Photocatalysis: a promising route for 21st century organic chemistry

Giovanni Palmisano,[ab] Vincenzo Augugliaro,*[a] Mario Pagliaro[b] and Leonardo Palmisano*[a]

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One of the main goals of 21st century chemistry is to replace environmentally hazardous processes with energy efficient routes allowing to totally avoid the use and production of harmful chemicals and to maximise the quantity of raw material that ends up in the final product. Selective photocatalytic conversions will play a major role in this evolution and this account shows how photocatalysis is offering an alternative green route for the production of organics.

1 Introduction

Photocatalysis by polycrystalline semiconductor oxides is an unconventional technology that has traditionally been applied (sometimes coupled to other technologies) to degrade organic and inorganic pollutants both in vapour and liquid phase.[1] Its main advantages consist not only in general mild conditions, but also in the possibility to abate refractory, very toxic and

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[a] *"Schiavello-Grillone" Photocatalysis Group, Dipartimento di Ingegneria Chimica dei Processi e dei Materiali, Università degli Studi di Palermo, Viale delle Scienze, 90128, Palermo, Italy.*
E-mail: augugliaro@dicpm.unipa.it; palmisano@dicpm.unipa.it;
Fax: +39 091 6567280; Tel: +39 091 6567246
[b] *Istituto per lo Studio dei Materiali Nanostrutturati, Consiglio Nazionale delle Ricerche, Via U. La Malfa 153, 90146, Palermo, Italy*

Giovanni Palmisano

Giovanni Palmisano, born in 1981, is PhD student in Chemical and Materials Engineering at the University of Palermo under the supervision of Prof. Vincenzo Augugliaro and Dr Mario Pagliaro. He received his high degree in Chemical Engineering cum laude in April 2005 and currently works in sol–gel materials and reactors for selective photo- and electro-catalytic conversions.

Vincenzo Augugliaro

Vincenzo Augugliaro is Full Professor of Transport Phenomena at the University of Palermo. In the course of his scientific activity he has contributed to the following fields: chemical absorption kinetics, biochemical reactor modelling, diffusional kinetics in metalliding alloys, chemical kinetics of heterogeneous photocatalytic systems, modelling of heterogeneous photoreactors, radiation field modelling in absorbing–reacting media, advanced oxidation processes for environment remediation. He is author of hundreds of papers published in international journals and books and oral or poster communications in National and International Conferences.

Mario Pagliaro

Mario Pagliaro is a research chemist and educator based in Palermo at Italy's Research Council (the CNR). He leads the new Institute for Scientific Methodology (www.i-sem.net) and coordinates the research work of a Group collaborating with researchers in eleven countries. His research focuses on the overlap of biology, chemistry and materials science and has resulted in a number of findings now partly available on the market.

Leonardo Palmisano

Leonardo Palmisano is Full Professor of Chemistry at the University of Palermo. His main field of interest is heterogeneous photocatalysis and he is author of hundreds of papers published in international journals and books and oral or poster communications in National and International Conferences. He has been invited as Visiting Researcher (Bradford University, UK), Visiting Professor (Hokkaido University, Japan) or Lecturer in many universities all over the world. He is also co-author of the didactic book "Fondamenti di Chimica" published in Italy by Edises and in Spain by Ariel Ciencia.

non biodegradable molecules. Many semiconductor materials have been tested as photocatalysts but it is generally accepted that TiO_2, due to its low cost and high activity and stability under irradiation, is the most reliable material.

Applications of heterogeneous photocatalysis as a synthetic route have also been tested but they are less common because semiconductor photocatalytic reactions have always been considered as highly unselective processes, especially in water. Nevertheless many selective reactions were carried out by employing not only titanium dioxide, but also other semiconductors and silica.[2] On the other hand, a number of selective syntheses mediated by different irradiated organic species have been studied.

Increasingly stringent environmental limitations for chemical processes are driving researchers to find alternative synthetic routes based on heterogeneous, leach-proof catalysts affording high yields of the wanted product in environmentally benign solvents such as water or (supercritical) carbon dioxide. As recent literature shows, organic chemistry is moving this way as well, bearing in mind that, in many cases, both water-soluble and water-insoluble molecules can react faster in water and, sometimes, higher reaction rates are found with water-insoluble substrates.[3]

In this scenario new perspectives are open for the development of medium to large-scale green photocatalytic processes in the synthesis of a number of organic species, widely used in pharmaceutical, food and cosmetic industries.

The advantages of these different types of reactions, especially when carried out in organic-free solvents, are massive: only consider the possibility to avoid environmentally and unhealthy dangerous heavy metal catalysts, strong chemical oxidant/reducing agents and the benefit coming from the use of the sun as a free green light source.

In this feature article we report several studies on photocatalytic selective reactions, both in gas and in liquid media. Some organic syntheses here cited produced only micro to millimolar amounts of chemicals; even if they have been performed on a more analytical than on a preparative scale, they merit to be mentioned as the related investigations strongly demonstrate the synthetic ability of photocatalysis. Most of studies report on oxidations or reductions. In the former case hydrocarbons and alcohols mainly have been oxidised, in the latter case CO_2 conversion to useful organics along with some nitrogen-containing organics reductions have been intensively investigated.

Among the employed photocatalysts, SiO_2 and semiconductors such as TiO_2, ZnO, WO_3, CdS and NiO are very common. These catalysts are often metal-doped in order to shift the radiation absorption towards higher wavelengths and supported over various materials (*e.g.* silica and zeolites) in order to increase the surface area and hence the reaction rate. Similarly inorganics like uranyl(VI) and polyoxometalates are extensively applied along with various organic compounds. Porphyrins and phthalocyanines are organic species with large potential as selective photocatalysts.

This article emphasises the recent advances on selective photocatalytic conversions of interest for organic chemistry and ends with economic considerations of practical utility in evaluating application of these types of reaction.

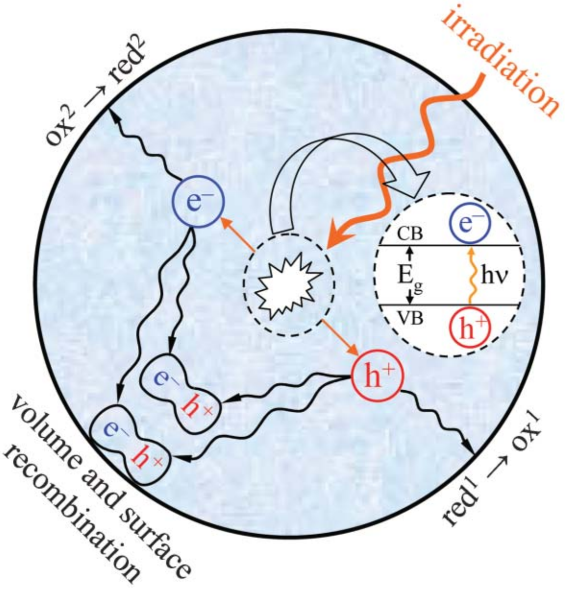


Fig. 1 Representation of a semiconductor-photocatalyzed reaction.

2 Photocatalysts

Fig. 1 shows the representation of a semiconductor photocatalyzed reaction. By simplifying the process under irradiation can be divided in four steps: absorption of light followed by the separation of the electron–hole couple, adsorption of the reagents, redox reaction, desorption of the products.[1]

It is generally accepted that the following steps occur on semiconductor catalysts (SC) irradiated with energy higher or equal to the band gap (E_g), causing the formation of a hole (h^+) in the valence band (vb) and an electron in the conduction band (cb):

$$SC + h\nu\ (\geqslant E_g) \longrightarrow h^+–e^-$$

$$h^+–e^- \longrightarrow h_{vb}^{\ +} + e_{cb}^{\ -}$$

$$h^+ + OH^- \longrightarrow {}^{\bullet}OH$$

$$e^- + O_2 \longrightarrow O_2^{\bullet -}$$

Fig. 2 reports the band gap energy and the redox potentials of the most common semiconductors, used as photocatalysts.

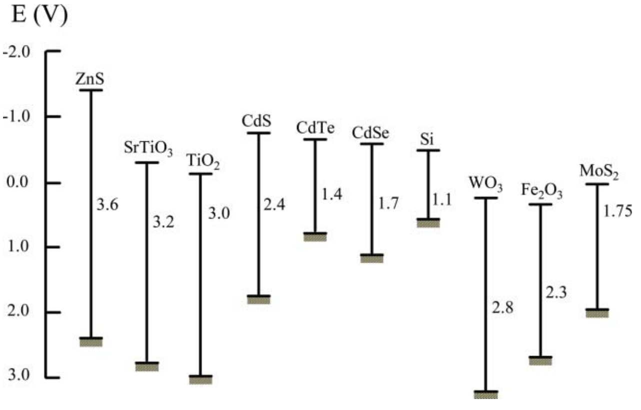


Fig. 2 Band gaps and redox potentials (*vs.* NHE) at pH = 1.

Compared to its crystalline analogue, poorly crystalline TiO_2 (excitation wavelength, λ_{exc} = 385 nm) improves significantly its selectivity in some partial oxidations.[4] Many types of highly dispersed metal oxide species on supports such as SiO_2 and Al_2O_3/SiO_2 as well as mixed oxides and zeolites exhibit good selectivities for partial oxidations. This is ascribed to the high dispersion of photoactive sites, surrounded by insulator supports, so that the exciton is localized and isolated.[2b]

An example of a homogeneous inorganic catalyst is represented by UO_2^{2+} (λ_{exc} = 385 nm), which absorbs visible light to produce a long-lived, strongly oxidizing excited state, $*UO_2^{2+}$, which is capable[5] to catalyse the aerobic oxidation of cyclopentane to cyclopentanone:

$$UO_2^{2+} + h\nu \rightarrow *UO_2^{2+}$$

$$*UO_2^{2+} + C_5H_{10} \rightarrow UO_2^{2+} + C_5H_9^{\bullet} + H^+$$

$$C_5H_9^{\bullet} + O_2 \rightarrow C_5H_9O_2^{\bullet}$$

$$C_5H_9O_2^{\bullet} \rightarrow C_5H_8O + 1/2\ H_2O_2$$

$$2\ UO_2^{2+} + O_2 + 2\ H^+ \rightarrow 2\ UO_2^{2+} + H_2O_2$$

Polyoxometalates (POMs) also induce reversible redox reactions upon irradiation, acting as multielectron and oxygen relays.[6] The reaction route commonly proposed for the conversion of organic substrates (mainly alcohols) is H-abstraction, as shown in the case of 2-propanol oxidation:

$$\mathrm{POM} + h\nu \rightarrow \mathrm{POM}^*$$

$$\mathrm{POM}^* + \mathrm{Me_2CHOH} \rightarrow \mathrm{POM}\ (e^-) + \mathrm{Me_2COH}^{\bullet} + H^+$$

$$\mathrm{POM} + \mathrm{Me_2COH}^{\bullet} \rightarrow \mathrm{POM}\ (e^-) + \mathrm{Me_2CO} + H^+$$

Finally, phthalocyanine and porphyrin complexes have been widely studied as photocatalysts for hydrocarbon aerobic oxidation such as in the case of iron(III) mesotetrakis(2,6-dichlorophenyl)porphyrin (Fig. 3), working in aqueous solutions of appropriate surfactants to form micelles, where the oxygenation of alkenes to epoxides smoothly takes place.[7]

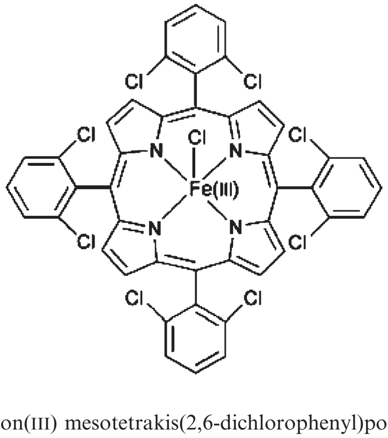


Fig. 3 Iron(III) mesotetrakis(2,6-dichlorophenyl)porphyrins.[7]

3 Oxidation reactions

Photooxidation is by far the most studied reaction class. In photocatalytic reactions carried out in non-aqueous systems it is usual to obtain rather high chemical yields of oxidation products, although sometimes with very low quantum yields/efficiencies (especially in the case of semiconductors). Industrial processes for oxidation reactions have generally been conducted using stoichiometric amounts of heavy metal reagents (*e.g.* Cr and Mn salts or V_2O_5) or moisture-sensitive oxidants.[3]

Most studies dealt with aliphatic and aromatic alkanes and alkene derivatives and particular attention has been devoted to the selective oxidation of alcohols to carbonyls.

3.1 Aromatic hydroxylation

The hydroxylation of aromatics is of particular interest to the chemical industry. Hydroquinone, for example, is a widely used commercial chemical. A typical industrial process for hydroquinone production is based on the oxidation of aniline by manganese dioxide and sulfuric acid. This is then followed by reduction typically using Fe/HCl.

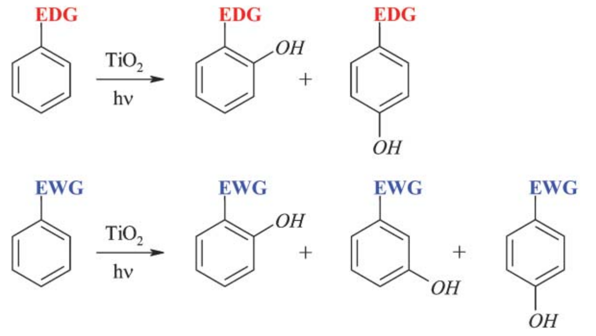
This process is not atom efficient (*i.e.*, only a modest part of the atoms consumed in the process are present in the final product) and generates a massive quantity of wastes (namely iron(II) oxide, manganese sulfate, ammonium sulfate).

One of the greatest advances in catalysis since the early 1980s was the discovery of titanium silicate catalysts by chemists at Enichem (Italy). These versatile oxides already have a wide range of industrial applications including epoxide formation, ammoximation and hydroxylation.[3e] In particular they are used for the production of dihydroxylated benzenes, by using hydrogen peroxide.

Among photocatalytic aromatics oxidations,[8–12] the conversion of benzene to phenol is perhaps the most interesting reaction, since the latter is widely used as a disinfectant, precursor of resins and preservative for pharmaceutical aid. Hence its yearly global production amounts to *ca.* 5×10^6 tonnes yr^{-1}. A recent heterogeneous photocatalytic oxidation of benzene to phenol[8] in water–acetonitrile suspensions reaches 11% yield by employing TiO_2 along with polyoxometalate $PW_{12}O_{40}^{3-}$. The secondary products are hydroquinone and catechol.

Attempts to selectively oxidise benzene were also carried out with transition metal-exchanged BEA zeolites dispersed in benzene–acetonitrile–water mixtures;[9] and by means of UO_2^{2+} and H_2O_2 affording phenol with an optimal quantum yield of 0.7.[10]

Similarly, TiO_2-catalyzed photocatalysis can be used to obtain mono-hydroxylated aromatic derivatives in fairly to good yields.[11,12] Under irradiation, the aromatic compounds adsorbed on the catalyst surface undergo two competing reaction pathways: (i) hydroxylation of the aromatic ring or, (ii) multi-step oxidation reactions to complete mineralization. Scheme 1 shows that, in the case of compounds containing an electron donor group, the OH radical attack follows the selectivity rules known for homogeneous electrophilic aromatic substitution, obtaining the only *ortho-* and *para-*isomers. In the absence of an electron donor group, instead, the attack is unselective, and a mixture of all the three possible isomers is



Scheme 1 Main hydroxylated products obtained during the photocatalytic oxidation of aromatic compounds containing either an electron donor (EDG) or an electron withdrawing group (EWG).[11,12]

obtained. This is a general behaviour, confirmed by all the intermediate compounds detected in investigations on aromatic photocatalytic oxidations.[12]

3.2 Hydrocarbon oxidation

Direct conversion of alkanes into highly desirable oxygenates such as alcohols, ketones, aldehydes and carboxylic acids is of great significance to the future chemical industry, and photocatalysis shows large promise to become the technology of choice.[5,7,13–24]

One of the most relevant result makes use of water suspensions of commercial TiO_2 Degussa P25 to afford high selectivities in the oxidation of toluene, cyclohexane, methylcyclohexane and ethylbenzene (see Table 1).[13] Justification of outstanding results could be the high volume (2 ml) of substrate present in the reactor, compared with the water volume (13 ml) together with the low power (5.5 W) of the used lamp (a quartz Pen-Ray, low-pressure, cold cathode mercury lamp). Neither carbon oxides nor open-ring products were produced during the reaction time (2 h).

Photocatalytic oxidation of cyclohexane to cyclohexanol and cyclohexanone in TiO_2 slurries[15] is largely influenced by the solvent. Cyclohexanone is an important intermediate in ε-caprolactam synthesis, which is used in the manufacture of nylon polymers. The product formation rate notably increases by employing a solvent that does not compete with cyclohexane over the active reaction sites. Moreover the rate was also enhanced by solvents, such as dichloromethane, that were strongly adsorbed and formed reactive radicals on irradiated TiO_2. Dichloromethane was the best solvent with regard to the formation rate of cyclohexanol and cyclohexanone. The most unfavourable solvents were isopropanol, chloroform and benzene; the first and the second ones adsorbed quite strongly on TiO_2 forming radicals reacting with other solvent molecules.

Table 1 Liquid-phase photocatalyzed oxidation of hydrocarbons[13]

Substrate	Product	Selectivity (mol%)	Conversion (mol%)
Toluene	Benzyl alcohol	9	12
	Benzaldehyde	91	
Cyclohexane[a]	Cyclohexanol	30	4
	Cyclohexanone	44	
	2-Cyclohexenone	5	
	1,1′-Bicyclohexane	21	
Methylcyclohexane	1-Methylcyclohexanol	16	8
	2-Methylcyclohexanol	8	
	3-Methylcyclohexanol	16	
	4-Methylcyclohexanol	5	
	2-Methylcyclohexanone	15	
	3-Methylcyclohexanone	24	
	4-Methylcyclohexanone	11	
	1-Methanolcyclohexane	56	
Ethylbenzene	Acetophenone	100	7

[a] 3.0 ml 30% H_2O_2 added.

The proposed reaction mechanisms for the formation of cyclohexanol are reported starting with the alkyl radical, which can be formed by reaction between the hydrocarbon with either a hole or a hydroxyl radical:

$$^{\bullet}RH + {}^{\bullet}OH \rightarrow RHOH$$

$$^{\bullet}RH + O_2 \rightarrow RHOO^{\bullet}$$

$$RHOO^{\bullet} + RH_2 \rightarrow RHOOH + HR^{\bullet}$$

$$RHOOH + e^{-} \rightarrow HRO^{\bullet} + OH^{-}$$

$$HRO^{\bullet} + RH_2 \rightarrow RHOH + HR^{\bullet}$$

As far as the cyclohexanone formation is concerned the authors hypothesised the subsequent reactions:

$$RHOH + 2\ {}^{\bullet}OH \rightarrow RO + 2\ H_2O$$

$$RHOO^{\bullet} + e^{-} \rightarrow RO + OH^{-}$$

$$^{\bullet}RH + O_2^{\bullet -} \rightarrow RO + OH^{-}$$

$$^{\bullet}RH + HO_2^{\bullet} \rightarrow RO + H_2O$$

TiO_2 film reactors were used for the partial oxidation of cyclohexane in gas phase as well.[16] The films were prepared *via* four different methods (dip coating using titanium isopropoxide and commercially available titanium dioxide particles, sol–gel process, and flame aerosol process) and irradiated with UV-light. Best results in terms of activity for the formation of cyclohexanol and cyclohexanone (expressed in μmol per gram of catalyst per minute) were those of flame aerosol films, reaching the value of 0.964 μmol g^{-1} min^{-1}, with a selectivity towards the two products of 98%. The best selectivity was 99%, achieved with films obtained by the sol–gel method, but in this case the activity value was very low, 0.025 μmol g^{-1} min^{-1}.

Transition metal oxides systems have also been often used aiming to selectively photooxidise hydrocarbons to the respective alcohols, aldehydes and ketones. Recent results with sol–gel silica-entrapped Cr employed in the partial oxidation of cyclohexane under visible-light irradiation[18] in acetonitrile indicate that the highest turnover number (2.5) and selectivity (68%) for cyclohexanone production were obtained with catalyst containing 0.1% Cr when only traces of CO_2 were detected. Even if some TiO_2 systems show higher selectivity, typically considerable amounts of CO_2 are formed whereas these Cr-silica systems prevent cyclohexane decomposition. The silica-entrapped Cr catalyst, characterized by

Table 2 Turnover numbers and selectivities for hydrocarbon photocatalytic oxidation[19]

Substrate	Product(s)	Turnover number[a,b]	Selectivity[b] (mol%)
Toluene	Benzaldehyde	76 ± 11	100
Cumene	Acetophenone	143 ± 10	55
	Cumyl alcohol	116 ± 14	45
Diphenylmethane	Benzophenone	160 ± 25	100
Dihydroanthracene	Anthracene	235 ± 37	100
Fluorene	Fluorenone	287 ± 34	100

[a] Turnover number represents the total moles of product per mole of catalyst. [b] Values obtained after 18 h photolysis.

diffuse-reflectance spectroscopy, showed three distinct absorption bands at 245, 330 and 460 nm, assigned to ligand-to-metal charge transfer from O_2^- to Cr^{6+} transitions of chromate species, which are highly dispersed on silica matrixes and isolated from each other. Increasing the Cr content resulted in red-shifted absorption at 500–800 nm, which could be assigned to the d–d transition of octahedral Cr^{3+} in the Cr_2O_3 cluster, indicating that these catalysts contained polymerized Cr^{3+} species.

Aerobic visible-light photocatalytic selective oxidation of various hydrocarbons (see Table 2) by a photo-stable diiron(III) bisporphyrin complex (λ_{exc} = 425 nm) was recently reported to proceed with high turnover numbers and complete selectivities.[19] The conversion of toluene to benzaldehyde, followed by measuring the solution absorption, is qualitatively shown in Fig. 4, along with the redox cycle of the catalyst. The main drawback of this oxidation is represented by the use of the unsafe solvent pyridine in the photoreactions.

The simplest hydrocarbon, methane, is a valued, abundant fuel, whose oxygenate derivative methanol can be used as building block for a variety of chemicals.[21] The major source of methane is natural gas, which is copiously present in nature. Industrial processes usually convert natural gas to synthesis gas (a mixture of CO and H_2), formed through a process known as steam reforming, carried out under severe temperature conditions (973–1373 K). Synthesis gas, once obtained, may be used to produce methanol which in turn is used to synthesise crucial compounds as formaldehyde, acetic acid, and MTBE (methyl *tert*-butyl ether). The latter, for instance, is used as an additive to produce cleaner burning gasoline. Methanol itself is employed as a fuel source in fuel cells.

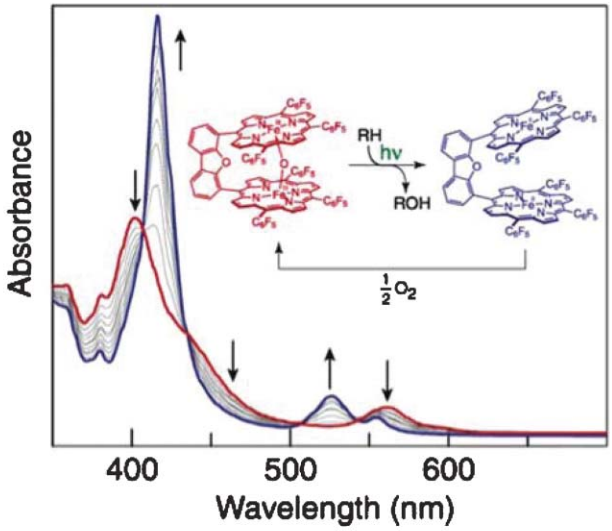


Fig. 4 Time course of the changes in the absorption profile accompanying the photoconversion (λ = 425 nm) of anaerobic pyridine solutions of (DPDF)Fe_2O (7×10^{-6} M) in the presence of toluene (1.0 M) at room temperature. (Reprinted with permission from ref. 19. Copyright 2006, American Chemical Society.)

Low yield photocatalytic oxidation of methane has been achieved mainly by using semiconductors such as TiO_2, WO_3 and NiO.[22–24] Methane conversion to methanol, hydrogen and acetic acid, by La-doped WO_3 in the presence of an electron transfer molecule in aqueous irradiated suspensions (at *ca.* 367 K)[22] is thought to proceed as reported below:

$$La/WO_3 \xrightarrow{h\nu, \lambda > 410\ nm} e_{cb}^- + h_{vb}^+$$

$$e_{cb}^- + MV^{2+} \rightarrow MV^{\bullet +}$$

$$h_{vb}^+ + H_2O \rightarrow H^+ + {}^{\bullet}OH$$

$$MV^{\bullet +} + H^+ \rightarrow 1/2\ H_2 + MV^{2+}$$

$$CH_4 + {}^{\bullet}OH \rightarrow CH_3^{\bullet} + H_2O$$

$$CH_3^{\bullet} + H_2O \rightarrow CH_3OH + 1/2\ H_2$$

where MV stands for methyl viologen. Conversion of methane is low (*ca.* 4 and 10% in the presence of hydrogen peroxide) and no reaction is observed at room temperature. A significant advancement then uses[23] methane hydrates (see Fig. 5), now obtaining significant conversions even at very low temperatures (268 K). Methane hydrates form in the ocean at depths between *ca.* 280 and 4000 m enabling higher concentrations of methane in water, higher even than that obtained in water–methane pressurised systems. Hence the produced methanol in this case was more than four-fold than that of the methane–water system. The author also observed that irradiating the suspensions with UV-vis rather than visible light lowered the quantity of alcohol, causing an overoxidation of methanol.

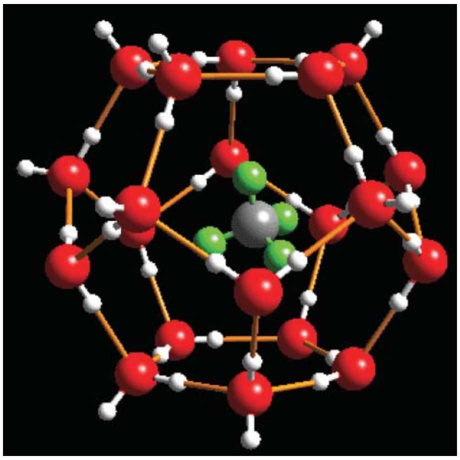


Fig. 5 Structure of methane hydrate.

Table 3 Irradiation of acetonitrile solutions of benzyl alcohol (100 mM) in the presence of catalytic concentrations of the anions $[S_2M_{18}O_{62}]^{4-}$ (M = W, Mo)[26]

Complex [mol%]	Light source[b] [irrad. time]	Conversion (%)	Aldehyde yield (mol%)	Acid yield (mol%)
$S_2W_{18}O_{62}{}^{4-}$ [2.0]	Solar light [25 days]	29	25	3
$S_2Mo_{18}O_{62}{}^{4-}$ [4.0]	Solar light [25 days]	4	3	Negligible
$S_2W_{18}O_{62}{}^{4-}$ [1.9][a]	12.5 W [48 h]	24	21	3

[a] Concentrations for the last entry were: 79 mM benzyl alcohol and 1.52 mM $[S_2M_{18}O_{62}]^{4-}$. [b] Artificial light: λ = 312–700 nm.

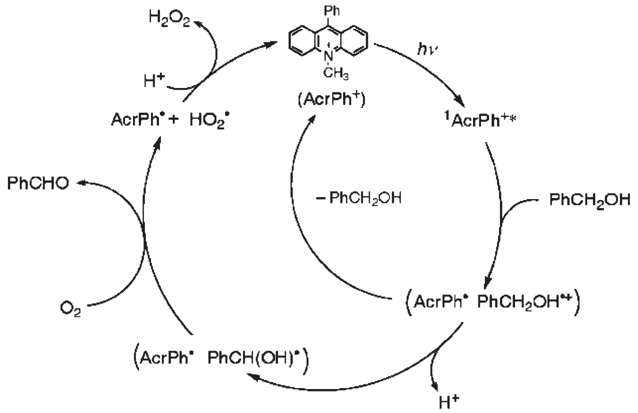
3.3 Alcohol oxidation

A number of new efficient processes for aerobic alcohol oxidation to carbonyl compounds mostly based on Ru and Pd–Au have been recently developed.[25] By photocatalysis, promising results in the oxidation of aromatic alcohols make use of heteropolyoxometalates catalysts of the form $[S_2M_{18}O_{62}]^{4-}$ (M = W, Mo) irradiated both by solar and UV-vis light in acetonitrile.[26,27] Results (Table 3) point to good activity and yield of $S_2W_{18}O_{62}{}^{4-}$ with both solar and UV-vis light, whereas $S_2Mo_{18}O_{62}{}^{4-}$ gave very low conversion.

Even better, a large variety of aromatic alcohols can be successfully converted in yields ranging from 50 to 97%[27] using a heterogeneous catalyst ($H_3PW_{12}O_{40}/SiO_2$) with O_2 as the unique oxidising agent. Notably no overoxidation to carboxylic acids was observed and the catalyst was proved to be leach-proof.

At room temperature and under visible light irradiation the solvent-free oxidation of benzyl alcohol to benzaldehyde by 9-phenyl-10-methylacridinium perchlorate as photocatalyst proceeds with O_2 as unique oxidant[28] with 35 ± 5% quantum yields. The reaction mechanism (Scheme 2) involves the photoactive species $AcrPh^+$ that under irradiation converts into the singlet excited state $^1AcrPh^{+*}$, which is further quenched by electron transfer from the alcohol in the solvent cage, yielding $AcrPh^•$ and $PhCH_2OH^{•+}$. The latter undergoes fast deprotonation producing $PhCH(OH)^•$ that reacts with O_2 to afford PhCHO and $HO_2{}^•$. Subsequently the protonation of $HO_2{}^•$ and the regeneration of $AcrPh^+$ occur, thus closing the cycle.

Selective photooxidation of alcohols to the corresponding aldehydes and ketones was performed either in gas phase[29] or in liquid phase using acetonitrile as solvent[27,30] or without solvent.[31] The first remarkable selective photocatalytic oxidation of alcohols to aldehydes in water[4] at room temperature concerns the selective oxidation of 4-methoxybenzyl alcohol to the corresponding aldehyde in water suspensions of home-prepared TiO_2. 4-Methoxybenzaldehyde (or *p*-anisaldehyde) is a fragrance and an intermediate in many different industrial processes. The nanostructured catalyst synthesised by boiling aqueous solutions of $TiCl_4$, in mild conditions, showed a yield much higher (42% mol for conversions of *ca.* 65%) than that obtained with TiO_2 commercial samples (see Table 4). The only by-products present were traces of 4-methoxybenzoic acid (only for long-lasting runs) and open-ring products, CO_2 being the other main oxidation product.



Scheme 2 Photocatalytic mechanism of solvent-free oxidation of benzyl alcohol with O_2.[28]

UV-vis light was used to compare the various catalysts for reproducibility reasons, but similar selectivities were observed in experimental runs performed by solar light.

Results are summarised in Table 4. Two commercial TiO_2 samples were compared with home-prepared (HP) catalysts obtained by simply boiling $TiCl_4$ solution for different times. Increasing the boiling time resulted in a higher crystallinity and activity of the catalyst, which afforded progressively lower yields in aldehyde due to a higher production of CO_2. Selectivity values obtained with commercial catalysts drastically decreased with irradiation time and decreasing the catalyst amount of commercial samples did not result in significant enhancement of selectivity to aldehyde. Conversely the poorly crystalline home-prepared samples gave rise to yields of *ca.* 35% even when the conversion was *ca.* 80%. Finally no catalyst deactivation was observed by the authors in any case.

Various aliphatic and aromatic alcohols (*e.g.* 1-pentanol, cyclohexanol, benzyl alcohol, 1-phenylethanol) can be aerobically oxidised to the corresponding carbonyls by using light-activated TiO_2 in an annular gas phase reactor at *ca.* 463 K in moderate yield (37%) but with selectivities >95%.[29] Oxidation of 1-phenylethanol notably gave styrene (with a selectivity of 87% and a conversion of 97%).

Table 4 Photocatalytic oxidation of 4-methoxybenzyl alcohol to aldehyde. Alcohol initial concentration: 1 mM[4]

Catalyst[a]	Boiling time/h	SSA[b]/ $m^2\ g^{-1}$	Irrad. time[c]/h	Yield[c] (mol%)
TiO_2 Merck	—	10	5.2	12
TiO_2 Degussa P25	—	50	0.9	9
TiO_2 HP	0.5	235	7.7	42
TiO_2 HP	2.0	226	4.7	37
TiO_2 HP	4.0	220	3.9	36
TiO_2 HP	6.0	206	2.8	31
TiO_2 HP	8.0	108	3.2	32

[a] "HP" stands for home prepared. [b] SSA = BET specific surface area. [c] These values refer to a conversion of *ca.* 65% and a catalyst amount of 0.2 g l^{-1}.

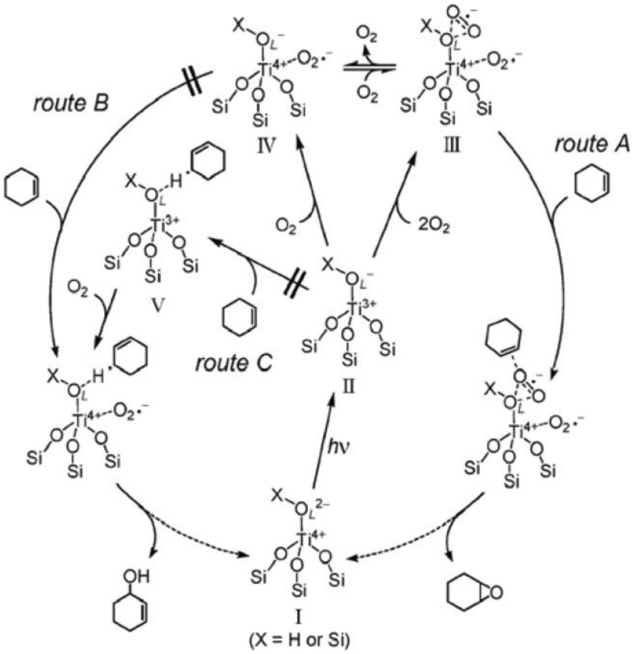
3.4 Alkene epoxidation

Commercially important alkene epoxidation[32] can be induced also photocatalytically, mostly using TiO_2 as catalyst and oxygen as the unique oxidant.[33–35] Photocatalytic epoxidation of propene over TiO_2-dispersed SiO_2 catalysts, prepared either *via* impregnation or by the sol–gel process, proceeds best over the sol–gel catalyst with a 57% selectivity towards propene oxide at 9% propene conversion. Comparable conversions were obtained with the catalyst prepared *via* impregnation but the selectivity was only 41%.[33]

Similar catalysts of highly dispersed TiO_2 in a SiO_2 matrix (prepared *via* a sol–gel method)[34] employed in the gas phase epoxidation of styrene, afford styrene oxide along with benzaldehyde and CO_2. The TiO_2/SiO_2 catalysts compared with TiO_2 Degussa P25, gave selectivities of 62, 23 and 15% toward styrene oxide, benzaldehyde and CO_2 with a styrene conversion of 18% whereas the commercial catalyst degraded 95% of the substrate affording 98% CO_2 and 2% benzaldehyde.

Remarkable control of the chemistry by materials shape is offered by the performance of a novel catalyst made of Ti entrapped in the hexagonal channels of MCM-41 silica in the acetonitrile-assisted photocatalytic epoxidation of various alkenes.[35] The relatively poor selectivity (*ca.* 60%) reached in previous studies depended on alkenes and $O_2^{\bullet -}$ radicals promoting formation of side products such as alcohols and ketones. Photocatalytic epoxidation of various cyclic and linear olefins within the porosity of the novel catalyst proceeds with unprecedented selectivity (>98%) and stereoretentivities (selectivity >99%) in the oxidation of *cis*- and *trans*-2-hexene. In Scheme 3 the three hypothesised possible reaction routes are reported (O_L indicates lattice oxygen atoms).

In route A the direct addition of $O_3^{\bullet -}$ to cyclohexene occurs. The O_L^- (formed by electron transfer between O_L^{2-} and Ti^{4+}) acts as a positive hole. Cyclohexene radical is formed by reaction with the electrophilic O_L^-, which is in turn transformed in O_L^{2-}. Then the alkene radical reacts with $O_2^{\bullet -}$ to afford allylic oxidation products (routes B and C). The influence of acetonitrile on selectivity could be ascribed to the selective suppression of the cyclohexene radical formation on the O_L^- site.



Scheme 3 Acetonitrile-assisted selective olefin epoxidation on photo-activated Ti-O_4 species.[35]

4 Reduction reactions

Photocatalytic reduction is intrinsically safer compared to chemical reductions usually conducted by using harmful or environmentally unsafe species, such as iron ammonium chloride, sulfides, hydrogen, borohydrides, carbon monoxide and in general activated metals.[36]

Yet, photocatalytic reductions are less frequent than oxidations most probably because the reducing ability of a conduction band electron is considerably lower than the oxidizing one of a valence band hole.

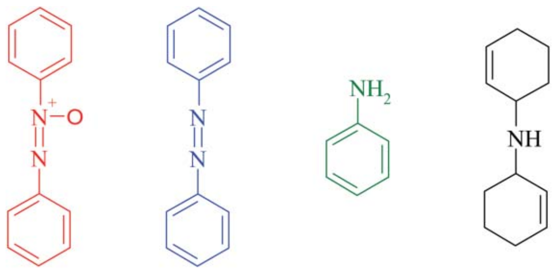
4.1 Nitro-aromatic reduction

Photoinduced nitro-aromatics reduction has attracted much attention.[37–41] For instance, the reduction of nitrobenzene and its derivatives over irradiated TiO_2 surface has been largely described in the last decade.

In the conversion of nitrobenzene, 3- and 4-nitrotoluene and nitrobenzonitrile in the presence of TiO_2 aqueous slurries,[37] methanol or 2-propanol play the role of electron donors and identical rates and selectivities are achieved in both cases, revealing the minor relevance of the chemical nature of the alcohol. High yields in anilines were obtained in the case of nitrobenzene and nitrotoluenes, whereas low selectivities were found in the conversion of nitrobenzonitriles.

Nitrobenzene reduction in the presence of cyclohexene[38] induces interesting functionalisations of the nitro-organic. Nitrobenzene/cyclohexene mixtures were irradiated by UV-light at room temperature and pressure in the presence of various semiconductors (TiO_2, WO_3 and CdS). Fig. 6 represents the four identified products that amount to about 90% of the reduced substrate. **I** and **IV** were the most abundant products under homogeneous conditions, whereas **II**, **I** and **III** are predominant by using TiO_2, WO_3 and CdS, respectively.

No reactivity is observed without cyclohexene or irradiation. The presence of a semiconductor inhibited the formation of **IV**, probably because the high surface coverage by intermediates drastically reduced the chance of reaction between a



I **II** **III** **IV**

Fig. 6 Products of nitrobenzene photoreduction.[38]

reduction product of nitrobenzene, as $C_6H_5NH^{\bullet}$, and an oxidation product of cyclohexene, as $C_6H_9^{\bullet}$, that could lead to **IV**. Moreover the highest yield in reduced compounds was obtained by using CdS, *i.e.* the most powerful reducing semiconductor.

4-Nitrophenol can be reduced to 4-aminophenol with almost complete selectivities in different alcohols (methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol)[39] in TiO_2 Degussa P25 suspensions irradiated by UV-light. The influence of solvent properties (viscosity, relative permittivity, refractive index and polarity/polarisability) on reaction rate is very impressive. Viscosity and polarity/polarisability parameter, *i.e.* the ability of a solvent to stabilise a charge or dipole by means of its dielectric effect, were found to play an important role in the conversion rate. An increase in the polarity/polarisability parameter corresponds to a better stabilization of the produced charged intermediate species and hence to a higher reaction rate.

Reduction of aryl azides to amines,[41] photocatalysed by CdS or CdSe nanoparticles in water, takes place with high quantum yields (near to 0.5) and with almost complete selectivities towards amines, at room temperature and pressure and at neutral pH. A simplified mechanism of the reaction is depicted in Scheme 4. Sodium formate is used as electron donor (oxidised to CO_2 during the reaction).

4.2 CO_2 reduction

The environmental problems caused by the continuously increasing concentration of CO_2 in the atmosphere have brought researchers to find new solutions to convert the high amounts of the exceeding CO_2 into useful chemicals. Therefore photocatalytic reduction of CO_2 by using photoactive species is clearly highly desirable.[42–58]

Previous research has shown that transition metal complexes catalyse the reduction of carbon dioxide by some hydride complexes, where the activated hydrogen is originating from water.[42] Actually the larger part of such reactions results in a partial reduction of carbon dioxide to carbon monoxide, whereas the possibility of producing formaldehyde, methanol and methane is of particular interest because of the large use of these valued chemicals.

In photocatalysis both liquid[43–51] and gas[52–58] systems were extensively used with different catalysts. For example, reduced high pressure CO_2 in aqueous 2-propanol solutions in which TiO_2 Degussa P25 was suspended mostly affords methane and acetone (the latter from 2-propanol oxidation).[43] The proposed reaction mechanism is as shown below:

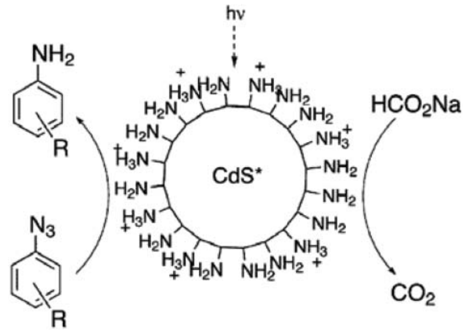
$$TiO_2 \xrightarrow{h\nu} e_{cb}^- + h_{vb}^+$$

$$-\ \text{oxidation}: h_{vb}^+ + (CH_3)_2CHOH \rightarrow 2H^+ + (CH_3)_2CO$$

$$-\ \text{reduction}: e_{cb}^- + CO_2 \rightarrow {}^{\bullet}CO_2^- \xrightarrow{H^+ + e^-} CO + OH^-$$

$$CO + OH^- \xrightarrow{2H^+ + 2e^-} {}^{\bullet}C + H_2O \xrightarrow{2H^+ + 2e^-} {}^{\bullet}CH_2$$

$${}^{\bullet}CH_2 \xrightarrow{2H^+ + 2e^-} CH_4$$



Scheme 4 Photoreduction of azides to amines by using CdS or CdSe as catalysts and sodium formate as a sacrificial electron donor.[41]

The major drawback of CO_2 photocatalytic reduction process lies in the rather low energy conversion efficiencies. A gain can be obtained for instance using gel films of TiO_2 nanocrystals embedded in SiO_2 matrixes (Ti/Si mole ratio = 0.1) irradiated with a UV-vis lamp ($\lambda > 300$ nm) and with 2-propanol as electron donor. The reduction of CO_2 in the presence of nitrate ions yields hydrogen, formate, CO, ammonia and urea at 10 μmol h^{-1} when the TiO_2 present in the film was about 7.0 μmol.[45] Comparing the performance in different solvents (water, ethylene glycol, acetonitrile, sulfolane, propylene carbonate), a linear correlation between the dielectric constants and the photogenerated electrons in the formation of the various products is observed. Hence, raising the dielectric constant results in significant increase of ammonia and urea production and strong decrease of formate and CO up to negligible concentrations, thus demonstrating that the *selectivity* of a photocatalytic process can be easily tuned by *adjusting the reaction ambient*.

An improved synthesis of methanol from carbon dioxide uses UV-irradiated copper-doped commercial TiO_2 (Degussa P25), suspended in CO_2-saturated water. CuO provides the best influence on both yield in methanol (2655 μmol per gram of catalyst after 6 h irradiation) and quantum efficiency (19.2%) serving as an electron trap preventing recombination of electrons and holes. It should however be considered that CO_2 conversion, indeed, is a reversible reaction and the produced methanol can be easily reoxidised to hydrogen and CO_2.[46]

Metal bipyridine (bpy) complexes,[49,50] porphyrins and phthalocyanines[51] also work as proficient catalysts for CO_2 reduction. These species are best excited by visible light. For example, high-pressure reduction of CO_2 to CO in dimethylformamide mediated by [*fac*-Re(bpy)(CO_3)Cl] affords an optimal yield of 99.5 μmol and a turnover number of 41.8 ($\text{mol}_{CO}\ \text{mol}_{cat}^{-1}$) after 25 h irradiation at 2.45 MPa.[49] An advanced application makes use of a heterogeneous system in which $[Co(bpy)_3]^{2+}$ plays the role of homogeneous catalyst and $[Ru(bpy)_3]^{2+}$ is fixed to a cation exchange polymer acting as photosensitizer (Fig. 7).[50] Remarkably the reaction takes place at atmospheric pressure and temperature giving CO and H_2 as the sole products with about half the yield of the analogous homogeneous system where both the complexes were dissolved in the solvent.

The immobilization of catalysts is a major goal of current chemistry since it offers several advantages, such as avoiding a separation step from the reacting environment, thus facilitating and speeding up the catalyst reusability, which is essential

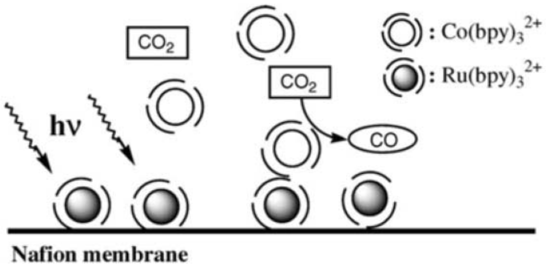


Fig. 7 Representation of photocatalytic CO_2 to CO conversion, in which the Ru and Co complexes act as photosensitizer and catalyst, respectively. (Reproduced with permission from ref. 50. Copyright 2002, Elsevier Science B.V.).

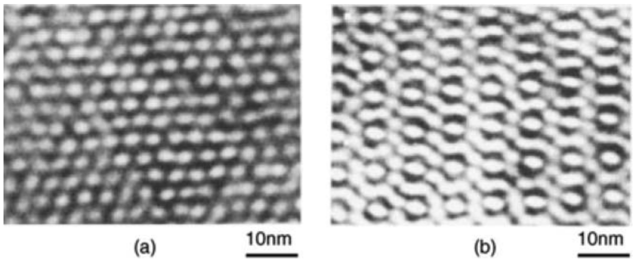


Fig. 8 TEM images of mesoporous Ti-containing silica transparent films. (Reproduced with permission from ref. 56*b*. Copyright 2003, Elsevier B. V.).

in view of industrial applications. Aiming to this purpose, the preparation of TiO_2/SiO_2 mesoporous films *ca.* 50 μm thick[56] is a noteworthy result, since higher yields and quantum yields were obtained with respect to those observed by using the same samples in powdered form. Transparent self-standing thin films prepared by a surfactant-template sol–gel process are obtained as highly ordered mesostructures, with hexagonal (Fig. 8(a)) or cubic (Fig. 8(b)) symmetries depending on the amount of water present in the starting mixture.[56b] These films, applied in the photoconversion of CO_2 and H_2O to CH_4 and CH_3OH as main products at 323 K have a high surface area (*ca.* 900 $m^2\ g^{-1}$) and produced methane and methanol in *ca.* 70 and 15 μmol $g_{Ti}{}^{-1}$, respectively (after 6 h irradiation) with a total quantum yield of almost 30%. As yields drastically reduced upon grinding the films to powder the high performance is due to the pronounced absorbance of light by the shaped film.

A fixed-bed gas-solid photocatalytic reactor (see Fig. 9) was employed[57] with commercial TiO_2 pellets, irradiated by UV-light, for the reduction of CO_2 to CH_4, CO and H_2 being the reaction by-products. The reaction was performed at room conditions at two different wavelengths: switching the light from 253.7 to 365 nm resulted in lowering the CH_4 concentration from 200 to 100 mg l^{-1}. CO was formed approximately in the same concentration as CH_4, while the ratio H_2/CH_4 was *ca.* 0.6. The authors emphasized that the presence of H_2 was a clear clue that the TiO_2 pellets also promoted water photo-splitting. Comparing the results obtained by the authors with previous studies it could be noticed that, even if their product yield seemed to be worse (0.1 μmol $g_{cat}{}^{-1}$ after 48 h irradiation), the very low power of the lamps used must be taken into account (only 4.8 W).

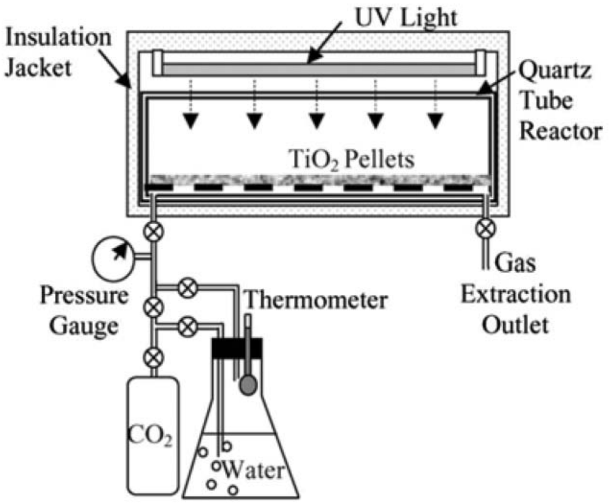


Fig. 9 Schematic drawing of the experimental setup applied in the reduction of CO_2 in the gas phase. (Reproduced with permission from ref. 57. Copyright 2006, Elsevier B.V.).

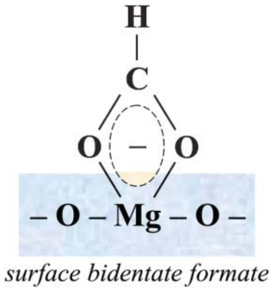


Fig. 10 Photoactive species in the reduction of CO_2 to CO catalysed by MgO and UV-light.[58]

TiO_2 however is not the only metal oxide that catalyses CO_2 photoreduction in the gas phase. Photocatalytic conversion of CO_2 to CO over particulate MgO occurs at room temperature[58] with a CO yield of *ca.* 10 μmol $g_{cat}{}^{-1}$ (after 5 h irradiation) although in the presence of a strong UV irradiation (500 W). The reaction mechanism is supposed to involve activation of CO_2 adsorbed on MgO to a CO^{2-} radical by UV-light, and subsequent reduction to the surface bidentate formate (see Fig. 10), identified as the photoactive species.

5 Other reactions

TiO_2[59–67] and also other catalysts[67–72] have been applied to many conversions, generally in organic solvent, although a few syntheses were performed in water[63] or ethanol.[64]

Dehydrogenation

Dihydropyrazine and 2-methylpiperazine photocatalytic syntheses were[59] conducted over UV-irradiated semiconductor/zeolite by bubbling oxygen in alkyl diamine solution in acetonitrile. The maximum yield in dihydropyrazine (Fig. 11, **I**) was 20% with 2 wt% TiO_2 supported on Hβ (a zeolite with a ratio SiO_2/Al_2O_3 = 20), whereas 32% yield of 2-methylpiperazine (Fig. 11, **II**) was obtained with 5 wt% TiO_2 supported on

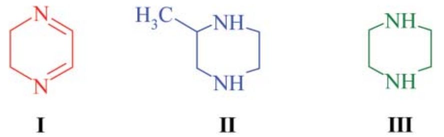
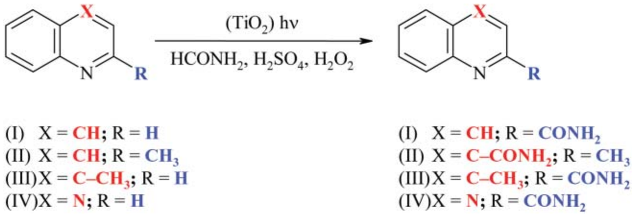


Fig. 11 Reaction products in semiconductor/zeolite photocatalysed syntheses.[59]



Scheme 5 Sunlight induced functionalization of heterocyclic bases.[62a]

Hβ. In the last case piperazine (Fig. 11, **III**) was also formed with a yield of 15%.

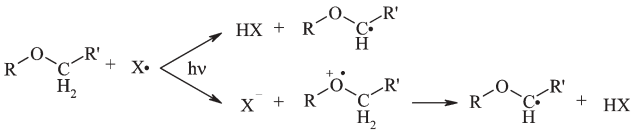
Heterocycle functionalisation

Sunlight induces functionalisation of heterocyclic bases by reacting amides[62a] or ethers[62b] in water or water–acetonitrile mixtures in the presence of TiO_2. Acid and H_2O_2 assist in the reaction mechanism involving the formation of an amide radical (see Scheme 5) attacking the heterocyclic base while hydrogen abstraction is due to photocatalytically formed OH radical.

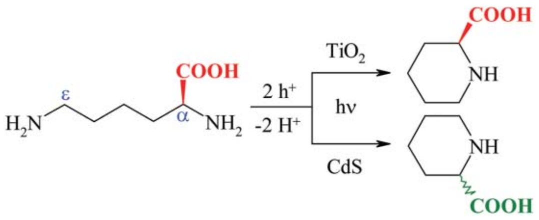
Simple production of valuable heterocyclic aldehydes by acidic hydrolysis is thus enabled by reacting heterocyclic bases (*e.g.* quinoline, quinaldine and lepidine) with ethers (*e.g.* tetrahydropyran, dioxane, dioxolane, diethyl ether and trioxane).[62b] The α-oxyalkyl radical generated either by hydrogen abstraction from the α-carbon or by electron transfer from the oxygen followed by deprotonation from the carbon α to the oxygen radical cation (Scheme 6) is responsible for the high selectivity observed and yields up to 75% are common.

One-pot cyclizations

Amino acids in deaerated aqueous suspensions[63] of TiO_2 and CdS (Scheme 7) are successfully cyclized *via* a combination of oxidation and reduction with full retention of (*S*)-configuration in the product (pipecolinic acid) when the reaction was promoted by TiO_2 (a racemate was formed in CdS-catalysed reaction). The highest selectivity of 77% was reached with a hydrothermal crystallised TiO_2 at conversion >90%. Hence, a crucial intermediate in the preparation of biologically active heterocyclic species (used for example as anaesthetics) is directly and selectively obtained in aqueous medium.



Scheme 6 Hypothesised mechanism of formation of the α-oxyalkyl radical in the presence of TiO_2.[62b]



Scheme 7 Photocatalytic cyclization of lysine to pipecolinic acid by using two different semiconductors.[63]

Carbonylation

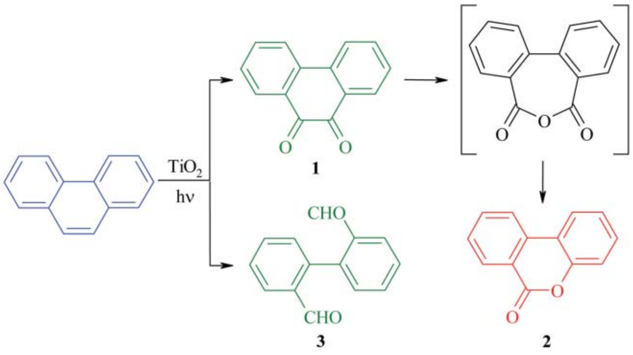
p-Nitrotoluene to carbamate conversion can be achieved at room temperature and pressure in neat ethanol, with suspended TiO_2.[64] The reached selectivity is *ca.* 85% with conversions of *ca*. 26%. The secondary product (selectivity *ca.* 15%) was *p*-toluidine. This reaction allows one to avoid the use of a poisonous and corrosive gas such as phosgene, used in industrial preparations of aromatic isocyanates, which instead can be obtained by easy cracking of carbamates. In place of phosgene, in this reaction carbon monoxide is generated by ethanol, which is first oxidised by $^{\bullet}OH$ to acetaldehyde, that undergoes hydrogen atom abstraction, eventually forming CO and $^{\bullet}CH_3$.

Coumarin compound synthesis

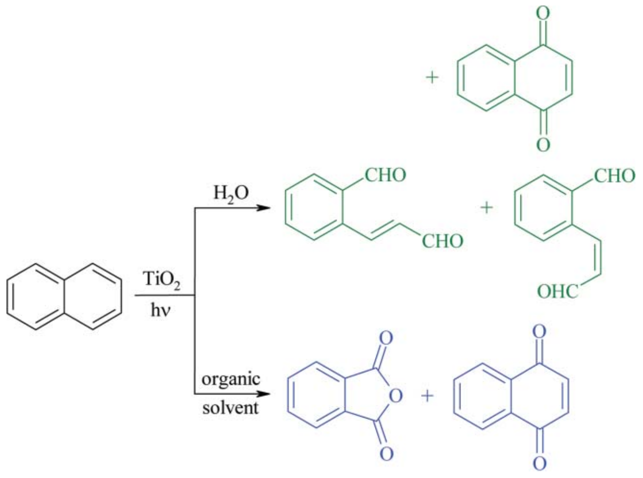
Irradiating solutions of phenanthrene and acetonitrile ($\lambda >$ 340 nm) in the presence of TiO_2 yields a coumarin compound at room conditions, with 8% water and oxygen as oxidant.[65] This type of compound retains appeal since they are intermediates for many chemicals, including pharmaceuticals and fluorescent dyestuffs. The reaction mechanism is illustrated in Scheme 8 and the main product (**2**) was obtained with a yield of 45%. The estimated quantum efficiency is around 17% by using light of *ca.* 365 nm. Finally the production of **2** in this one-pot reaction is attractive because the conventional syntheses of such species from commercial compounds require many steps.

Naphthalene oxygenation

Water (containing 1% CH_3CN) and organic solvents give different selectivities in the attractive oxidation of naphthalene



Scheme 8 Photocatalytic oxidation of phenanthrene to a coumarin compound.[65]



Scheme 9 Photocatalytic oxidation of naphthalene in aqueous and organic solvents.[66b]

and its derivatives.[66b] In the former case 2-formylcinnamaldehydes together with 1,4-naphthoquinone were formed, with a maximum yield of 11% when conversion was *ca.* 50%. Conversely when using organic solvents the main product was phthalic anhydride and considerable quantities of 1,4-naphthoquinone were also formed (Scheme 9). In this case, however, the reaction rate was one order of magnitude lower probably both for a less favoured adsorption on the semiconductor and for a less efficient electron transfer. The reaction selectivity and the hypothesised mechanism suggest that in organic solvents the primary pathway is an electron transfer one, while the C–C bond breakage occurs only in water, probably because this process involves a significant charge separation.

Addition-cyclization reactions of aromatic tertiary amines

Excited semiconductors such as TiO$_2$ and ZnS have been used as photochemical sensitizers for the radical addition of tertiary amines to electron deficient alkenes.[67] The reaction of various α,β-unsaturated lactones with methylpyrrolidine was carried out with high conversion rates and yields.

In order to improve the selectivity of radical reactions in organic chemistry, photochemical methods have been efficiently tested for the stereoselective radical addition of tertiary amines to electron deficient double bonds[67a] and radical tandem reactions.[67b] In particular the diastereoselective tandem addition–cyclization reaction of *N*,*N*-dimethylaniline with menthyloxyfuranone was performed.

Unsaturated α-amino esters synthesis

Novel unsaturated *N*-phenyl-α-amino esters can be obtained by irradiation at $\lambda > 350$ nm of silica-supported CdS methanolic suspensions. The involved reagents are methyl (2*Z*)-phenyl(phenylimino)acetate and various cyclic olefins (represented by RH in Scheme 10). Supporting the catalyst over silica results in a three-fold increase in reaction rate. Scheme 10 shows the main product obtained together with the only by-product. The C–C hetero-coupling steps taking place in this reaction generate two chiral carbon centers, yielding a mixture of four diastereoisomers. The highest yield (referred only to the main product) obtained was 49% and no reaction took place in the absence of catalyst showing the distinct photocatalytic feature of this process.

Scheme 10 Photocatalytic synthesis of unsaturated α-amino esters.[69c]

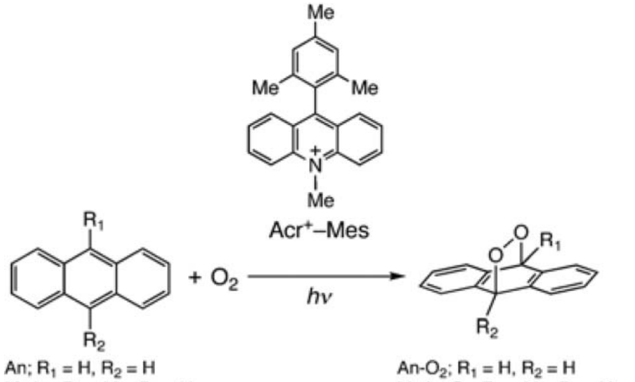
Anthracene and olefin oxygenation

Visible light ($\lambda > 430$ nm) irradiated 9-mesityl-10-methylacridinium ion (Acr$^+$–Mes, Scheme 11) and oxygen promote the oxygenation of anthracenes and olefins.[72] Acr$^+$–Mes initiates the reaction with the formation of the electron-transfer state Acr$^•$–Mes$^{•+}$. Subsequently two simultaneous electron transfers from anthracenes (or olefins) to the Mes$^{·+}$ moiety and from Acr$^•$ to O$_2$ take place. The synthesised products from anthracenes (with yields of 99, 46 and 75% for Me$_2$An, MeAn and An, respectively) are epidioxyanthracenes. The reached quantum yields in the processes represented in Scheme 11 are rather high, ranging from 62 to 91%. Anthrone and anthraquinone derivatives are formed for long-lasting runs. In Fig. 12 the trends of reagent and products are showed in the case of anthracene.

As far as the oxygenation of olefins is concerned they can be converted to dioxetanes and, upon prolonged irradiation times, ketone derivatives.

6 Conclusion and outlook

This feature article, in which only some of the several works concerning photocatalytic selective reactions are summarized briefly, shows that photocatalysis can be applied as a green synthetic route in organic chemistry.



Scheme 11 Photocatalytic oxygenation of anthracenes with dioxygen. (Reprinted with permission from ref. 72. Copyright 2004, American Chemical Society.)

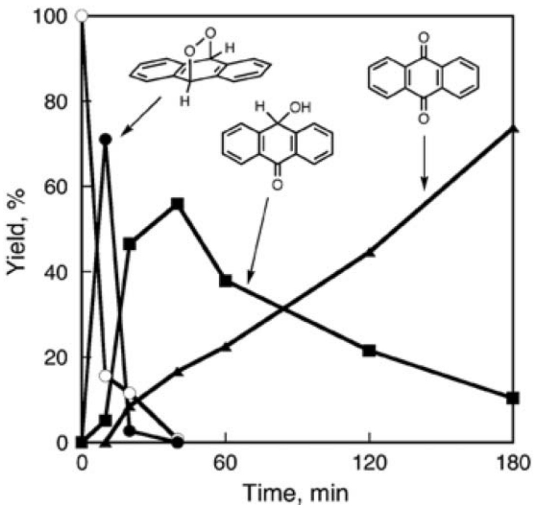


Fig. 12 Photooxygenation of anthracene (10^{-2} M) in the presence of Acr$^+$–Mes (10^{-3} M) in O_2-saturated acetonitrile. Anthracene (○), An-O_2 (●), 10-hydroxyanthrone (■), and anthraquinone (▲). (Reprinted with permission from ref. 72. Copyright 2004, American Chemical Society.)

Despite the pervasiveness of a few applications, the controlled use of light to cause chemical reactions is in its infancy. Theoretically the stage was set for dramatic growth in photochemistry when the laser was invented in the early 1960s but in practice commercial applications of laser-based chemistry have proved elusive in the following half century. Photocatalysis is emerging as a potent synthetic route in organic chemistry. Both semiconductors and various organic species can be used as catalysts with increasingly good results in terms of yields and selectivity. Heterogeneous metal oxides catalysts however are more easily recyclable, since they can be simply separated and usually are not readily deactivated or when deactivation occurs it is a reversible process.

The long-term low selectivity issue typical of traditional photochemical processes is being addressed by taking control of the state of excited species. This is done by control of the reaction environment as the medium influences their competition against fast decay of the Franck–Condon excited species. As pointed out by Liu and Hammond, "confinement does not necessarily lead to inhibition of reactions of the trapped substrate";[73] and we have discussed elsewhere why photochemistry in doped sol–gel oxides will play a major role in this evolution.[74] Yet, economic competitive advantage drives industrial innovation, and not sustainability or simple technical feasibility. Hence, in order to find wider application, photocatalytic processes need to be made cheaper. Employment of sunlight is of course an option even if solar photons, as Archimedes first showed some twenty-three centuries ago, need to be concentrated, especially in scaled up processes. Yet, mimicking Nature's photosynthesis as a route to harness solar photons for use in conventional synthesis seems most promising. When this will be accomplished, rapid global spread of photochemical synthesis will take place. By highlighting some of the principles of photocatalysis emerging from current research, the aim of this article is to accelerate this evolution.

Acknowledgements

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