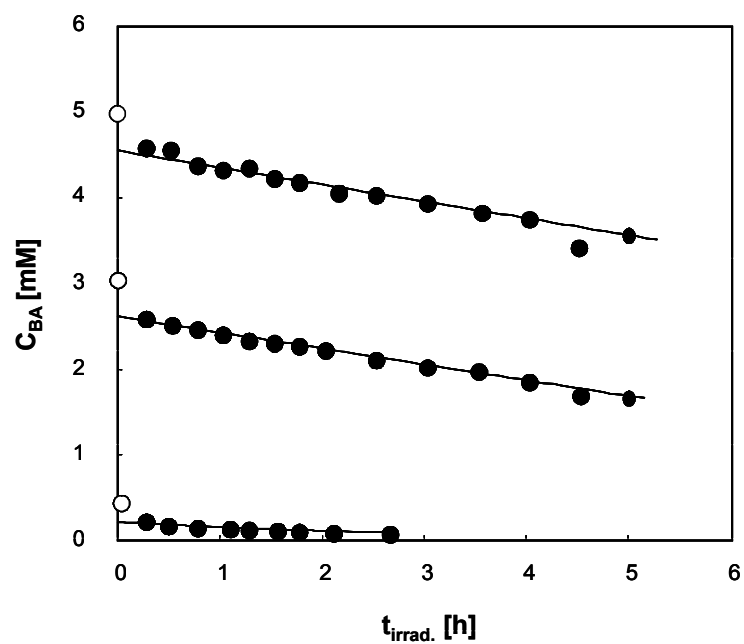


Figure 3.37. Experimental values of benzyl alcohol concentration vs. irradiation time. HP0.5 amount: 0.4 g/L, lamp power, 500 W. The empty symbols indicate the concentration of starting solution. The solid lines represent the Langmuir photoadsorption model (eq 1.24)

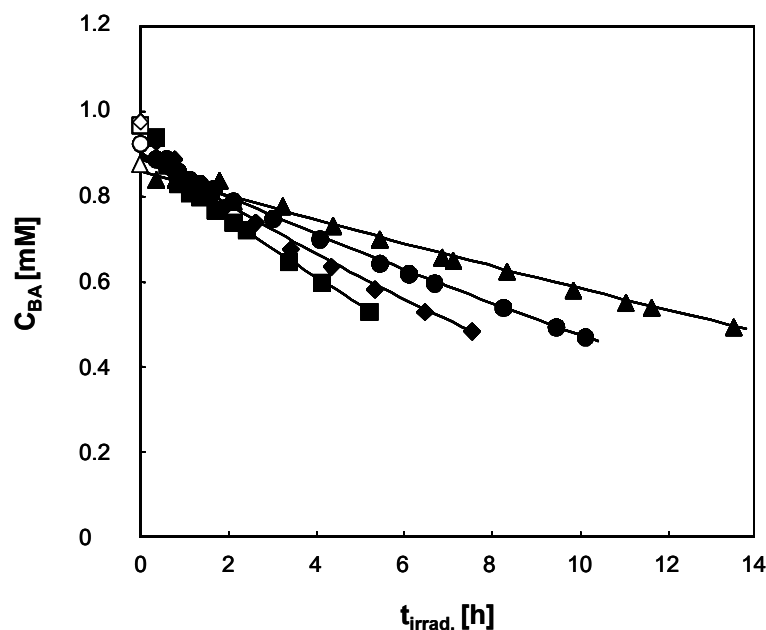


Figure 3.38. Experimental values of benzyl alcohol concentration vs. irradiation time. HP0.5 amount: ($\blacktriangle$) 0.1 g/L; ($\bullet$) 0.2 g/L; ($\blacklozenge$) 0.6 g/L; ($\blacksquare$) 0.8 g/L. Lamp power, 125 W. The empty symbols indicate the concentration of starting solution. The solid lines represent the Langmuir photoadsorption model (eq 1.24)

BAD was the intermediate product detected in the course of BA photocatalytic oxidation, CO_2 being the other oxidation product. No other intermediates were detected in all the course of the runs indicating that at the used experimental conditions the produced aldehyde does not compete with alcohol for photoadsorption and oxidation. This feature implies that the BA kinetics did not change in the course of the runs due to the accumulation of intermediate products in the reaction ambient.

Figure 3.38. reports the results obtained from runs carried out with different amounts of catalyst; for all these runs the same initial benzyl alcohol concentration and lamp power were used.

Figures 3.39 and 3.40 report the photoreactivity results obtained from representative runs carried out at different initial phenol concentrations (with the same amount of catalyst) and at different amounts of catalyst (with the same initial phenol concentration), respectively.

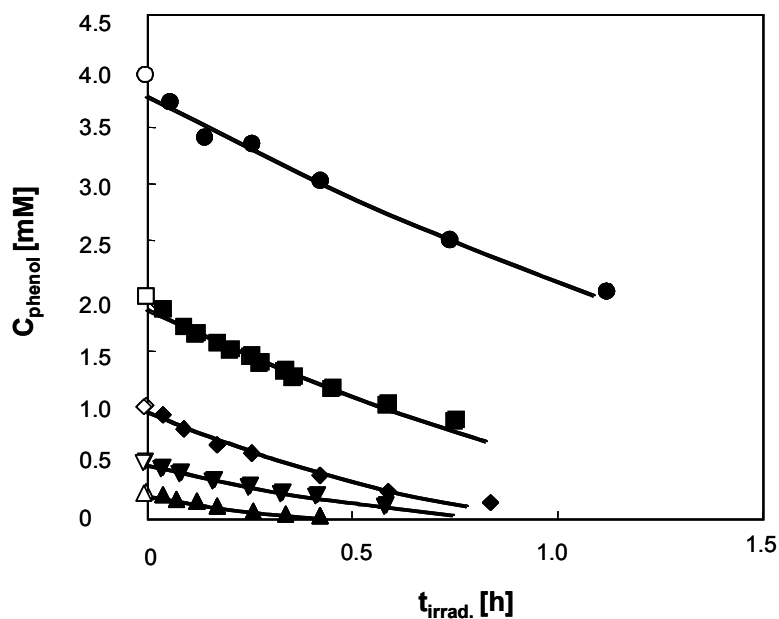


Figure 3.39. Experimental values of phenol concentration vs. irradiation time. TiO_2 P25 catalyst amount: 0.32 g/L, lamp power, 500 W. The empty symbols indicate the concentration of starting solution. The solid lines represent the Freundlich photoadsorption model (eq 1.49)

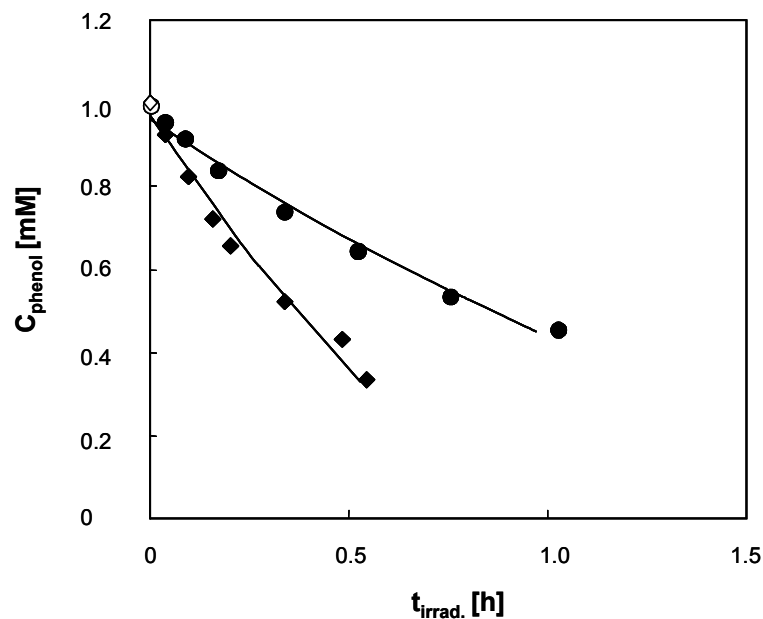


Figure 3.40. Experimental values of phenol concentration vs. irradiation time. TiO_2 P25 catalyst amount: (●) 0.05 g/L and (◆) 0.64 g/L. Lamp power, 500 W. The empty symbols indicate the concentration of starting solution. The solid lines represent the Freundlich photoadsorption model (eq 1.49)

In Figures 3.39 and 3.40 the phenol concentration values reported for the zero time correspond to those of the starting solution, i.e. without catalyst and irradiation. It is useful to report that the adsorption of phenol in the dark is negligible so that the phenol concentration in the solution did not change after the addition of the catalyst.

In the course of phenol photocatalytic oxidation, the main products determined through TOC and HPLC analyses were CO₂, hydroquinone and catechol, as expected having in mind that the photocatalytic oxidation of organic compounds on illuminated TiO₂ proceeds via [•]OH attack on the substrate. The experimental results indicate that since the start of irradiation two parallel reaction pathways take place: direct mineralization of phenol to CO₂ (occurring through a series of reactions taking place over the catalyst surface and producing intermediates not desorbing to the bulk of solution) and partial oxidation to hydroxylated compounds (Salaices et al. 2004).

The carbon balance between reacted phenol and produced CO₂ and dihydroxylated compounds was satisfactorily satisfied (>98%) for phenol conversion less than 60%. On this basis it may be assumed that at the used experimental conditions the stable intermediate products of phenol photodegradation do not compete with phenol for photoadsorption and oxidation, at least in the time needed for 60% conversion.

This feature implies that the phenol degradation kinetics did not change in the course of the runs due to the accumulation of intermediate products in the reaction ambient. As a consequence only the phenol concentration values relative to conversion below 60% have been taken into account in the course of photoadsorption modelling.

3.5.2. Benzyl Alcohol and Phenol Photoadsorption

Non-linear optimization techniques have been applied to determine isotherm parameters. It is well known (Ncibi 2008) that the use of linear expressions, obtained by transformation of non-linear one, distorts the experimental error by creating an inherent error estimation problem. In fact the

linear analysis method assumes that: (i) the scatter of points follows a Gaussian distribution; and (ii) the error distribution is the same at every value of the equilibrium liquid-phase concentration. Such behaviour is not exhibited by equilibrium isotherm models since they have non-linear shape; for this reason the error distribution gets altered after transforming the data to linear. Non-linear regression method avoids such errors, making this analysing technique the most appropriate to obtain more realistic isotherm parameters.

In this work, among different error functions the Marquardt's percent standard deviation (MPSD) was used to enable the optimization process to determine and evaluate the fit of the isotherm equation to the experimental data. This error function is similar to a geometric mean error distribution which is modified to allow for the number of degrees of freedom of the system. For each case the isotherm parameters were determined by minimising the MPSD function across the liquid phase concentration range using the DataPlot solver (Heckert and Filliben 2003a; Heckert and Filliben 2003b). It was assumed that both the liquid phase concentration and the solid phase concentration contribute equally to weighting the error criterion chosen for the model solution procedure.

3.5.2.1. Benzyl Alcohol Photoadsorption

The fitting of the Langmuir, Freundlich and Redlich-Peterson models to the data has been firstly applied to the photoreactivity results obtained from runs carried out at equal mass of catalyst and lamp power. For the Langmuir model, the following procedure has been followed. In order to have an estimate of parameters values, the data at high initial concentration of benzyl alcohol have been fitted to eq 1.30 and those at low initial concentration to eq 1.37. The parameters obtained by these fitting procedures have been used to determine K_L^* and N_s^* by means of eq 1.42. As inequalities 1.25 and 1.31 were not strongly satisfied, the fitting procedure has been repeated by using the general equation of the proposed model (eq 1.24).

For the runs carried out at different catalyst amounts the general equations for the liquid concentration profile (eqns. 1.24, 1.49, and 1.57) have been used.

For Freundlich and Redlich-Peterson isotherms the fitting obtained for each run was quite satisfactory ($R^2 > 0.98$); however for the runs carried out at equal amount of catalyst, the Freundlich and Redlich-Peterson parameters values showed a dependence on initial benzyl alcohol concentration; on the contrary same values were obtained for Langmuir parameters. On this basis the Langmuir isotherm seems to best describe the photoadsorption phenomenon of benzyl alcohol on HP0.5. The continuous lines drawn through the data of Figures 3.36-3.38 represent eq 1.24 and a very satisfactory fitting ($R^2 > 0.99$) may be noted. The values of kinetic and Langmuir parameters (k , K_L^* and N_s^*), obtained by the best fitting procedure, are reported later (see Figure 3.43).

The suitability of Langmuir model to describe the photoadsorption phenomenon has been further checked by using the linear form of Langmuir equation (1.42). Figure 3.41 reports the values of the $C_{L,0}/(C_{T,0} - C_{L,0})$ group obtained from runs carried out at equal mass of catalyst and lamp power versus the benzyl alcohol equilibrium concentration. The straight lines drawn through the data represent eq 1.42 and a very good fitting ($R^2 > 0.99$) may be noted.

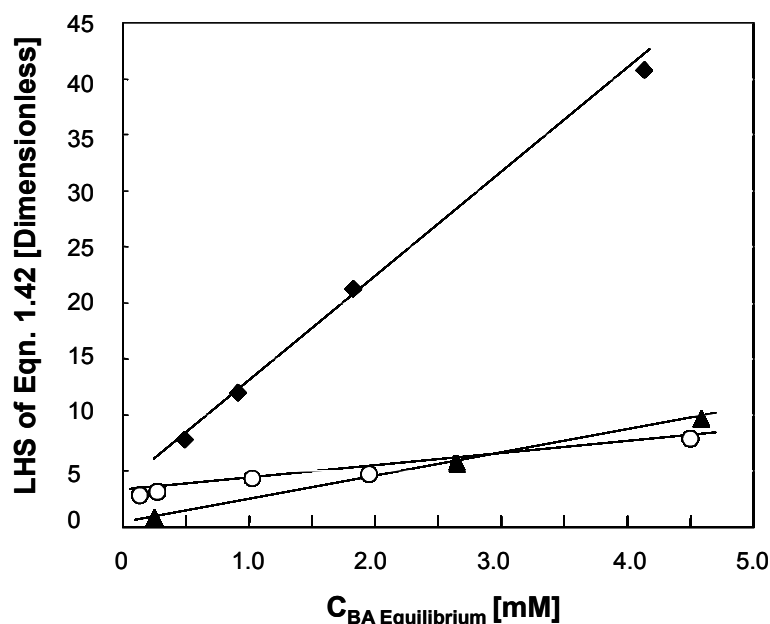


Figure 3.41. Linear form of Langmuir model. The left hand side of eq 1.42, $C_{L,0}/(C_{T,0} - C_{L,0})$, versus $C_{L,0}$ for runs carried out under irradiation with lamp power of 125 W ($\blacklozenge$), 500 W ($\blacktriangle$) and in the dark ($\circ$). The dark data are multiplied for 10^{-3} . The solid lines represent the Langmuir photoadsorption model (eq 1.42)

The slopes and linear coefficients of lines allow to determine the N_s^* and K_L^* values corresponding to these runs; these values are almost the same of those determined by means of eq 1.24 (error percentage, $\pm 4\%$). Figure 3.41 also reports the adsorption results obtained in the absence of irradiation, i.e. in the dark. A least-squares best fitting procedure allows to determine the values ($R^2 > 0.99$) of the Langmuir equilibrium constant and the maximum adsorption capacity in the absence of irradiation, i.e. $K_L = 350\text{ M}^{-1}$ and $N_s = 4.57 \cdot 10^{-6}\text{ mol per gram of catalyst}$.

The effect of catalyst amount on photoadsorption capacity is shown in Figure 3.42. This Figure reports the benzyl alcohol moles photoadsorbed per unit mass of catalyst versus the catalyst amount; the reported data refer to runs carried out at equal initial benzyl alcohol concentration and lamp power. From the observation of data of Figure 3.42 it may be noted a decrease of specific photoadsorption capacity by increasing the catalyst amount, differently from that expected on thermodynamic basis for which an increase of catalyst amount determines a corresponding increase of adsorbed substrate.

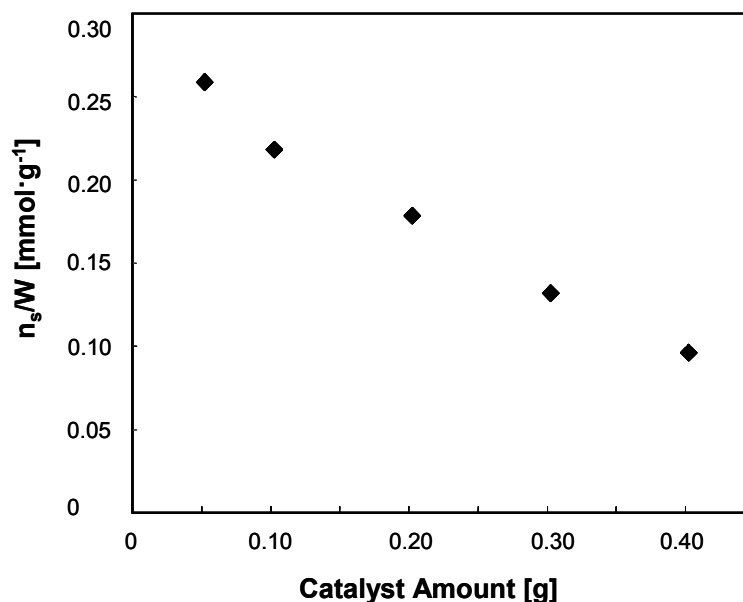


Figure 3.42. Photoadsorbed amount of benzyl alcohol per unit mass of catalyst, n_s/W , versus the mass of catalyst. Initial benzyl alcohol concentration, 1 mM, lamp power, 125 W

This finding may be explained by considering that an increase of catalyst amount determines an increase of photons absorbed by the suspension but the photon flow absorbed by the unit mass of catalyst decreases. As photoadsorption is likely to be strongly dependent on absorbed photon flow, the increase of catalyst amount is eventually detrimental for specific photoadsorption.

The consideration that the photon flow absorbed by the unit mass of catalyst is the parameter mainly affecting the photoadsorption phenomenon is strengthened by the results reported in Figure 3.43. This Figure reports the values of the model parameters, K_L^* , N_S^* and k , versus the absorbed photon flow per unit mass of catalyst. The K_L and N_S values obtained from dark experiments are also reported. It may be noted that all parameters increase by increasing the specific photon absorption. While it is known that in thermal catalysis a temperature increase determines an increase of kinetic and equilibrium adsorption constants, the results of Fig. 3.43 also show a beneficial effect of absorbed photons on the photoadsorbed amount of solute. This effect is very noticeable if a comparison is done between irradiated and dark conditions. The values of K_L^* and N_S^* are one and two orders of magnitude, respectively, higher than those obtained in the absence of irradiation.

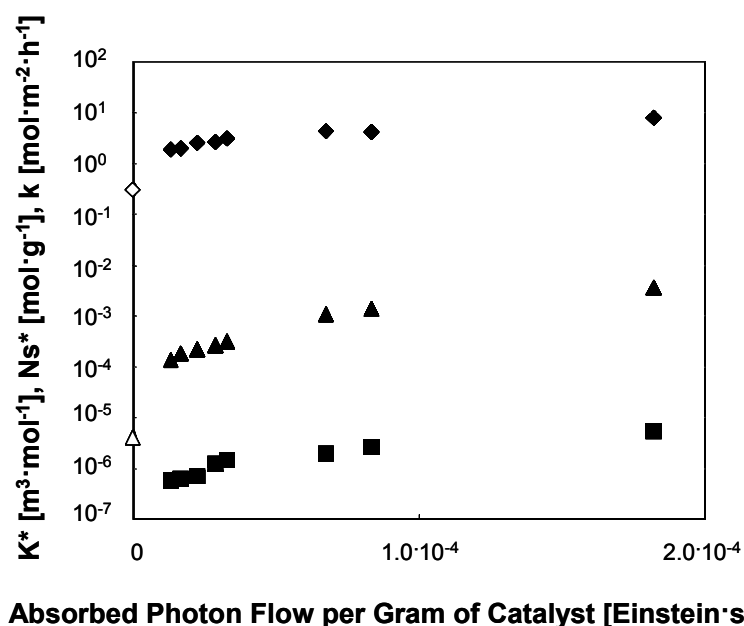


Figure 3.43. Values of kinetic and Langmuir model parameters (see eq 1.24) versus the absorbed photon flow per unit mass of catalyst. $\blacklozenge$, K^*_L ; $\blacktriangle$, N_s^* ; $\blacksquare$, k . The empty symbols refers to dark conditions

3.5.2.2. Phenol Photoadsorption

The fitting of photoreactivity data obtained from runs carried out at equal mass of catalyst and at different catalyst amounts has been carried out by applying the general equations of Langmuir, Freundlich and Redlich-Peterson isotherms (eqns. 1.24, 1.49, and 1.57). For Langmuir and Redlich-Peterson isotherms the fitting obtained for each run was quite satisfactory ($R^2 > 0.98$); however for the runs carried out at equal amount of catalyst, the Langmuir and Redlich-Peterson parameters values showed a dependence on initial phenol concentration; on the contrary same values were obtained for Freundlich parameters. On this basis the Freundlich isotherm seems to best describe the photoadsorption phenomenon of phenol on commercial TiO_2 catalyst (Degussa P25). The continuous lines drawn through the data of Figures 3.39 and 3.40 represent eq 1.49 with $n = 2$ and a satisfactory fitting ($R^2 > 0.98$) may be noted.

The suitability of Freundlich model to describe the photoadsorption phenomenon has been further checked by using the Freundlich equation (eq 1.43) in its linear form. Figure 3.44 reports the values of the n_s/W group

obtained from runs carried out at equal mass of catalyst versus the square root of phenol equilibrium concentration. The straight line drawn through the data represents eq 1.43; the slope value of this line, equal to the $(K_F^* \cdot N_s^*)$ product, is 0.0112, very near to the 0.0107 value obtained from the best fitting procedure.

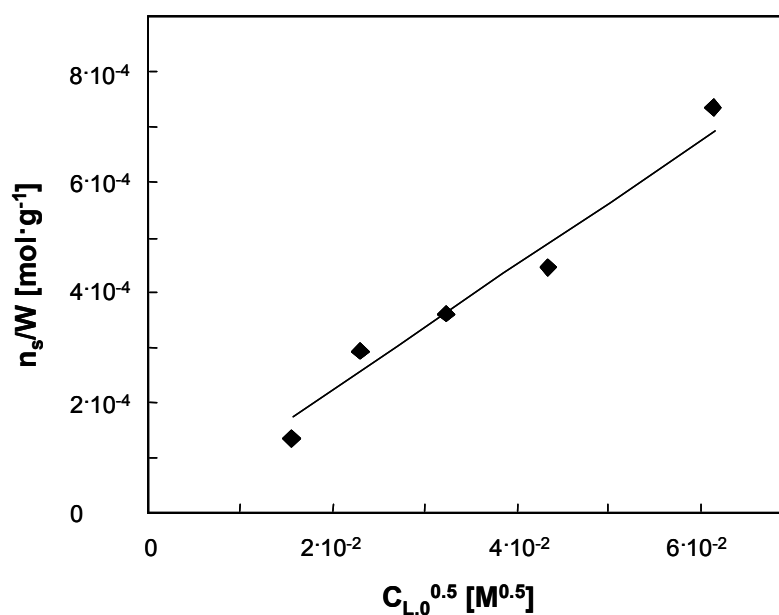


Figure 3.44. Linear form of Freundlich model. The left hand side of eq 3.24, n_s/W , versus $C_{L,0}^{0.5}$ for runs carried out under irradiation with lamp power of 500 W. The solid line represents the Freundlich photoadsorption model (eq 1.43)

The values of kinetic and Freundlich parameters (k , K_F^* and N_s^*), obtained from runs carried out with different amounts of catalyst, are reported in Figure 3.45 versus the absorbed photon flow per unit mass of catalyst. These values show the same feature of Langmuir parameters obtained for benzyl alcohol oxidation, i.e. they decrease by decreasing the photon flow absorbed by the unit mass of catalyst. As in the case of benzyl alcohol, the consideration that the photon flow absorbed by the unit mass of catalyst is the parameter mainly affecting the photoadsorption phenomenon is strengthened by the results reported in Figure 3.45.

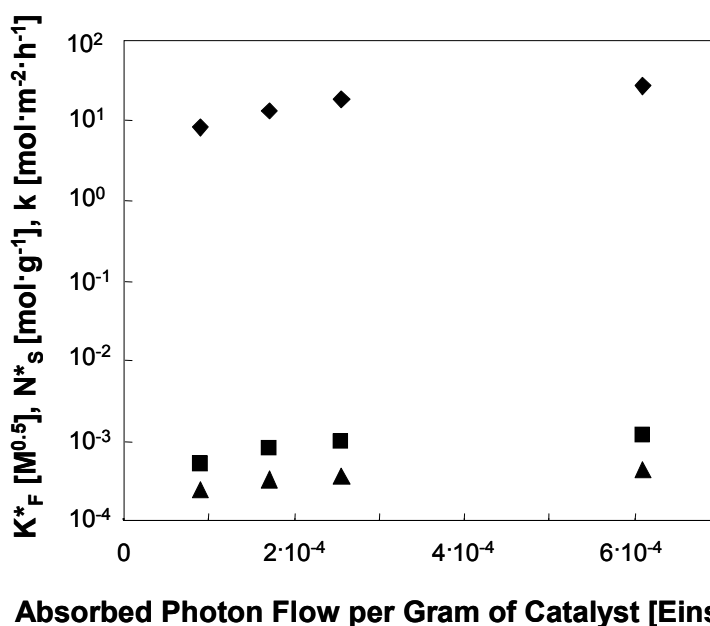


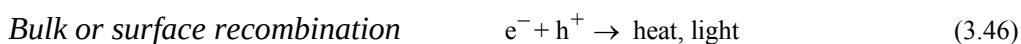
Figure 3.45. Values of kinetic and Freundlich model parameters (eq 1.49) versus the absorbed photon flow per unit mass of catalyst. ◆, K_F^* ; ▲, N_s^* ; ■, k

3.5.3. Reaction Mechanism

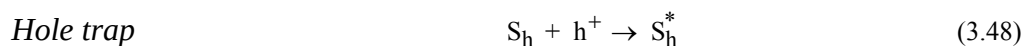
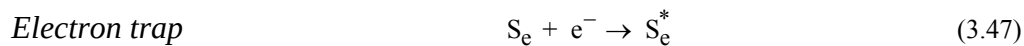
According to the preceding discussion, the primary events occurring at the photocatalyst surface may be described by the following mechanism. The primary photochemical act, following the light absorption by the semiconductor, is the generation of electron/hole pairs. The light absorbed by the unit surface of catalyst and unit time produces equivalent bulk concentrations of charge carriers, e^- and h^+ :



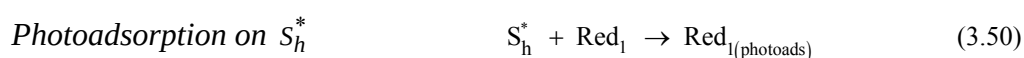
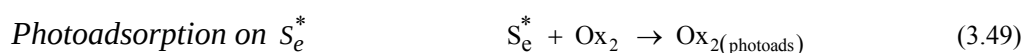
The charge carriers can recombine either in the bulk or in the surface:



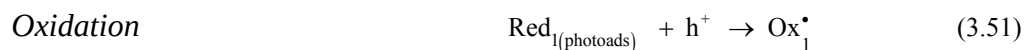
or migrate to the surface where they are trapped by suitable electron and hole traps forming the corresponding active centers:



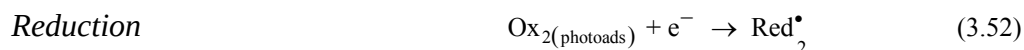
If electron acceptors (Ox_2 , like oxygen) or electron donors (Red_1 , as organic substrates) are present at the surface, they can be photoadsorbed on the active centers:



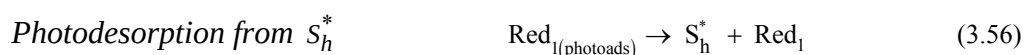
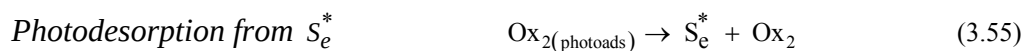
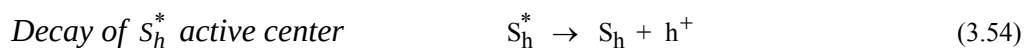
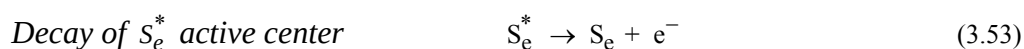
The photoadsorption steps are followed by oxidation of the organic substrate:



and by reduction of the oxidant species:



Competitive with reactions 3.47-4.50 are the back reactions:



The combined reactions 3.45 and 3.46 or 3.47, 3.48, 3.53 and 3.54 or 3.49, 3.50, 3.55 and 3.56 yield a net cycle, where there is not useful use of the absorbed photons.

The radicals formed through reactions 3.51 and 3.52 may be further transformed either by subsequent reaction with photogenerated active species, or through reaction with solvent, other species present in solution (such as O_2 , H_2O_2 , O_2^-), elimination of molecular groups or ions (Piccinini et al. 1997; Calza et al. 1997) or dimerisation (Minero et al. 1995). The additional transformations may lead to the complete degradation of the organic compound to CO_2 and inorganic anions. In addition to all the preceding reactions, which hold for a substrate that can only be oxidized, there are possible concurrent oxidative and reductive reactions, as observed for halomethanes degradation (Calza et al. 1997).

4. CONCLUSIONS

The first part of thesis reports some investigations in order to establish a link between photocatalysis and organic chemistry using new selective home made titanium photocatalysts and performing for selective photocatalytic oxidation of some aromatic alcohols to corresponding aldehydes in water. The mild experimental conditions used, consisting of aqueous suspensions free of any organic co-solvents, absence of heavy metals, high temperatures or pressures, can propose this process as a green route for partial alcohol oxidation. These studies could be a landmark in TiO_2 photocatalysis in general and partial oxidation in particular (Yurdakal et al. 2008; Augugliaro et al. 2008a; Yurdakal et al. 2009b). In addition, an industrial process by using continuous annular fixed bed reactor which includes home-made TiO_2 covered spheres was investigated and modelled for partial oxidation of MBA in water (Yurdakal et al. 2010).

The second part of thesis has been devoted to selective oxidation of BA to BAD in the presence of small amount of some aliphatic alcohols as hole trap in water by using irradiated HP and commercial TiO_2 catalysts in order to study hole trap effect onto selectivity and activity depend on the catalysts. Moreover, in order to investigate the reason why HP TiO_2 catalyst are much more selective than commercial ones and hole trap effect onto the selectivity were studied very deeply by performing photoelectrochemical and *in situ* ATR-FTIR measurements (Augugliaro et al. 2008b; Augugliaro et al. 2008c).

At the last part of the thesis, the first time a quantitative method able to determine the amount of substrate photoadsorbed onto the catalyst surface in liquid-solid systems under reaction conditions was investigated. The influence of substrate concentration, catalyst amount and irradiation power on photoadsorption is considered. The equilibrium data of photoadsorption capacity is fitted versus the liquid-phase substrate concentration by using Langmuir, Freundlich, and Redlich-Peterson adsorption isotherms. By taking into account the photoadsorption phenomena, the kinetic modelling of the photooxidation processes are carried out for each of these adsorption isotherms and the parameters of the models are determined. Moreover since photoadsorption could

give information for catalyst surface and subtract under real experimental condition, the work have another importance from other surface determination techniques, such as FTIR, NMR or TEM. (Yurdakal et al. 2009a; Augugliaro et al. 2009).

4.1. Green Synthesis: Selective Photocatalytic Oxidation of Aromatic Alcohols

At this part of the investigation, the photocatalytic oxidation of BA and MBA has been performed in pure water by using commercial TiO₂ samples (Rutile Sigma-Aldrich, Merck, Degussa P25) and rutile TiO₂ prepared from TiCl₄ at low temperature (333K) and characterized by using BET, SEM and XRD analyses. A particular attention has been devoted to the identification of the produced aromatic compounds along with the formed CO₂. Oxidation products, such as the corresponding aromatic aldehyde and acid, as well as mono- and di-hydroxylated aldehydes have been detected. The HP rutile sample gave a marked selectivity towards the formation of the aromatic aldehyde (38% and 60% for BA and MBA, respectively), resulting in a 3 to 7 fold improvement with respect to commercial samples, the only by-product being CO₂. This catalyst was found to be the most selective in the formation of aldehyde in water. By using the commercial or the calcined HP samples many hydroxylated aromatics were detected besides the aldehyde and the acid. This finding points to a higher selectivity performance of the HP rutile with respect to the commercial TiO₂ samples. Some of the HP samples were also dialyzed to check the influence of the presence of Cl⁻ species on catalyst reactivity and selectivity. The results show that Cl⁻ ions help to increase the selectivity very less amount, however increase the reaction rate almost two times. The very different selectivities (60% and 38% for MBA and BA, respectively) were justified by considering the presence of an electron donor group in the former case and the hydrophobic nature of BAD.

Then, in order to increase the selectivity toward aldehyde, other HP rutile TiO₂ catalysts were prepared at room temperature by using water and TiCl₄ as precursor, at different H₂O/TiCl₄ ratios, without addition of additives, and

characterized by using BET, SEM and XRD analy. The catalysts were used for carrying out the selective photocatalytic oxidation of MBA to MBAD in aqueous suspension, free of any organic co-solvent. The selectivities showed by the HP catalysts were in the 45-74 % range, up to 4 times higher than that of a commercial rutile TiO_2 sample, the reaction rates being comparable. By using the most selective photocatalyst, the oxidation of benzyl, 4-methylbenzyl, and 4-nitrobenzyl alcohol was also carried out in order to investigate the influence of the substituent group on the oxidation rate and selectivity. The presence of $-\text{OCH}_3$ group positively influenced the selectivity whereas $-\text{NO}_2$ group showed to have a detrimental effect. The Hammett relationship well describes the influence of substituent group on the kinetic constant of partial oxidation of aromatic alcohols to aldehydes.

By concluding the reported results of first part indicate that heterogeneous photocatalytic method may be used for synthesis of valuable organic compounds with selectivities as high as 74%; moreover the process conditions can be considered green synthetic ones as neither organic solvents nor heavy-metal catalysts have been used. The investigation of the effect of the aromatic alcohol substituent on the partial oxidation performance shows that this effect is well described by the Hammett's relationship, whose validity is widely confirmed for homogeneous reacting systems but for very few cases (Sangchakr et al. 1995; Tanaka and Reddy 2002) in heterogeneous photocatalytic systems.

Moreover, a industrial process was investigated for oxidation of aromatic alcohols. In this aim a fixed bed continuous photoreactor containing Pyrex beads covered by a thin film of HP TiO_2 photocatalyst prepared and used for photocatalytic oxidation of MBA in aqueous solution. The results show that the oxidation occurs through two parallel routes: the first is the partial oxidation producing *p*-anisaldehyde and the second one is the mineralization. The kinetic modelling of partial oxidation and mineralization results has been made by using equations like to the LH model. The values of model parameters have been obtained by applying a least-squares best fitting procedure to all the experimental data. The observed dependence of parameters on absorbed photons clearly outline that the assumptions of LH model are not valid in the present case. A further limit

of the present kinetic model is that it does not explicitly takes into account the dependence on the radiation intensity profile. In fact, while the photocatalytic bed does not present axial variations in the local volumetric rate of photon absorption, the radial variations are surely important, especially for HP2 bed irradiated with 500 W lamp. On this ground the $S_{PO} \cdot k_{2,PO}$ and $S_{MIN} \cdot k_{2,MIN}$ values here reported are values averaged on the radial radiation profile. Work is in progress on this specific point.

4.2. Selectivity Enhancement by Aliphatic Alcohols with Intrinsic and Surface Features of Catalysts

The photoreactivity results indicate that the aromatic alcohol molecules participate to two parallel oxidative processes on the catalyst surface: The first one is the partial oxidation giving rise to the aldehyde and the second one is the complete oxidation producing eventually CO_2 . In the first pathway the adsorbed aromatic alcohol is transformed into the corresponding aldehyde which desorbs from the surface, while in the second one the substrate is mineralised through consecutive oxidation steps producing species which remain adsorbed onto the surface. The addition to the reacting system of an aliphatic alcohol (methanol, ethanol, 2-propanol or tert-butanol) determines a significant improvement of the photoprocess selectivity towards aldehyde. The aliphatic alcohols, as they are hole-traps, favourably compete with aromatic alcohols for the mineralizing pathway thus determining the increase of aldehyde selectivity.

The present investigation clearly indicates that a low-weight aliphatic alcohol such as methanol (or better the safe ethanol), added in small amounts in aqueous TiO_2 suspensions, can relevantly improve the photoprocess selectivity towards partial oxidation without production of intermediates that could give rise to interferences in the subsequent separation steps of the products. To the best of our knowledge this is the first work reporting as the aliphatic alcohols are able to enhance the selectivity of heterogeneous photocatalytic oxidation processes in water, opening intriguing perspectives also for green synthetic aims.

The photoelectrochemical characterization of HP catalysts clearly indicates that the semiconducting properties of HP0.5, HP2, HP4 and HP6 did not appreciably vary with the preparation procedure contrarily to sample HP8. The different photoactivities and selectivities exhibited by the photocatalysts could arise hence more from different properties of their surfaces rather than from semiconducting ones. From the ATR-FTIR analysis, it can be concluded that two main differences between HP0.5 and Degussa P25 surfaces exist. On one hand, their dissimilar hydrophilicity is relevant. A much higher amount of molecular water is indeed present on the former sample in comparison to the latter. On the other hand, the ability in adsorbing the organic compounds deriving from BA photocatalytic oxidation is quite lower for the HP catalyst as compared to the commercial one. On this basis, the highest selectivity of HP0.5 sample towards BA partial oxidation can be ascribed not only to its low affinity for BAD adsorption, but also to the lowest mineralization promoted. It can be postulated that the higher hydrophilicity of HP0.5 sample compared to Degussa P25 plays an important role in connection with the latter effect, as the high coverage of the HP0.5 surface by water molecules might result in a competition for adsorption sites. Bearing in mind the difficulty of stating clear correlations between photoreactivity and catalysts features, the following considerations may be drawn. The photoactivity results obtained with HP0.5 catalyst show a low oxidation rate of BA but a high selectivity to BAD. The present study shows that the surface of HP0.5 catalyst is rich in molecularly adsorbed water, which is able to displace BA molecules in the dark. Under irradiation, water displaces BA more effectively and determines a very low coverage of alcohol molecules on HP surface. It is likely that this low coverage is responsible for the low oxidation rate of BA. On the other hand, the high water content might account for the high selectivity to BAD, assuming that water competes with BA molecules for the adsorption on mineralization sites. The presence of ethanol lowers the BA amount on HP surface, thus determining a strong decrease of the overall alcohol oxidation rate. Molecularly adsorbed water is also partly displaced by ethanol but the selectivity to BAD is increased. One plausible explanation is that ethanol is predominantly adsorbed on mineralization sites. For Degussa P25 the reactivity results indicate

that the mineralization pathway predominates over the partial oxidizing one. As compared to HP0.5, this catalyst shows a higher coverage of BA and smaller water content so that the ratio between water and BA is low and, therefore, it is likely that mineralization sites are not preferentially occupied by water molecules. The addition of ethanol determines a strong decrease of BA coverage while the water content is poorly modified. For this catalyst neither the BA oxidation rate nor the selectivity to BAD is affected by ethanol so that it may be hypothesized that under irradiation the BA and water coverages on P25 surface remain unaltered and therefore also the partial oxidation and mineralization pathways.

4.3. Determination of Photoadsorption Capacity of Polycrystalline TiO₂ Catalyst in Irradiated Slurry

The method here proposed for the determination of photoadsorption capacity under reaction conditions gives valuable information on the influence of absorbed photons on kinetics and thermodynamics of a photocatalytic reaction. The consideration that the photon flow absorbed by the unit mass of catalyst is the parameter mainly affecting the photoadsorption phenomenon is strengthened by all the results. Under irradiation the catalyst surface undergoes noticeable changes (for example, from hydrophobic to hydrophilic character), these changes depending on photon absorption. The photoadsorbed amount of solute shows firstly a sharp increase with absorbed photons, this increase being less important at high photon absorption. This behaviour appears to indicate that the number of photoactive sites increases with photon absorption until a value is reached for which an increase of absorbed photon does not affect the amount of photoadsorbed substrate. This limiting amount should be characteristic of the catalyst surface and the physicochemical features of solute and medium (such as pH, ionic strength, etc.).

The basic assumptions of model are that: i) the TiO₂ surface, once firstly irradiated, needs a certain time to reach a thermodynamic equilibrium with the surrounding medium; and ii) photoadsorption is fast with respect to the reaction. The best fitting procedure suggests that the Langmuir isotherm is the most

suitable one for describing BA photoadsorption while the Freundlich isotherm better describes phenol photoadsorption. In both cases the other tested isotherms (Freundlich and Redlich-Peterson ones for BA and Langmuir and Redlich-Peterson ones for phenol) did not give a satisfactory fitting. It must be outlined, however, that it is likely that the chemical features of solute determine the most suitable isotherm for modelling the photoadsorption phenomenon.

The modelling results indicate that the parameters of the Langmuir and Freundlich models depend on the absorbed photon flow. In order to take into account the dependence on photon flows it would be necessary to develop a kinetic model based on the proposed reaction mechanism in which the photon appear as reactants.

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