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Photocatalysis with Organized Systems for the Oxofunctionalization of Hydrocarbons by O_2

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I. Introduction

A great deal of attention has been devoted in the last years to photocatalytic processes both in the homogeneous phase and in heterogeneous systems. In its broadest sense, photocatalysis concerns the use of light to induce chemical transformations on organic or inorganic substrates that are transparent in the wavelength range employed.[1−3] Radiation is absorbed by a photocatalyst whose electronically excited states induce electron- or energy-transfer reactions able to trigger the chemical reactions of interest.

Wastewater decontamination, solar energy conversion, and photoelectrochemical processes are main research targets in the field of photocatalysis.[4−11] However, the possibility that this technique could also provide an alternative to more conventional synthetic pathways has attracted the growing interest of many researchers.[12−25] Significant examples of photocatalytic processes employed for synthetic purposes are oxidation and reduction processes, isomerization reactions, C−H bond activations, and C−C and C−N bond-forming reactions. This review aims to cover recent advances in the use of photocatalysis for the oxofunctionalization of hydrocarbons with molecular oxygen. A carefully examination of literature data shows that this synthetic issue has been confronted only in a few cases and has not been recently examined in a systematic way.

The use of solar light as a reagent in oxidative catalysis is particularly relevant to realizing innovative and economically advantageous processes for conversion of hydrocarbons into oxygenates and, at the same time, to move toward a “sustainable chemistry” that has a minimal environmental impact. This is true for at least three main reasons: (i) Solar light represents a totally renewable source of energy. (ii) Photochemical excitation requires milder conditions than thermal activation. (iii) Photochemical excitation allows one to conceive shorter reaction sequences and to minimize undesirable side reactions. The second key reagent employed in the oxygenation processes considered herein is the molecule of O_2. In this connection, it is important to underline that the search for new catalysts capable of inducing the oxofunctionalization of hydrocarbons with this environmentally friendly and cheap reagent represents a major target from the synthetic and industrial points of view.[26−32] On the basis of pure thermodynamic considerations, most organic compounds are not stable with respect to oxidation by O_2. There are, however, kinetic limitations in this process mainly imposed by the triplet ground state of the O_2 molecule, which is not consistent with the singlet states of many organic substrates. In the following, we will show that activation of both O_2 and the organic substrate may be achieved by photochemical excitation with light of the visible or of the near-ultraviolet regions ($\lambda > 300$ nm).

It is a fact that selectivity is a key issue in the catalysis of fine chemicals production. To pursue this objective, all the steps of the oxidation process must be optimized. Generally speaking, the use of heterogeneous and organized systems is a suitable way to control efficiency and selectivity of catalytic processes

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Andrea Maldotti received the Doctoral degree in Chemistry from the University of Ferrara in 1976. At the same place he acquired experience in photochemical research under the guidance of Prof. Vittorio Carassiti. Since 1992 he has been Associate Professor of General and Inorganic Chemistry at the Faculty of Science of the University of Ferrara, where his teaching load includes courses on general and inorganic chemistry, bioinorganic chemistry, and chemistry laboratory. His current research interest is mainly focused on homogeneous and heterogeneous photocatalysis (including oxidation reactions, photoelectrocatalysis, and the reactivity of modified surfaces) as well as bioinorganic chemistry.

Alessandra Molinari was born in Ferrara, Italy, in 1968. She received her degree in Chemistry at the University of Ferrara in 1994 and her Ph.D. degree in Chemistry from the same University in 1998, under the direction of Prof. Vittorio Carassiti and Prof. Andrea Maldotti. During that period, she spent a period in the lab of Dr. Daniel Mansuy in Paris getting experience in the synthesis of silanized metal porphyrin complexes. Since 1999 she has been at the Chemistry Department of the University of Ferrara as a postdoctoral fellow. Her current research field is heterogeneous photocatalysis based on the use of polyoxometalates, semiconducting oxides, and metal porphyrins, covering aspects of preparation and optimization of the organized catalysts, study of the reaction mechanisms, and photochemical characterization. A. Molinari is the coauthor of more than 20 articles on these subjects in international journals and of a book chapter. She is a member of EPA (European Photochemistry Association) and GIF (Italian Group of Photochemistry). She has been awarded the Enichem Award (1994) and the Italian National Federchimica Award (1995).

through the control of the microscopic environment surrounding the catalytic center. In particular, the nature of the reaction environment may affect numerous physical and chemical functionalities of the photocatalytic system such as the absorption of light, the generation of elementary redox intermediates, the rate of competitive chemical steps, and the adsorption−desorption equilibria of substrates, intermediates, and final products. Moreover, another fundamental role of a solid support is to make the photocatalyst more easily handled and recycled.

Rossano Amadelli received his degree in Chemistry from the University of Ferrara (Ferrara, Italy) and his Ph.D. degree in Chemistry (1982) under the guidance of Prof. Ernest B. Yeager from Case Western Reserve University, Cleveland, OH. Afterward he moved back to Italy where he obtained a position as a research fellow of the Italian National Research Council (CNR) at the “Centro di Fotoreattività e Catalisi” (CSFC) in Ferrara. Since 1991 he has held the position of Director of Research at the same Research Center, now a section of the ISOF–CNR Institute. His earlier research activities had focused on studies of adsorption of organic compounds at the metal–solution interface (Hg, In–Ga) and on the reduction of oxygen on noble metals. Later research interests have concerned mainly catalysis, in particular, (i) photocatalysis and photoelectrocatalysis on semiconductors, especially for the oxidation of hydrocarbons and for the degradation of pollutants, and (ii) electrocatalytic processes (ozone formation, oxidation of organic compounds) at high potentials on conductive oxides (PbO_2) and metal electrodes (Pt, Ni).

The optimal tailoring of organized photocatalysts benefits from examination of a large number of materials such as photosensitive semiconductors, neutral organic polymers, ion exchange membranes, inorganic polymers as linear and cyclic polysilicate (clay, zeolites, etc.), and molecular aggregates composed of surfactants or lipids. Here, we attempt to summarize and classify the significant features of different organized systems able to induce photocatalytic hydrocarbon oxygenations.

We will emphasize the versatility and the growing interest of this research, largely dealing with the recent literature. Wherever needed, we will discuss the reaction mechanisms and the catalyst stability in view of reuse in multiple catalytic cycles. Moreover, we point out that both the comprehension of the mechanism and the building up of stable photocatalytic systems are of interest in a variety of other applications of photocatalysis, included environmental pollution control through oxidative mineralization of organics.

II. Photocatalysis Based on One-Step Redox Processes

A. Common Primary Photochemical Processes

The photochemical behavior of the photocatalysts described in this section is characterized by some common features. Absorption of light by the ground state of the photocatalyst (P) produces an excited state (eq 1), from which oxidation of molecular or anionic species (S) and reduction of O_2 simultaneously occur (eq 2), with an efficiency that depends on the possibility that the excited photocatalyst reacts successfully before its deactivation (eq 3). The process occurs in a cyclic way and leads to the formation of the intermediates $S^{\bullet+}$ and the O_2-reduction species, which take part effectively in the subsequent oxofunctionalization of organic substrates.

$$P + h\nu \rightarrow P^* \quad (1)$$

$$P^* + S + O_2 \rightarrow S^{\bullet+} + \text{reduction products of } O_2 + P \quad (2)$$

$$P^* \rightarrow P + h\nu'/\Delta T \quad (3)$$

The following discussion concerns photocatalytic systems based on the use of molecular species as well as heterogeneous semiconductors. It is easy to see the close relationships between the excited states of these two classes of compounds. Irradiation of a molecular species promotes an electron from a filled (HOMO) to an unfilled (LUMO) molecular orbital. The so produced excited state is a more powerful reductant and oxidant than the ground state, since the excited electron may be easily removed, and the photogenerated "hole" may accept more easily an additional electron. In a heterogeneous photoactive semiconductor a set of closely spaced, filled molecular orbitals form the valence band and a set of closely spaced, empty molecular orbitals form the conduction band. Photoexcitation with light of energy equal to or greater than the band-gap energy promotes an electron from the valence band to the conduction band (e^-_{CB}) leaving an electron deficiency or "hole" in the valence band (h^+_{VB}). Interfacial electron-transfer processes may, then, occur with adsorbed substrates.

B. Biomimetic Approach

A number of studies carried out in homogeneous phase have demonstrated that Fe(III) porphyrin complexes ($Fe^{III}P$) are able to photocatalyze the oxidation of alkanes and alkenes (RH_2) through the general mechanism schematized by eqs 1−3.[33−43] Photoexcitation ($\lambda = 300-400$ nm) in axial ligand (L) to metal charge-transfer bands may induce the homolytic cleavage of the Fe(III)−L bond, which causes the oxidation and the detachment of L as radical species and the reduction of Fe(III) to Fe(II) (eq 4).[33,34,38,43,44] The photoreaction quantum yields range from 10^{-4} to 10^{-1} and depend on the nature of the iron compounds, on the efficiency of the charge separation occurring in competition with the radiationless deactivation of the excited state, and on the possibility for the radical $L^\bullet$ to escape from the first coordination sphere of the metal before cage recombination.

$$Fe^{III}(L)P + h\nu \rightarrow Fe^{II}P + L^\bullet \quad (4)$$

The so obtained radical species $L^\bullet$ are able to initiate chain autoxidation processes via hydrogen abstraction from the substrate (eq 5). The reaction of $RH^\bullet$ with O_2 would yield peroxo species $RHOO^\bullet$ and RHOOH, which, typically, lead to the formation of the corresponding alcohols and ketones. These processes are not characterized by very high quantum yields ($10^{-2}-10^{-1}$) since chain autoxidation processes via hydrogen abstraction from the substrate are not favored at room temperature.

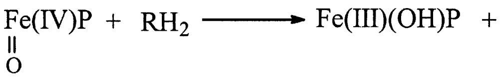
$$L^\bullet + RH_2 \rightarrow HL + RH^\bullet \xrightarrow[RH_2]{O_2} RHOOH + RH^\bullet \quad (5)$$

It has been demonstrated that oxidation yield and product distribution depend on the contribution of additional oxidation reactions, to which the iron porphyrin intermediates in different oxidation states take part directly. In this framework, the possibility to form high-valent species, which are key intermediates in the catalytic cycles of natural oxygenases, makes the reactivity of photoexcited iron porphyrin of interest in biomimetic catalysis.[44,45]

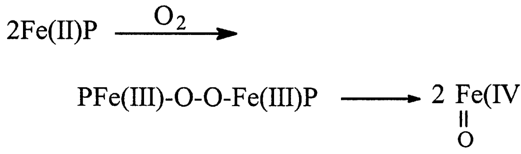
Oxoiron(IV) complexes ($PFe^{IV}{=}O$), able to generate, in turn, radical species through (eq 6), may be originated from thermal decomposition of μ-peroxo dimers (eq 7), as well as from photodisproportionation of μ-oxo derivatives (eq 8). Highly reactive oxoferryl porphyrinate π cation radicals ($^{+\bullet}PFe^{IV}{=}O$) may induce the hydroxylation of alkanes and the epoxidation of alkenes (eqs 9 and 10). The formation of these oxidizing intermediates may occur through the reaction sequence (11), when the presence of sterically hindered substituents on the porphyrin ring prevents the formation of μ-oxo dimers and polar solvents favor intramolecular decomposition of Fe(III)−peroxoalkyl complexes. The final product distribution may also be affected by the reactions between peroxide species and the iron complex both in its ferrous and ferric forms (eqs 12−14).

Work in the past decade has demonstrated that heterogenization of iron porphyrins offers a number of advantages in the selection of one oxidation pathway in thermal catalysis.[45,46] In this context, some efforts have been done to verify the possibility to use the photocatalytic approach. The most significant results are summarized in Table 1.

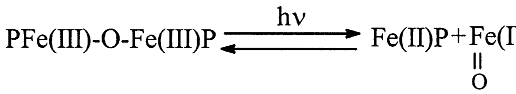
Weber and co-workers reported that iron porphyrins are able to photocatalyze enantiodiscriminating oxygenation reactions when employed in an organized molecular system. They investigated the photocatalytic behavior of an iron tetraarylporphyrin connected to heptakis(2,6-di-*O*-methyl)-β-cyclodextrin through a spacer group.[47,48] Some hours irradiation under aerobic conditions of this modified porphyrin dissolved in acetonitrile containing a racemic mixture of *R*-(+)-α-pinene and *S*-(−)-α-pinene causes oxidation of *S*-(−)-enantiomers in good excess. The authors proposed that the iron porphyrin should assist both the photooxidation of the axial ligand Cl^- to $Cl^\bullet$ radical according to eq 4 and the catalyzed direct epoxidation by high-valent oxygenating species. However, the nature of the products strongly suggests that other nonenantioselective reactions via free radical chain oxidation must be involved. The observed products along with their enantiomeric excess depend on the employed solvent. Thus, in the photocatalytic oxygenation of pinene using the chiral complex, enantiomeric discrimination is higher in acetonitrile than in benzene. This is likely due to the polarity of the former solvent, which forces the apolar substrate into the hydrophobic cyclodextrin cavity.



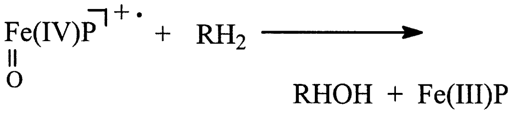
$$\underset{\overset{\|}{\mathrm{O}}}{\mathrm{Fe(IV)P}} + \mathrm{RH_2} \longrightarrow \mathrm{Fe(III)(OH)P} + \mathrm{RH^{\bullet}} \quad (6)$$



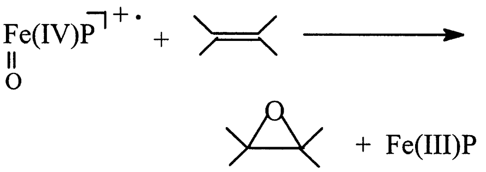
$$2\mathrm{Fe(II)P} \xrightarrow{\mathrm{O_2}} \mathrm{PFe(III){-}O{-}O{-}Fe(III)P} \longrightarrow 2\,\underset{\overset{\|}{\mathrm{O}}}{\mathrm{Fe(IV)P}} \quad (7)$$



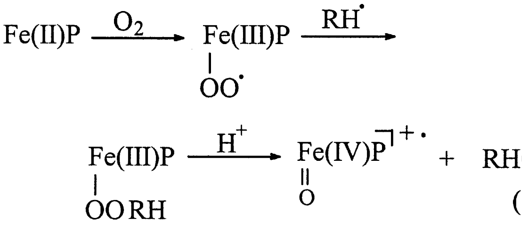
$$\mathrm{PFe(III){-}O{-}Fe(III)P} \underset{}{\overset{h\nu}{\rightleftarrows}} \mathrm{Fe(II)P} + \underset{\overset{\|}{\mathrm{O}}}{\mathrm{Fe(IV)P}} \quad (8)$$



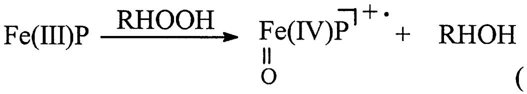
$$\underset{\overset{\|}{\mathrm{O}}}{[\mathrm{Fe(IV)P}]^{+\bullet}} + \mathrm{RH_2} \longrightarrow \mathrm{RHOH} + \mathrm{Fe(III)P} \quad (9)$$



(10)



$$\mathrm{Fe(II)P} \xrightarrow{\mathrm{O_2}} \underset{\mathrm{OO^{\bullet}}}{\underset{|}{\mathrm{Fe(III)P}}} \xrightarrow{\mathrm{RH^{\bullet}}} \underset{\mathrm{OORH}}{\underset{|}{\mathrm{Fe(III)P}}} \xrightarrow{\mathrm{H^+}} \underset{\overset{\|}{\mathrm{O}}}{[\mathrm{Fe(IV)P}]^{+\bullet}} + \mathrm{RHOH} \quad (11)$$



$$\mathrm{Fe(III)P} \xrightarrow{\mathrm{RHOOH}} \underset{\overset{\|}{\mathrm{O}}}{[\mathrm{Fe(IV)P}]^{+\bullet}} + \mathrm{RHOH} \quad (12)$$

$$\mathrm{Fe(III)P} + \mathrm{RHOOH} \longrightarrow \mathrm{Fe(II)P} + \mathrm{RHOO^{\bullet}} + \mathrm{H^{+}} \quad (13)$$

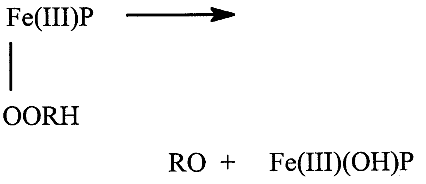
$$\mathrm{Fe(II)P} + \mathrm{RHOOH} \longrightarrow \mathrm{Fe(III)P} + \mathrm{RHO^{\bullet}} + \mathrm{OH^{-}} \quad (14)$$

The biomimetic approach to induce hydrocarbon oxofunctionalization with organized systems has been followed by our research group in the last 10 years. The main significant results have been obtained using the iron(III) *meso*-tetrakis(2,6- dichlorophenyl)-porphyrin ($\mathrm{Fe^{III}TDCPP}$). An interesting peculiarity of this complex is that the chlorine atoms in its *meso*-aryl groups prevent the formation of μ-oxo dimers and provide a steric protection of the porphyrin ring against its radical induced oxidative degradation. We found that $\mathrm{Fe^{III}TDCPP}$ could be hosted inside different heterogeneous or microheterogeneous systems. In all cases the primary photochemical act has been identified as the photoinduced reduction of Fe(III) to Fe(II) with the simultaneous oxidation of the axial ligand to radical species according to eq 4. On the other hand, the reaction environment may control some of the main parameters affecting the reactivity of these intermediates and, therefore, the chemoselectivity of the oxidation processes.

$\mathrm{Fe^{III}(Cl)TDCPP}$ could be physically entrapped inside cross-linked polystyrene utilizing solvent-dependent swelling. This kind of heterogenization did not cause any change of the photocatalytic properties of the iron porphyrin.[49] In fact, as shown in Table 1, the formation of allylic oxidation products through radical chain autoxidation processes prevails. The oxidation process occurs with good turnover value and quantum yield (2.2×10^{-2} at 365 nm).

More recently, we investigated the photocatalytic behavior of $\mathrm{Fe^{III}TDCPP}$ in micellar aggregates.[50] As outlined by Kalyanasundaram,[51] these systems can be considered “heterogeneous” at the “microscopic” level. The main positive implications of the use of micellar aggregates are the possibility to employ (i) optically transparent solutions readily amenable to photochemical investigation, (ii) water as a medium for carrying out organic transformations, and (iii) reagents and reaction intermediates confined in small hydrophobic cavities.

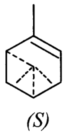
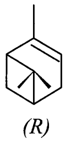
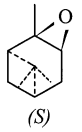
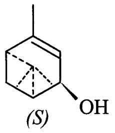
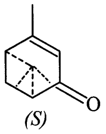
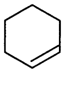
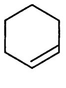
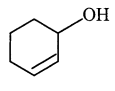
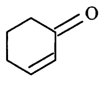
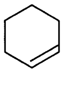
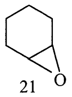
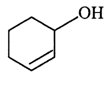
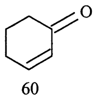
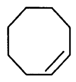
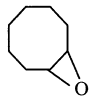
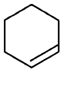
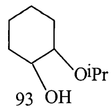
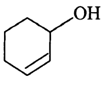
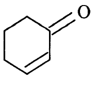
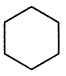
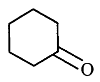
We found that aqueous solutions of *N*,*N*-dimethyltetradecylamine *N*-oxide ($\mathrm{C_{14}H_{29}NO(CH_3)_2}$, DTAO) are able to dissolve both $\mathrm{Fe^{III}(Cl)TDCPP}$ (2×10^{-5} M) and considerable amounts of cyclohexene or cyclooctene (up to 5×10^{-2} M). Irradiation ($\lambda > 350$ nm, 4 h) in the presence of oxygen leads to the formation of cyclohex-2-en-1-one as main oxidation product of cyclohexene (third row in Table 1).[50] We inferred that the photocatalytic process occurs mainly in the nonpolar region of the micelles, where the heterolytic cleavage of the Fe(III) porphyrin cyclohexenyl peroxide intermediate is not favored (reaction sequence (11)). Rather, it undergoes an intramolecular decomposition, giving the starting Fe(III) porphyrin complex and the corresponding ketone (eq 15).[43,52] Cyclohexene and cyclooctene are also oxidized to the corresponding epoxides, with a selectivity higher than 90% in the case of cyclooctene.



$$\underset{\mathrm{OORH}}{\underset{|}{\mathrm{Fe(III)P}}} \longrightarrow \mathrm{RO} + \mathrm{Fe(III)(OH)P} \quad (15)$$

Nafion (a Du Pont Nemours registered trademark) is an optically transparent polymer consisting of a perfluorinated backbone connected to sulfonic groups through short chains of a perfluoropropylene ether. The monocationic iron porphyrin $\mathrm{Fe^{III}(Pr^{i}OH)TDCPP}$ can be caged inside the anionic cavities of Nafion simply by swelling the membrane in an alcoholic medium.[44,53] This system is expected to favor oxidation reactions in the proximity of the metal center as well as to inhibit autoxidation processes in the solution bulk. Therefore, contrary to what is observed in homogeneous solution, its irradiation ($\lambda > 350$ nm, 6 h) in $\mathrm{Pr^{i}OH}$−cyclohexene results in the formation of more than 90% *trans*-cyclohexane-1,2-diol mono-

Table 1. Photocatalytic Oxidations with Iron Complexes

Organized photocatalyst	Solvent or dispersing medium	Substrate	Product distribution %[a]	Turn over[b]	Ref
Cyclodextrin-linked Fe(III)P	CH_3CN	 (S)  (R)	 (S) 51(11)  (S) 26(18)  (S) 23(3)	15	47, 48
FeTDCPP/ polystyrene			 43  57	2500 (4000)	49
FeTDCPP/ DTAO	H_2O		 21  19  60	10 (35)	50
FeTDCPP/ DTAO	H_2O		 >90%	12 (40)	50
Fe(Cl)TDCPP/ Nafion	Pr^iOH		 93  6  1	90 (800)	44, 53
$FeCl_3$ in aqueous emulsions	H_2O		 > 90%	< 1	54

[a] For the system of cyclodextrin-linked Fe(III) porphyrin, the number within parentheses is the enantiomeric excess. [b] Within parentheses are the mol of oxidized substrate/mol of destroyed iron complex.

ethyl ether and of only minor amounts of allylic oxidation products. It is worth noting that the heterogenization inside Nafion significantly improves both the efficiency and the stability of the iron porphyrin photocatalyst; in particular, the amount of oxidized cyclohexene and the turnover of the metal complex increase by 1 order of magnitude. The presence of cyclohexane-1,2-diol monoalkyl ether among the products indirectly reveals the formation of cyclohexene epoxide, which, in the strong acidic environment inside Nafion, undergoes a nucleophilic attack by the alcohol, inducing epoxide ring opening. Formation of epoxide is, in turn, an indication of the involvement of oxo−ferryl intermediates in the overall oxygenating photoprocess.

Some iron chloride salts are able to promote photocatalytic aerobic oxidation of hydrocarbons.[54] When aqueous emulsions of cyclohexane are irradiated ($\lambda > 300$ nm, 3 h) in the presence of $FeCl_3 \cdot 6H_2O$, cyclohexanone is obtained with high selectivity (>90%). On the contrary, analogous experiments carried out in homogeneous phase (CH_3CN−cyclohexane) lead to the formation of a mixture of ketone, alcohol, and hydroperoxide. The authors assume that ROOH is the primary product obtained as a consequence of radical chain oxidation processes initiated by the primary photoproducts Fe(II) and $Cl^•$. This peroxide should be selectively transformed into cyclohexanone under the employed conditions, through a mechanism that remains unclear. The main limitation of this system is its very low efficiency in comparison with the homogeneous phase systems, while the major advantage is the use of relatively cheap iron compounds.

C. Semiconductors

1. Basis of Semiconductor Photocatalysis

Heterogeneous photocatalysis on semiconductors has experienced an impressive growth in the last 20 years, and several review papers and books illustrate the enormous achievements in this field,[11,55−57] which is now mature enough as to be credited among the most promising advanced oxidation technologies (AOT) for environment remediation.

Studies focusing on environmental cleanup by far and large lead the research in this area. On the other hand, researchers in the field of semiconductor photocatalysis have always been conscious of its potentiality for photosynthetic applications,[6,14,58] although studies in this direction have probably been less systematic compared to those aiming at full mineralization. The awareness of the importance of green chemistry has given a boost to the pursue of environmentally friendly alternative processes under mild conditions, which avoid stoichiometric consumption of expensive oxidants.[19,59,60] Attention of recent studies has been concentrated mainly on TiO_2 since it combines unique characteristics, such as stability and environmental tolerance, that make it the ideal material for most applications despite the fact that it absorbs a small fraction of visible light.

The particular type of heterogeneous photocatalysis described here uses semiconductors in the form of dispersions or supported films to drive oxidation and reduction reactions; in this respect it can be considered as a particular case of photoelectrochemistry at open circuit conditions. Both for a photoelectrode or a semiconductor suspension, absorption of light creates electron−hole pairs that will recombine unless charge separation is maintained.

While in a n-type photoelectrode electrons can be conveyed through an external circuit and holes will be sufficiently long-lived to oxidize a large variety of substrates, in a suspension of the same semiconductor both charges have to be transferred through the interface to independent (acceptor and donor) species. This means that, for charge transfer to compete with recombination, the transfer of at least one of the photogenerated charges to species in solution must be a fast process. Due to its unlimited availability, oxygen is the common electron acceptor, and its role in the photocatalytic oxygenation of hydrocarbons will be discussed here. Among other important parameters that affect the photocatalytic processes are (i) composition of the reaction medium, (ii) adsorption, (iii) the kind of semiconductor and its crystallographic and morphological characteristics, and (iv) semiconductor bulk and surface modification.

2. Role of Oxygen and Adsorption

Adsorption of the substrate is an important factor that can control the reaction mechanism and the formation of products. In turn, adsorption is influenced by the nature of the reaction medium, e.g. polarity of the solvent for reactions in a liquid phase and humidity for reactions that are run at the gas−solid interface.

In photocatalytic processes using dispersed semiconductors oxygen is the straightforward electron acceptor independently of whether the target is mineralization or photosynthesis, and its reduction mechanism has been examined in a number of publications (eqs 16−19).[61−66]

$$TiO_2 \xrightarrow{h\nu} (e^-/h^+) \tag{16}$$

$$O_2 + e^- \rightarrow O_2^{-} \tag{17}$$

$$2O_2^{-} + 2H_2O \rightarrow H_2O_2 + 2OH^- + O_2 \tag{18}$$

$$H_2O_2 + e^- \rightarrow OH^\bullet + OH^- \tag{19}$$

It soon became evident that the role of O_2 is not just that of scavenging the photogenerated electrons and that its reductive activation is fundamental: it produces the so-called active oxygen species while the simultaneous oxidation of an organic substrate yields radical intermediates[62] as follows:

$$RH_2 + h^+ \rightarrow RH^\bullet + H^+ \tag{20}$$

$$(OH^-)_{surf} + h^+ \rightarrow (OH^\bullet)_{surf} \tag{21}$$

$$RH_2 + (OH^\bullet)_{surf} \rightarrow RH^\bullet + H_2O \tag{22}$$

$$RH^\bullet + (OH^\bullet)_{surf} \rightarrow (HROH)_{ads} \tag{23}$$

$$(HROH)_{ads} + 2(OH^\bullet)_{surf} \rightarrow RO + 2H_2O \tag{24}$$

Then, following a mechanism that Kisch[59] calls type B photocatalysis, coupling reactions of oxidation and reduction intermediates lead to products of partial or total combustion, depending on experimental conditions (eqs 25−30).[6,67,68]

$$RH^\bullet + O_2 \rightarrow HRO_2^\bullet \tag{25}$$

$$HRO_2^\bullet + RH_2 \rightarrow RH^\bullet + HROOH \tag{26}$$

$$HRO_2^\bullet + e^- \rightarrow RO + (OH^-)_{surf} \tag{27}$$

$$RH^\bullet + O_2^{-} \rightarrow RO + OH^- \tag{28}$$

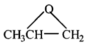
$$RH^\bullet + HO_2^\bullet \rightarrow RO + H_2O \tag{29}$$

$$HRO_2^\bullet + HO_2^\bullet \rightarrow HROOH + O_2 \tag{30}$$

There are now several examples illustrating the role of O_2 in processes of hydrocarbons photooxygenation on semiconductors. In an earlier work, Ward and co-workers[69] examined the selective oxidation of olefins to epoxides, alcohols, aldehydes, and ketones in a liquid medium. Although the oxidation of propylene was the main focus of this investigation, a large number of other olefins, having from 2 to about 20 carbon atoms, have been tested using illuminated suspensions of different semiconductors including TiO_2, MoO_3, WO_3, CdS, and $CuMoO_4$. Mixed catalysts, such as TiO_2−MoO_3, and metallized samples have also been employed.

As can be seen in Table 2, the choice of the electron acceptor (O_2, Cu^{2+}, or none) and the metal modification of the surface have an important effect on the distribution of products. It should be also pointed out that the overall formation of oxidation products decreased dramatically in the absence of O_2 and to a lesser extent when platinized TiO_2 was used. On the

Table 2. Effect of the Photocatalyst on Selectivity (mol %) in the Oxygenation of Propylene in Aqueous TiO_2 Suspensions[69]

Organized Photocatalyst	CH_3CHO	 $CH_3CH(O)CH_2$	$CH_2{=}CHCH_2OH$	CH_3CH_2CHO	CH_2CHCHO
TiO_2/O_2	78	18	4	-	-
$TiO_2/N_2/Cu^{2+}$	10	41	14	10	24
$TiO_2/O_2/Cu^{2+}$	32	51	1.1	6.2	10
$Pt\text{-}TiO_2/O_2$	82	13	1.5	3.3	-
$Pt\text{-}TiO_2/N_2$	1	28	8.2	63	-
$Pt\text{-}TiO_2/N_2/Cu^{2+}$	6.5	50	10	15	18
$TiO_2\text{-}MoO_3/O_2$	10.4	58.1	-	-	31.5

other hand, when a mixed H_2O-CH_3CN solvent was used, the yield of monooxygenated products and the selectivity toward acrolein production increased sensibly on increasing the amount of acetonitrile in the medium.

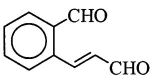
Research in our laboratories showed that the presence of oxygen is indispensable for the photooxidation of cyclohexane to cyclohexanol and cyclohexanone on titanium dioxide.[70] According to the mechanism proposed, the main route leading to cyclohexanone involves peroxy radicals intermediates that are formed by reaction of the hydrocarbon radicals (eqs 25−30) with activated oxygen species or O_2 itself. In contrast, cyclohexanol results from the reaction of species formed via valence band oxidation processes (eqs 20−24).

Reactivity of cyclohexane and selectivity depend markedly on the medium in which TiO_2 is dispersed. In neat cyclohexane the ketone represents more than 90% of the monooxygenation products. When the photooxidation is carried out in $C_6H_{12}-CH_2Cl_2$, the overall conversion of the parent hydrocarbon increases with increasing the content of CH_2Cl_2, as does the selectivity toward ketone and alcohol formation versus total degradation to CO_2. At the same time, a decrease in adsorption strength of the alcohol causes an increase of the $C_6H_{11}OH/C_6H_{10}O$ ratio as a function of the amount of CH_2Cl_2 in the mixed solvent. Further development in this area may involve kinetic studies for the complete comprehension of cyclohexane oxidation.

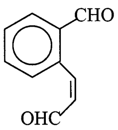
The results of the above research on the effect of adsorption were confirmed by Almquist and Biswas,[71] who carried out the oxidation of cyclohexane in different solvents. It is interesting that chloroform among these strongly inhibits the photooxidation process due to the fact that it can compete with the hydrocarbon for oxidation and with O_2 for reduction.

Titanium dioxide photocatalyzed partial oxidation of hydrocarbons by O_2 in an aqueous medium has been reported.[72] Selectivity in the formation of benzaldehyde from toluene is high, in agreement with earlier data,[73] while no cyclohexane oxygenation occurs unless hydrogen peroxide is added to the suspension. In this case, cyclohexanol and cyclohexanone are obtained with a selectivity of 30 and 44%, respectively, and this product distribution is strongly reminiscent of homogeneous phase autooxidation processes, likely due to light absorption by H_2O_2 itself. In addition, the relatively high yields of 1,1′-bicyclohexane and of dehydrogenation products seem to suggest that the reaction medium was poorly oxygenated.

Chart 1



1



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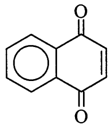

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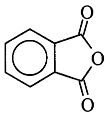


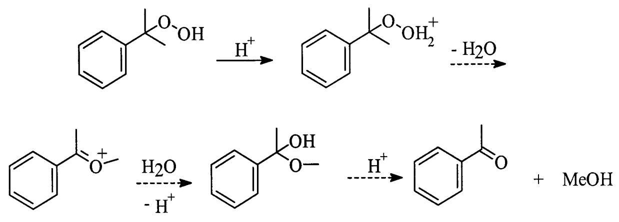
4

The role of O_2 and of solvent in the distribution of products of naphthalene photooxygenation on TiO_2 has been investigated by Soana and co-workers.[74] The oxidation of the hydrocarbon is initiated by addition of photogenerated $OH^{\bullet}$ radicals and the resulting organic radicals react with O_2 and/or the products of its reduction, i.e., O_2^{-} and $^{\bullet}HO_2$. The products that are formed via these coupled processes depend on the reaction medium (Chart 1). In an aqueous medium, 2-formylcinnamaldehydes (**1** and **2** in Chart 1) and naphthoquinone (**3**) are the main products, and selectivity is poor; in contrast, chemoselectivity is observed in organic solvents although the reaction is slower. Thus, only traces of the dialdehydes are formed while phthalic anhydride (**4**) is the main product in acetonitrile and, especially, in dichloromethane (about 20% of the intermediate products). In the first case, a significant amount of naphthoquinone is also formed. Furthermore, in the organic media, photooxidation is inhibited by electron-withdrawing groups in substituted naphthalenes.

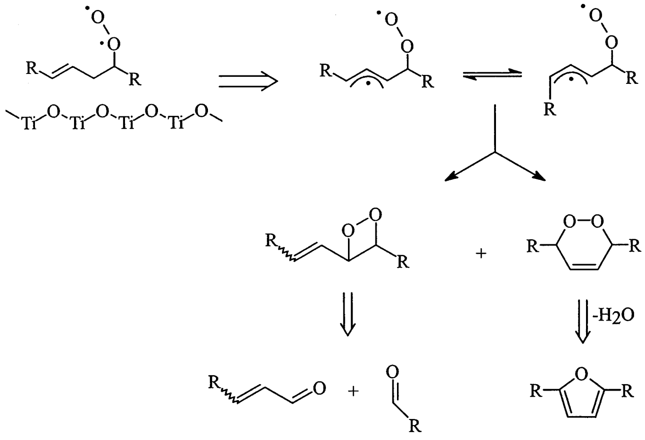
A highly efficient photocatalytic process of linear olefins epoxidation by molecular oxygen, using TiO_2 suspensions, has been reported by Ohno and co-workers.[75] The yield (epoxide produced/olefin consumed) increased with a decrease of chain length and in solvents with high donor number as follows: hexane < nitromethane < acetonitrile < butyronitrile. The last effect is attributed to a stabilization of cation radicals intermediates by the solvent. It should however be noted that Ermolenko and Giannotti[76] reported that nitrile solvents have a strong tendency to form hydroperoxides in the presence of irradiated polyoxotungstates; in particular, the high reactivity of propionitrile and isobutyronitrile is mentioned. It may well be that the data reported by Ohno[75] can also be explained by a process that is mediated by the solvent hydroperoxides.

A mechanistic analysis of acetophenone formation from the photooxidation of cumene in acetonitrile has been published by Wittenberg and co-workers.[77] From a detailed IR and XPS analysis of cumene adsorption on TiO_2, the authors conclude that an interaction of the benzene ring with surface OH groups takes place without appreciable dehydration or dehydroxylation of the surface. Acetophenone and CO_2 are the only reaction products detected, and the reaction proceeds with the intermediate of a hydroperoxide, according to the mechanism of Scheme 1.

Scheme 1



Scheme 2



The only way to account for the formation of acetophenone is to invoke the migration of a methyl group, which is in marked contrast to the phenyl group migration that explains the reaction mechanism of the industrial synthesis of phenol from the oxidation of cumene. This behavior is due to the fact that the phenyl group interacts with the surface and is not free to move.

O'Shea and co-workers[78] reported on the photooxygenation by O_2 of a number of substituted butadienes isomers over TiO_2 in acetonitrile. Reactivity is controlled by substituents which inhibit adsorption of the more reactive cis conformation. The authors propose that the diene radical cations are formed on the catalyst surface where they subsequently react with adsorbed superoxide radicals. In fact, reactions of the radicals with molecular oxygen is not considered likely since in a homogeneous phase the same radicals are insensitive to the presence of O_2. The radical cation−oxygen adducts diffuse away from the surface and undergo homogeneous phase bond rotations leading to loss of stereochemical and conformational identities (Scheme 2). The major products obtained from the oxidation of isomeric 2,4-hexadienes are acetaldehyde, *cis*- and *trans*-crotonaldehyde, and 2,5-dimethylfuran. Formation of cyclic oxygenated compounds also occurs via ring closure of the peroxyl radical adduct.

Several recent publications report on gas−solid photooxidations of hydrocarbons over TiO_2. In most cases the aim is photodegradation, but some studies also discuss the conditions that lead to the accumulation of oxygenated intermediates.

In the work by Augugliaro and co-workers[79] on the gas-phase photooxidation of toluene over TiO_2, partial oxidation of the hydrocarbons to benzaldehyde is observed rather than complete degradation. During the first hours of irradiation, the observation of benzene and CO_2 is attributed to decarboxylation of benzoic acid, in turn the product of benzaldehyde oxidation. Upon prolonged illumination a decrease in the rate of toluene conversion is attributed to poisoning of surface sites by reaction intermediates such as benzyl alcohol and benzoic acid. These same species block the surface sites that are responsible for the formation of benzoic acid, and the production of CO_2 and benzene stops after the first few hours. When toluene conversion reaches a steady state, only benzaldehyde is produced and no further catalyst deactivation is observed.

The role of water in the gas stream is discussed in the same work and in a later FTIR study.[80] With water present, at steady state, there is no decline in the formation of benzaldehyde, while for dry conditions the conversion of toluene to benzaldehyde is almost completely suppressed. The latter phenomenon is ascribed to an irreversible consumption of surface OH groups.

3. Influence of the Photocatalyst Type and Preparation

Some of the earlier publications present a screening of the activity of several semiconductor catalysts. Thus, Pichat and co-workers[81] describe the effect of the photocatalyst material on the partial oxidation of propene with oxygen. Several semiconductors were tested including TiO_2, ZrO_2, ZnO, V_2O_5, SnO_2, Sb_2O_4, CeO_2, WO_3, and Sn/Sb mixed oxides. Selectivity was found to obey the usual rule in catalysis, i.e., that of an increase as the oxidation yield decreases, and depended on the nature of the catalyst. Total oxidation to water and CO_2 was the predominant reaction over TiO_2, while partial oxidation was observed over SnO_2, WO_3, and Sb_2O_4. Partial photooxygenation of the olefin produced mainly acetaldehyde together with acrolein and acetone.

With reference to TiO_2, it is a generally recognized fact that it can present a rather different photocatalytic activity toward the same substrate in a liquid or gas phase. This is a question of differences in the crystallographic form (anatase or rutile) and morphology including shape and size of particles and surface area. The key issue is that active materials with ad-hoc characteristics for the use in photocatalysis are required, and the use of nanostructures with a mean particle size <20 nm, obtained by sol−gel methods, may meet this need at least in part.

The use of nanostructured semiconductors as photocatalysts offers a number of attractive characteristics such as (i) high absorption cross section, (ii) fast diffusion of carriers to the interface that, in principle, can reduce recombination, and (iii) high surface-to-volume ratios. Research in this field is intensive, and a large number of applications have been reported.[81−85]

As far as we are aware, the use of nanostructured semiconductors for the photosynthetic reactions of interest here is in its infancy. There are however few interesting publications. The effect of particle size is examined, for example, by Maira and co-workers[86] in the gas-phase photooxidation of toluene over TiO_2. The size of the particles (from 6 to 20 nm) is reported to influence the activity and selectivity of the photocatalyst. In particular, selectivity toward benzaldehyde production increases as the particle size increases.

Results are explained on the basis of the fact that the smaller particles are characterized not only by a larger surface area but also by a larger proportion of edges and corners that increases as size decreases. Edges and corners are expected to exhibit different catalytic and adsorption properties compared with the more planar surface sites.

The EPR technique is used to prove that the kind of oxygen species that are traps for electrons and holes depend on the size of the particles. Trapping of holes by lattice oxygen is considered to occur preferentially on larger size particles, while as size decreases holes become preferentially trapped by subsurface oxygen species. The involvement of $Ti^{4+}-O^{-}$ radicals is proposed to be the reason of the increase of selectivity to benzaldehyde as the particle size of the TiO_2 samples increases from 6 to 20 nm.

The mechanism of benzaldehyde formation from toluene was also a target of an interesting paper by Martra.[87] The author employed high-resolution TEM and FTIR to study the morphology of two types of TiO_2 having a mean particle size that falls into the micro- rather than in the nanoscale domain, i.e., 40 nm (P-25, Degussa) and 140 nm (Merck).

Size is found to affect the acid−base properties of surface hydroxyl groups: they are electron acceptor centers in the case of the Merck sample, while in P-25 they present a nucleophilic character. These differences are invoked to explain a difference in selectivity to benzaldehyde formation from the gas-phase photocatalytic oxidation of toluene. In particular, the lower selectivity observed with P-25 is ascribed to a stronger adsorption of the aldehyde.

On the basis of the cited studies on the photooxidation of toluene, it would seem possible to favor the accumulation of hydrocarbon oxygenated intermediates by using TiO_2 photocatalysts characterized by a relatively high mean particle size. However, Ohno et al.[75] seem to draw opposite conclusions in their work on the epoxidation of olefins, where higher yields are observed with TiO_2 samples having higher area. In the cited work by Almquist and Biswas[71] on the partial oxidation of cyclohexane, the mean particle size turned out to be ca. 11 nm.

Probably, for a complete scenario on this issue more data with diverse substrates are needed since, evidently, the phenomena are complex and results likely depend on the nature of the organic substrate and on its mode of interaction with the surface.

4. Effect of Bulk and Surface Modification

Necessity to optimize the performance of materials to meet specific characteristics for application has stimulated research both on new materials and on the modification of materials, such as TiO_2, whose photocatalytic behavior is well-known. Common strategies of altering a semiconductor to obtain a material with predictable properties are (i) doping with foreign metal species, (ii) surface modification with metal islands, and (iii) surface derivatization.

Doped Semiconductors. Doping of TiO_2 with a broad variety of foreign metals[88−90] has attracted a great deal of attention due, in part, to the need to extend its response to illumination with visible light. Methods of preparation include sol−gel coprecipitation[89,90] and, more recently, ion-implantation.[91] Generally, however, it appears from literature reports that doping of TiO_2 inhibits rather than improving its photocatalytic activity in both photodegradation and partial photooxidation processes.[89,92] For the case when partial oxidation of hydrocarbons is the research target, one exception in this trend is represented by Fe-doped TiO_2.

The preparation and performance of $Fe-TiO_2$ photocatalysts has been reviewed by Litter and Navio.[93] While this doped material does not show an enhanced response to visible light, some interesting changes in the photocatalytic activity are promising. It was observed, for example, that the product selectivity in the partial oxidation of toluene changes significantly in comparison with pristine titania.[94] The main partial oxidation product was benzaldehyde in all cases; benzyl alcohol and benzoic acid appear upon prolonged irradiation.

The photocatalytic activity of $Fe-TiO_2$ materials depends markedly on the doping level.[95] A relatively high amount of iron (5 wt % in Fe^{3+}) had an adverse effect on the activity of TiO_2 for toluene oxidation, whereas some positive effects are observed with a lower Fe^{3+} concentration (0.5 wt %). In particular, the yield in benzaldehyde was higher than for undoped TiO_2 under prolonged illumination, using a lower amount of dispersed catalyst.

Problems connected with the stability of $Fe-TiO_2$ photocatalysts have been mentioned in the cited review of Litter and Navio.[93] One major cause of a decrease in activity seems to be connected with photocorrosion leading to loss of Fe from the doped material

$$\equiv Fe(III) + e^{-} \rightarrow \equiv Fe(II) \rightarrow Fe(II)_{solution} \quad (31)$$

competing with the activation of oxygen:

$$Fe(II) + O_2 \rightarrow Fe(III)-O_2^{-} \quad (32)$$

Surface-Modified Semiconductors. Deposition of small metal particles on semiconductor surface has been widely studied as a means of increasing the efficiency of electron−hole separation by favoring reduction processes,[6,96] and beneficial effects are observed using platinized TiO_2 for the photocatalytic mineralization of organic compounds.[97−99] In contrast, the effect of surface metallization in partial photooxidation processes is seemingly more ambiguous. For example, the data of Table 2 show a remarkable effect of platinization on selectivity for propylene oxidation, while negative effects in cyclohexane monooxygenation have been reported by Herrmann and co-workers.[92]

Chemical derivatization represents an alternative method of semiconductor surfaces modification. A large amount of work has been done in the field of modified surfaces, directed at tailoring their catalytic activity. In the field of photoelectrocatalysis the

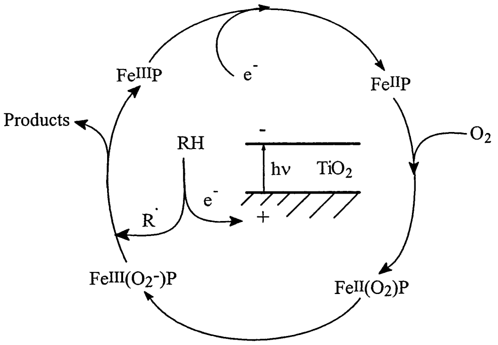


Figure 1. Photoinduced redox processes of the TiO_2−sil−FeP system.

search for new catalytic surfaces has been particularly active in view of improving the semiconductor surface stability against photocorrosion.

Surface derivatization for photoelectrosynthetic purposes is also gaining some new interest. In this case, the aim is that of controlling the reactivity and selectivity of the catalyst in a given process by linking non-light-absorbing molecules to the surface. This is well illustrated by an early work by Becker and coworkers,[100] which shows that the efficiency of α-methylstyrene photooxidation to acetophenone on TiO_2 increases considerably when the surface is modified by octyl groups.

A convenient way to immobilize molecular catalysts to surfaces is that of anchoring them via silane bond.[101] The photocatalytic behavior of TiO_2 surface modified by an anchored cobalt phthalocyanine was described by Hong et al.[102,103] Particularly, their study on the reduction of oxygen on the hybrid photocatalyst[103] was inspiring for our work on the photocatalytic formation of hydrocarbon oxygenates on TiO_2−iron porphyrin systems[104−106] where both the porphyrin and TiO_2 are able to function separately in the photocatalytic oxidation of hydrocarbons with molecular oxygen.

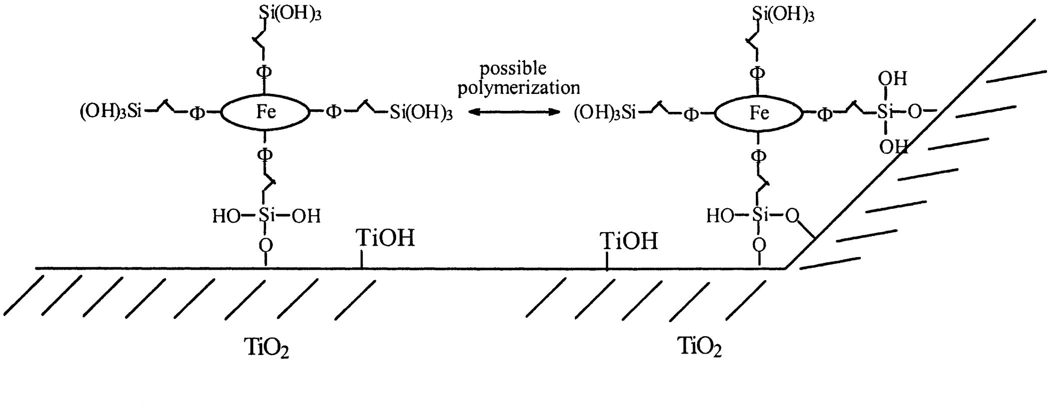
A Fe−porphyrin covalently linked to TiO_2 (TiO_2−sil−FeP) yielded a catalyst able to combine the high photochemical efficiency of the semiconductor with the biomimetic catalytic activity of the metal complex in the photooxidation of cyclohexane and cyclohexene.[104] Comparison with unmodified TiO_2 showed a higher selectivity to cyclohexanol formation and an increase in the yield in monooxygenated products of cyclohexene. On the other hand, in comparison with the porphyrin as a homogeneous phase catalyst, the yields of oxidation products formation are higher and, interestingly, the anchored porphyrin is more stable than in solution. Analogous experiments on the photooxidation of methylcyclohexane and *n*-heptane on hybrid TiO_2−sil−FeP photocatalysts features a different regioselectivity in the formation of ketones, along with a consistent decrease of CO_2 formation.[105]

In these systems, electrochemical experiments allowed to identify the porphyrin sites as the active centers for the reduction of O_2 according to Figure 1. In fact, the intermediate step in the derivatization process involves surface functionalization with silane functional groups, which results in a severe inhibition of O_2 reduction[104] (eqs 16−19) and of reactions 20−24 leading to hydrocarbon functionalization.

To avoid this drawback, an alternative synthetic route was adopted whereby the porphyrin ring itself bears silane functional groups[106] (Figure 2). With these alternative hybrid photocatalysts the overall concentration of partial oxidation products was twice that of the original TiO_2 in the case of cyclohexane and 3 times higher in the case of cyclohexene photooxidation.

Noteworthy this derivatization procedure avoids problems of extensive surface deactivation by silane groups and creates the conditions for cooperation among the free TiO_2 surface sites and the porphyrin centers. Elementary steps at these centers are essentially those of the biomimetic mechanism (eqs 6−14), involving an Fe(II)/Fe(III)-mediated reduction of O_2 and of peroxides and the formation of hypervalent Fe^{IV}=O intermediates that are efficient monooxygenating species. Interestingly, a similar mechanism is proposed for photooxidation processes at Fe-doped TiO_2, also involving formation of Fe(IV) as an active intermediate.[93]

Extension of the derivatization procedure[106] to nanocrystalline TiO_2 proved particularly fruitful since these light-transparent samples allowed elucidation of mechanistic details through the use of different spectroscopic techniques. It was established, in particular, that charge recombination via the iron center of the porphyrin strongly depends on the composition of the reaction medium: the rate is high in water while it is low in organic solvents that can



Φ = (2, 6 dichloro)phenyl-mSO$_2$NH

Figure 2. Schematic structure of the composite system TiO_2−sil−FeP.[106]

coordinate to, and thus stabilize, the porphyrin in its reduced form.

Stability of these composite catalysts is a particularly important issue. In fact, the iron porphyrin complex undergoes a slow degradation during photocatalytic experiments. Nevertheless, considering that porphyrins are widely employed as homogeneous phase catalysts, it is interesting to point out that the turnover number of 12 000, calculated in the heterogeneous process of photooxidation of cyclohexane, is about 2 orders of magnitude higher than in analogous experiments where the complex is used as the only catalyst in solution.

D. Supported Oxides

1. Polyoxoanions

It has often been stated that polyoxometalates can be considered soluble models of semiconductor metal oxide surfaces.[107] At the same time, the ability to undergo photoinduced multielectron transfers without changing their structure makes polyoxometalates very attractive catalysts in the oxidation of organic substrates in the presence of O_2.[76,108−113] Their use in heterogeneous catalysis is attracting more and more interest.[114−121]

We have reported[118,119,121] that $(^nBu_4N)_4W_{10}O_{32}$ can be successfully supported on silica by following a previously described “impregnation” procedure,[114] which results in the fixation of the polyoxoanion on the support through electrostatic interactions. The positive tetraalkylammonium cations likely act as a bridge between the negative surface and the decatungstate. Photoexcitation ($\lambda > 300$ nm) of powder dispersions of the $(^nBu_4N)_4W_{10}O_{32}/SiO_2$ system induces the oxygenation of cyclohexane[118] and cyclohexene[121] at 20 °C and 760 Torr of O_2. Cyclohexane is oxidized to comparable amounts of cyclohexanol and cyclohexanone, and cyclohexene is transformed to the corresponding cyclohexenyl hydroperoxide (about 90% of the overall oxidized substrate) and to cyclohex-2-en-1-one (about 6%). Important aspects of the use of polyoxometalate in its heterogenized form are the following: (i) There is more freedom in the choice of the dispersing medium. (ii) The photocatalyst can be reused several times without any significant loss of photochemical efficiency. (iii) This efficiency is comparable with that observed in homogeneous solution. (iv) Contrary to TiO_2, the heterogenized decatungstate does not cause any photomineralization of the substrate.

A reaction mechanism, which is summarized by eqs 33−40, has been proposed on the basis of previous work regarding the reactivity of decatungstate excited states[122] as well as homogeneous phase experiments.[76,123,124] Picosecond flash excitation of $W_{10}O_{32}^{4-}$ leads to formation of a LMCT excited state, which decays within 30 ps to a second transient ($W_{10}O_{32}^{4-}*$) persisting for more than 15 ns (eq 33). It has been demonstrated that this intermediate, which has a substantial charge-transfer character, is the primary photoreactant, because it is able to initiate the oxidation of the substrate through hydrogen abstraction (eq 34), generating a radical species which, in the presence of O_2, leads to the corresponding hydroperoxide (eq 35). The formation of intermediates and final products occurs mainly according to a photocatalytic cycle (eqs 36−40) where the decatungstate reacts in its oxidized and reduced forms, both in their ground states.

$$W_{10}O_{32}^{4-} \xrightarrow{h\nu} [\text{LMCT O} \rightarrow \text{W}] \rightarrow W_{10}O_{32}^{4-}* \quad (33)$$

$$W_{10}O_{32}^{4-}* + RH_2 \rightarrow HW_{10}O_{32}^{4-} + RH^\bullet \quad (34)$$

$$HW_{10}O_{32}^{4-} + RH^\bullet + O_2 \rightarrow W_{10}O_{32}^{4-} + RHOOH \quad (35)$$

$$RHOOH + HW_{10}O_{32}^{4-} \rightarrow RHO^\bullet + W_{10}O_{32}^{4-} + H_2O \quad (36)$$

$$RHO^\bullet + RH_2 \rightarrow RHOH + RH^\bullet \quad (37)$$

$$RH^\bullet + O_2 \rightarrow RHOO^\bullet \quad (38)$$

$$RHOH + 2W_{10}O_{32}^{4-}* \rightarrow RO + 2HW_{10}O_{32}^{4-} \quad (39)$$

$$RHOOH + W_{10}O_{32}^{4-}* \rightarrow [^\bullet ROOH + HW_{10}O_{32}^{4-}] \rightarrow RO + W_{10}O_{32}^{4-} + H_2O \quad (40)$$

The influence of alkali-metal cations on the redox properties of polyoxotungstates is well-known.[125] On this basis, we have recently investigated the effect of the countercation on the photocatalytic behavior of silica-supported $W_{10}O_{32}^{4-}$. In particular, the effect of Na^+ on the photooxidative properties of the decatungstate has been compared with that of some tetralkylammonium cations with different sizes and hydrophobicities.[119] The investigated heterogeneous systems are characterized by different and tunable photoreactivity, depending on the nature of the countercation. In particular, tetralkylammonium cations enhance the efficiency of cyclohexane photooxidation both to radical species and to the stable oxygenation products cyclohexanol and cyclohexanone. In fact, the cation makes the environment, where the photoactive anion is localized, more or less hydrophobic so influencing the possibility of approach of the substrate and, consequently, the photocatalytic efficiency of the process.

Recent developments in the use of mesoporous MCM-41-type materials as inorganic supports of catalytic interest[126−128] prompted us to investigate the preparation and the activity of heterogeneous photocatalysts based on the immobilization of $(^nBu_4N)_4W_{10}O_{32}$ on this material, which consists of uniform and hexagonal arrays of mesopores ranging from 20 to 100 Å[129] and shows a high surface area (about 1000 m^2/g).[120] Spectroscopic and N_2 adsorption−desorption experiments provide evidence that MCM-41 allows a better dispersion of $(^nBu_4N)_4W_{10}O_{32}$ than amorphous silica and that its ordered structure is maintained after the impregnation of the decatungstate up to 60%.

The photocatalytic activity of $(^{n}Bu_4N)_4W_{10}O_{32}$ in homogeneous solution and supported on MCM-41 or amorphous silica has been compared in the O_2 oxidation of cyclohexane and cyclododecane. Irradiations were carried out at $\lambda > 300$ for 120 min. A first important result is that heterogenization does not significantly reduce the photochemical efficiency of $(^{n}Bu_4N)_4W_{10}O_{32}$. Interestingly, $(^{n}Bu_4N)_4W_{10}O_{32}$ supported on amorphous silica is able to induce the oxidation of cyclododecane with an overall oxidation yield (46%) which is about double of that obtained in the homogeneous phase. The stability of the photocatalyst is demonstrated by the observation that it can be used at least three times without any loss of activity.

As far as the chemoselectivity of the photooxidation processes is concerned, the nature of the solid matrix has been found to control the ketone/alcohol ratio through modification of adsorption−desorption equilibria of reagents and reaction intermediates. In particular, the high surface area of the mesoporous material favors the reaction of the alcohol intermediates with the photoactive decatungstate to the corresponding ketones, leading to ketone/alcohol ratio higher (2.4) than when $(^{n}Bu_4N)_4W_{10}O_{32}$ is supported on amorphous silica (1.1).

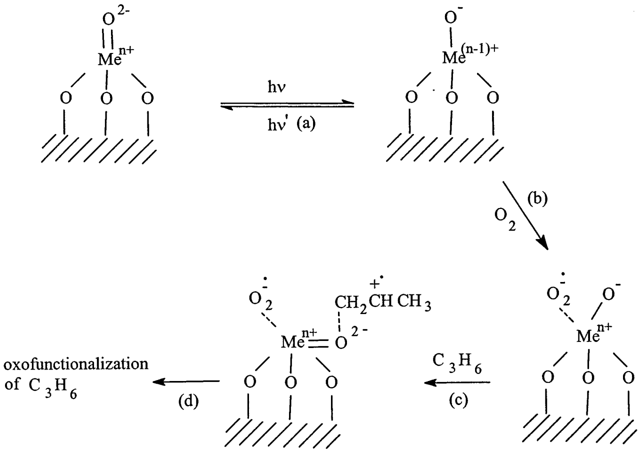
Another strategy for controlling the photoreactivity of polyoxotungstates consists of the use of multicomponent systems containing iron porphyrins. The presence of $Fe^{III}(Cl)TDCPP$ in catalytic amounts dissolved in the reaction medium was found to affect yield and selectivity of cyclohexene oxidation catalyzed by illuminated $(^{n}Bu_4N)_4W_{10}O_{32}$.[123] In particular, the iron porphyrin induces the following main effects: (i) The photochemical efficiency increases. (ii) A lower amount of allylic hydroperoxide is obtained. (iii) The sum of the alcohol and the ketone represents 40% of the overall oxidized cycloalkene. (iv) The ketone to alcohol concentration ratio decreases (from 4.1 to 1.6). The effect of the iron porphyrin has been ascribed to its ability to decompose allylic hydroperoxides to give the corresponding alcohols (see eqs 4−14). As far as the stability of the porphyrin complex is concerned, we did not observe any appreciable bleaching of its UV−vis spectrum, indicating that it did not undergo any significant degradation during the irradiation. This fact represents an important improvement with respect to the photocatalytic activity of the iron porphyrins alone.[43,44,53]

2. Highly Dispersed Metal Oxides

In this section, we describe the photocatalytic activity of some highly dispersed transition metal oxides. This activity is often significantly different from that typical of the parent bulk semiconducting oxides considered in section II.C.3.

$(Me^{n+}\ O)$−Si binary oxides have been prepared by both conventional impregnation and sol−gel procedures and characterized with a variety of spectroscopic methods (XRD, EXAFS, EPR, UV−vis, photoluminescence).[130−138] Generally speaking, the local structures of their active sites, as well as their photochemical properties, are strongly dependent on composition. More specifically, there is ample evidence that dispersed metal oxides may exist in a tetrahedral coordination. Photoexcitation results in the formation of a charge-transfer excited state of the isolated metal oxo species $[Me^{(n-1)+}-O^{-}]^{*}$ as shown by Scheme 3 (step a). The trapped O^{-} hole center and the $Me^{(n-1)+}$ electron center play a significant role in the subsequent photocatalytic oxofunctionalization processes (steps b−d), which, however, occur in competition with a radiative back-electron-transfer reaction (step a).

Scheme 3

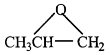
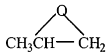
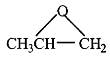
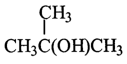
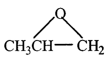
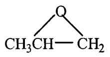


Some information about possible surface reactions that may occur after the primary photoprocess has been obtained with ESR investigations of $V_2O_5-SiO_2$ mixed oxides.[139,140] Excitation with UV light in the presence of O_2 gives ESR signals which have been attributed to O_2^{-} anion radicals adsorbed on the vanadium sites. Addition of C_3H_6 causes a gradual decrease of this signal. On the basis of these results, the authors proposed that O_2^{-} anion radicals should be produced on V^{4+} ions (step b), while propylene cation radicals are generated on the O^{-} ions of the anchored vanadium oxide species (step c). Subsequent reactions between O_2^{-} anion radicals and propylene cation radicals yield different oxidation products of the alkene.

The possibility of obtaining propylene oxide among the oxidation products is of great industrial importance. Some of the cases described in the following are shown in Table 3. It has been reported that irradiation of $V_2O_5-SiO_2$ prepared by conventional impregnation methods should cause the formation of propene oxide but only as an unstable precursor of the final aldehydic products.[141,142]

Good yield in propene oxide has been recently obtained with TiO_2[143] and ZnO[144] highly dispersed on silica through the sol−gel method (0.34 and 1.5 mol %, respectively) and irradiated in the presence of 15 Torr of propylene and 30 Torr of O_2 with an unfiltered Xe lamp. In both cases, the silica-supported metal oxide exhibits higher selectivity to propene oxide and lower conversion to CO_x than in its bulk forms. The stability of the systems was satisfactory since the product concentration still increased after 8 h of irradiation. Subsequent screening studies (not reported in Table 3) carried out on 50 different mixed oxides indicated that the TiO_2-SiO_2 and $ZnO-SiO_2$

Table 3. Photocatalytic Oxidations with Dispersed Metal Oxides

Organized photocatalyst	Light source (irradiation time)	Reaction medium	Conversion of substrate	Main products (%)	Ref.
V_2O_5- SiO_2	λ>300 nm (30’)	C_3H_6/O_2	41.5%	CH_3CHO 59 C_2H_5CHO 10 $CH_2{=}CHCHO$ 39	141, 142
TiO_2- SiO_2	Unfiltered xenon lamp (120’)	C_3H_6/O_2	9.2%	 57.5 CH_3CHO 21.1 CH_3COCH_3 5.8 CO_X 6.6	143
TiO_2	Unfiltered xenon lamp (60’)	C_3H_6/O_2	14.1%	COx 96.2	143
ZnO- SiO_2	Unfiltered xenon lamp (120’)	C_3H_6/O_2	8.6%	 33.4 CH_3CHO 17.9 CO_X 10.8 CH_3COCH_3 11.2 C_2H_5CHO 11.4	144
ZnO	Unfiltered xenon lamp (120’)	C_3H_6/O_2	1.25%	 1.9 CH_3COCH_3 20.8 CO_X 51.9	144
V_2O_5- SiO_2	Flow reactor λ>310 nm	C_3H_8/O_2	Total production rate: 0.5-0.6 μmol/min	CH_3CHO 32 CH_3COCH_3 26 C_2H_5CHO 26 C_2H_6 16	147
Rb-V_2O_5-SiO_2	Flow reactor λ>310 nm	C_3H_8/O_2	Total production rate: 1.2 μmol/min	CH_3COCH_3 33 C_2H_5CHO 9 CO_X 58	147
Rb-V_2O_5-SiO_2	Flow reactor λ>390 nm	C_4H_{10}/O_2	82.2%	CH_3COCH_3 54  $CH_3C(OH)(CH_3)CH_3$ 22	149
Cr-HMS	λ>270 nm (120’)	C_3H_8/O_2	10%-30%	$CH_2{=}CHCHO$ 6 CH_3COCH_3 7 CO_X 75	150
Cr-HMS	λ>450 nm (120’)	C_3H_8/O_2	10%-30%	$CH_2{=}CHCHO$ 10 CH_3COCH_3 25 CO_X 40	150
CrOx-SiO_2	λ>310 nm (120’)	C_3H_6/ O_2	12.5%	 33.9 C_2H_5CHO 9.2 CH_3CHO 30.7 CO_X 14.0	151
CrOx-SiO_2	λ>430 nm (120’)	C_3H_6/ O_2	7.7%	 31.8 C_2H_5CHO 9.2 CH_3CHO 30.8 CO_X 15.7	151
V_2O_5- Al_2O_3	unfiltered ultrahigh-pressure mercury lamp (300’)	C_6H_{12}/ CH_3CN (1:3 v/v) + O_2	2%	$C_6H_{11}OH$ 33 $C_6H_{10}O$ 67	152

systems are the most efficient photocatalysts for propene oxygenation, with high epoxide selectivity and low CO_2 yields.[145]

Photooxidation of benzene and cyclohexane has been investigated on TiO_2 pillared clays.[146] In agreement with the observations of the preceding paragraph, both activity and selectivity are found to depend markedly on the solvent composition. In particular, high yields of oxygenates are obtained in an aqueous environment. In addition, the clay host structure has a sensible effect not only on selectivity but also on the efficiency of the photooxygenation process. For the case of cyclohexane, the enhanced activity of the composite catalyst is explained on the basis of hydrophobic effects; it could be, however, that activity and selectivity are governed by topology of the reaction sites independently of the influence of hydrophobicity.

In addition to alkenes, alkanes too have been shown to undergo partial oxidation on various illuminated silica-supported oxides (C_3H_8 in Table 3). UV irradiation ($\lambda > 310$ nm) of $V_2O_5-SiO_2$ (2.5 wt %) induces the oxidation of propane to carbonylic products with only traces of CO_x.[147] Adsorption experiments and FTIR spectra indicated that an intermediate comprised of one molecule of propane and one molecule of oxygen is formed on the silica surface and that adsorption of propane generates an isopropoxide-like species.[148] Color changes of the catalyst after 60 min of irradiation suggested that deactivation processes occur, likely through reduction of vanadium cations.

Addition of Rb ions affects strongly the photocatalytic activity of the mixed oxide $V_2O_5-SiO_2$.[147] Three main effects were observed: (i) The alkaline ion makes the photocatalyst active under visible light too. (ii) It improves stability and efficiency of the mixed oxide. (iii) It affects the selectivity of the photocatalytic process, favoring, in particular, total oxidation of the substrate to CO_x. The effect on light absorption has been attributed to structural changes of vanadium species, which cause a decrease of the excitation energy of the charge transfer between vanadium and oxygen. The improvement of the stability of the photocatalyst has been explained by taking into account that vanadates in alkali-metal ion modified silica do not change their structure and that they are not poisoned by water molecules throughout the reaction. The effect of Rb ion on the yield in CO_2 is surprising and awaits further explanation.

The effect of Rb ions in controlling the selectivity of photoexcited $V_2O_5-SiO_2$ becomes of synthetic interest when the substrate is 2-methylpropane (C_4H_{10} in Table 3).[149] The most striking point is that the presence of these ions causes the formation of 2-methylpropan-2-ol in addition to carbonilic derivatives. Moreover, CO_x were detected only in negligible amounts. Although the mechanism is not completely defined, the authors suggested that a biomimetic oxygenation process may explain the formation of alcohol. Tracer investigations with $^{18}O_2$ showed that the oxygen atoms of 2-methylpropan-2-ol were from gaseous oxygen, whereas propanone contained ^{16}O, which originated from the lattice oxygen in the catalyst.[149]

It has been recently communicated that another mixed oxide able to operate under visible light irradiation is Cr-containing mesoporous silica (Cr−HMS), where isolated chromium moieties are tetrahedrally coordinated.[150] Photocatalytic experiments in the presence of propane and O_2 were carried out at $\lambda > 270$ nm or $\lambda > 450$ nm (2 h at 273 K) with Cr−HMS catalysts containing different amount of Cr (0.02−2.0 wt %). As shown in Table 3, oxidation of propane with high selectivity to oxygen-containing hydrocarbons such as propanone and acrolein proceeds under visible light irradiation, while further mineralization to CO_x occurs mainly under UV light irradiation. Cr−silica catalysts containing 0.1% of metal are also able to catalyze the photoepoxidation of propene to propene oxide by molecular oxygen.[151] As shown in Table 3, the major products are propene oxide, ethanal, propanal, and CO_x. The selectivity for epoxidation is of 30%. Interestingly, quantum yield measurements show that chromate species excited by visible light would promote propene epoxidation with the same efficiency of those excited by UV light.

V_2O_5 supported on various inorganic oxides has been investigated as a photocatalyst for the liquid-phase oxidation of cyclohexane to cyclohexanone with good selectivity (see also section II.C.3), which is a reaction of great industrial interest, as outlined by Teramura and co-workers.[152] After dispersion of these mixed oxides in a oxygenated acetonitrile/cyclohexane mixture, irradiations were carried out with a unfiltered ultrahigh-pressure mercury lamp. Among the photocatalysts investigated, the $V_2O_5-Al_2O_3$ system (2.5 wt %) exhibited the highest activity and the best selectivity for the ketone. In particular, the authors did not detect the formation of CO_2 and obtained a cyclohexanone to cyclohexanol concentration ratio of about 1.8 (last row in Table 3).

E. Constrained Systems

1. Zeolites as Photocatalytic Microreactors

Zeolites are crystalline aluminosilicates with a chemical composition represented by the formula $M_{2/n}O{\cdot}Al_2O_3{\cdot}xSiO_2{\cdot}yH_2O$, where M is usually a cation belonging to the groups IA or IIA. The building blocks of their structure are $[AlO_4]^{5-}$ and $[SiO_4]^{4-}$ tetrahedra, which are linked together through oxygen atoms so producing a three-dimensional network containing channels and cavities of strictly regular molecular dimensions. As each aluminum atom that is incorporated into the framework leads to the appearance of one negative charge in excess, charge-compensating cations must be introduced into the structure; these cations are not covalently bound to the zeolite but are located in the cages, cavities, and channels, and, therefore, they can be easily substituted with a variety of other cations. Their position, size, and number (which depends on the Si/Al ratio) can significantly affect the properties of the zeolite.

Zeolites are materials with attractive characteristics and can be considered as catalytic microreactors since they are characterized by high thermal stability, well-defined and rigid structure, large internal surface area, and ability to impose size and shape selectivity on the product distribution. On the other hand, they present also some specific limitations: (i) pore plugging; (ii) poisoning; (iii) migration; (iv) leaching; (v) structural defects involving guests in general.

Despite the variety of available zeolites, the faujasitic zeolites X and Y have been the most used for oxidative photocatalysis of hydrocarbons: they are constituted of tetrahedral arrangements of sodalite cages, which leads to the presence of supercages of approximately 12 Å in diameter, connected with each other via 12-membered ring openings of 7−8 Å dimension (pore window).

2. Primary Photochemical Steps

A molecule that has diffused inside the zeolite is subjected to many interactions. In particular, materials with low Si/Al ratios have a great number of compensating cations which will produce very high electrostatic fields and field gradients in channels and cavities. It has been calculated that electric fields could reach up to 6−7 V Å^{-1} at distances of a few angstroms from the cation site. Fields of this magnitude in the internal voids of the pores stabilize positive species in a similar way as highly polar, nonnucleophilic solvents. This is the reason several authors[153,154] have found that a variety of organic radical cations can be easily generated and stabilized in the zeolite Na−Y by γ-irradiation: γ rays produce an electron and a positive hole (zeolite(+); eq 41), which can be transferred to an adsorbed organic molecule to form the corresponding radical cation (eq 42).

$$\text{zeolite} \xrightarrow{\gamma} \text{zeolite}(+) + e^- \qquad (41)$$

$$\text{zeolite}(+) + RH_2 \rightarrow \text{zeolite} + RH_2^+ \qquad (42)$$

It has been demonstrated that molecular oxygen is a particularly suitable electron scavenger.[155] In fact, when it was added to systems consisting of a zeolite (H-mordenite, HY) and organic molecules with low ionization potential, such as polynuclear aromatic hydrocarbons,[156] pairs of interacting radicals ($RH^{\bullet+}$ and $O_2^{\bullet-}$) appeared under irradiation in the near UV region. It has been suggested that the oxidation of the substrate is initiated by a contact charge-transfer interaction between the hydrocarbon and the oxygen.[157] Illumination of these CT complexes results in an electron transfer with the formation of a cation radical and a superoxide anion radical.

The role of the zeolite is crucial because the high electric field mentioned above should stabilize the hydrocarbon−oxygen complex and should shift its absorption to longer wavelengths up to the visible region. Frei and co-workers were the first who discovered that dramatic red shifts of up to 300 nm of the tails of the CT absorption bands occurred in the supercages of zeolite Y, although the amount of visible light absorbed by the charge-transfer complexes is less than 0.5%.[158] They established that the onsets of the diffuse reflectance spectra shifts are strictly correlated to several factors: (i) ionization potential of the hydrocarbon (shifts to shorter wavelengths with increasing IP); (ii) Si/Al ratio; (iii) replacement of Na^+ with alkaline earth cations. In fact, electric fields in the proximity of doubly charged Ba^{2+} cations are expected to be substantially higher.

3. Hydrocarbon Photooxidation

Frei and co-workers demonstrated that charge-transfer photoprocesses within zeolites allow one to oxidize several small alkenes (2,3-dimethyl-2-butene,[159,160] *trans-/cis*-2-butene,[160] propylene[161,162]), aromatics (toluene[163,164] and etilbenzene[165]), and alkanes (cyclohexane,[166] propane and ethane,[162,167] and isobutane[168]). All photooxidation experiments were carried out placing zeolite wafers of NaY (or BaY) inside an infrared vacuum cell equipped with a cryostat and loaded with the gaseous substrate and O_2. Temperature was maintained in the range from 175 to 225 K. Irradiation was carried out with Ar ion lasers or with tungsten lamps, and photochemistry was monitored by FT-IR spectroscopy. In Table 4 some of the most significant results described in the following are reported.

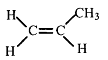
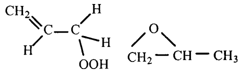
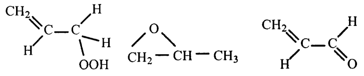
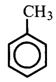
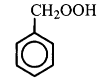
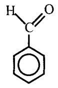
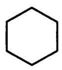
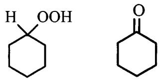
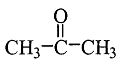
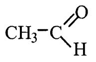
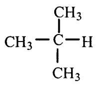
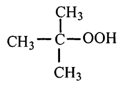
A general mechanism is proposed,[169] which is represented in Scheme 4 in the case of a generic alkene. The first step is a photoinduced electron transfer from the organic molecule to oxygen (step 1) followed by a proton transfer from the radical cation to O_2^-, to form an allyl radical and $HO_2^\bullet$ (step 2). The radical pairs so produced undergo cage recombination, without radical scrambling, to yield hydroperoxides, which are accumulated at low temperature (step 3). The observed great selectivity in the formation of hydroperoxide species is probably due to several factors: (i) Zeolites present diffusional constraints that may prevent undesired radical coupling reactions that dominate the chemistry in conventional fluid media. (ii) Use of visible light instead of UV photons would guarantee generation of the primary photoproducts with the least amount of excess energy, thus minimizing homolytic bond rupture and random coupling reactions. (iii) Secondary photolysis leading to product decomposition and overoxidation would be highly prevented.

Subsequent warming of the matrix to room temperature after photochemical reaction causes the hydroperoxide slow thermal decomposition with formation of water and of the corresponding carbonylic species (such as benzaldehyde from toluene, acetone from propane, cyclohexanone from cyclohexane) with a complete selectivity even when the photochemistry was monitored up to more than 20−30% conversion of the starting hydrocarbon.

However, the selectivity of photoprocesses carried out at room temperature is sometimes lower than those performed at 225 K, likely due to thermal reactions of the hydroperoxides with excess of the starting hydrocarbon still present inside the matrix. It is the case of propene which leads to the formation of the epoxide besides the expected acrolein. A noticeable exception is represented by isobutane, whose hydroperoxide is thermally stable, thanks to the lack of an α C−H group, which prevents thermal rearrangements. Photogenerated *tert*-butyl hydroperoxide has been exploited at room temperature for the in-situ epoxidation of *trans*- and *cis*-2-butene; the constrained environment of the zeolite warranted a complete diastereospecificity of the reaction.[168]

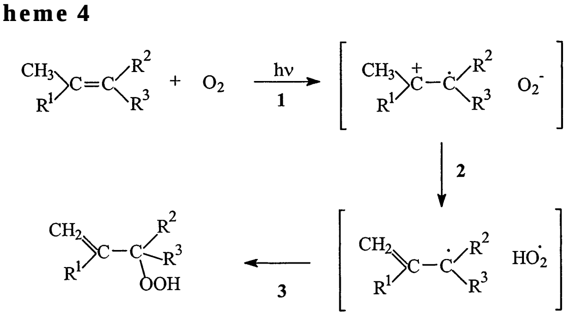
Another problem met with cyclohexane and propane is a dark thermal oxidation reaction occurring

Table 4. Photooxidation of Hydrocarbons in NaY, BaY, and CaY Zeolites and Their Product Distribution at Different Temperatures

Zeolite	λ_{exc} (nm)	Substrate	T (°C)	Product distribution [a]	Φ_{ox} [b]	Ref.
BaY	< 500		-100	 (87%) (13%)	0.2	161, 162
			25	 (38%) (36%) (26%)		
BaY	< 600		-70	 (100%)	0.1	162, 163
			25	 (100%)		
NaY	< 520	 [c]	25		0.03	166
BaY	< 500	$CH_3CH_2CH_3$ [c]	25	 $CH_3-\overset{O}{\overset{\parallel}{C}}-CH_3$ (100%)	[d]	167
CaY	< 500	CH_3CH_3	25	 $CH_3-C(=O)H$ (100%)	[d]	167
BaY	<520	 $(CH_3)_3C-H$	25	 $(CH_3)_3C-OOH$ (98%)	0.15	168

[a] It has been determined using FT-IR spectroscopy. [b] The reported quantum yields have been calculated as the ratio between the growth of the IR bands characteristic of the product and the number of adsorbed photons. [c] These photoreactions are complicated by dark thermal oxidation of the alkane inside the zeolite, for which the authors speculate some tentative explanations. [d] Percent product distribution has not been given by the authors; however, cyclohexyl hydroperoxide was found to rearrange thermally to cyclohexanone without side reaction.

Scheme 4

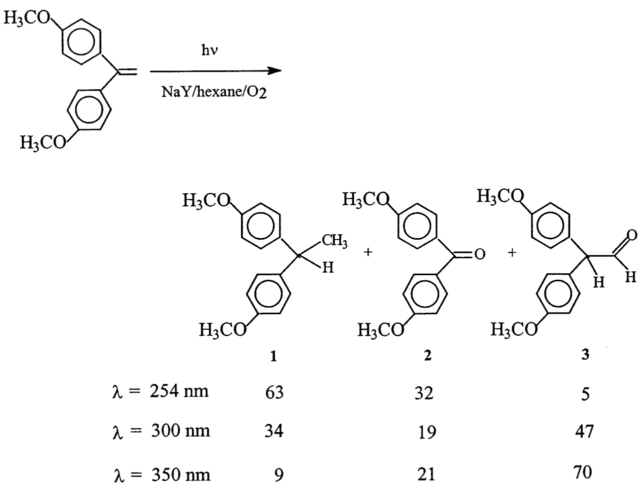


in oxygenated NaY[166] and BaY.[167] In a recent study,[170] Larsen and co-workers compared the kinetics of the thermal and photochemical oxidation of cyclohexane inside zeolites. For the thermal oxidation of this hydrocarbon in BaY and NaY, activation energies of 62(±9) and 85(±3) kJ/mol, respectively, were measured. The authors concluded that thermal oxidation of cyclohexane occurs as a consequence of the formation of precursors of the type $M^{n+}-O_2-$cyclohexane. On the contrary, when the hydrocarbon is more closely associated with the cation (as in the cases of toluene, propylene, etc.), the charge-transfer state (see Scheme 4) is less stabilized in energy and visible photoactivation is needed.

Larsen and co-workers continued the pioneering work of Frei, carrying out photoprocesses of the solid–gas phase.[171,172] In their investigation, the product distribution was determined in more detail by ex-situ ^1H NMR and GC-MS, after their removal from the zeolite. Ramamurthy and co-workers explored the use of a zeolite–hexane slurry approach, extending the study to aryl olefins.[173–177] Both groups focused their investigation on the factors that may influence product selectivity and formation, such as the effect of wavelength, temperature, parent zeolite, and alkene chain length considering, for example, the series of 1-alkenes (propylene, 1-butene, and 1-pentene). The most important conclusions can be summarized as follows:

Effect of Wavelength. Some diarylethylenes included in zeolite NaY under oxygen-saturated condi-

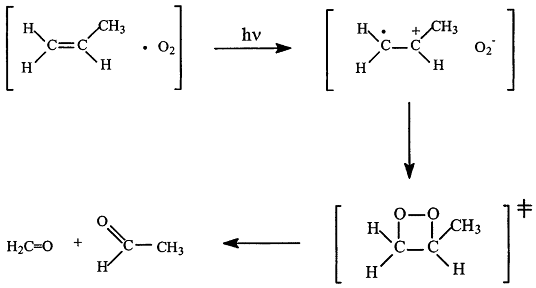
Scheme 5



	1	2	3
λ = 254 nm	63	32	5
λ = 300 nm	34	19	47
λ = 350 nm	9	21	70

tions have been irradiated at three different wavelengths (254, 300, and 350 nm, respectively). The results obtained with 1,1-bis(4-methoxyphenyl)ethylene are reported in Scheme 5. Two types of products are obtained: one is due to reduction (**1**), and the other two are due to oxidation (**2** and **3**). Irradiation at 254 nm gave **1** as the major product, while the change of the irradiation wavelength to 350 nm resulted in the predominant formation of oxidation products **2** and **3**. Ramamurthy and co-workers[173,174] assumed, in agreement with Frei, that the prevalence of products **2** and **3** upon long-wavelength irradiation may be ascribed to excitation of olefin−oxygen complex.

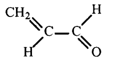
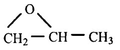
Scheme 6



Larsen and co-workers irradiated at different wavelength regions (>400 and > 285) BaY loaded with propylene and O_2.[171] The main products were acrolein and propylene oxide (Table 5), in full agreement with previous studies;[161,162] however, a decrease in the product selectivity was obtained irradiating with shorter wavelengths, as shown by the formation of nonselective saturated aldehydes. Similar trends have been also obtained for 1-butene and 1-pentene. The authors assumed that the formation of acrolein and epoxide occurred via Frei's mechanism, while the formation of the saturated compounds was attributed to a photooxidation mechanism involving a dioxetane intermediate, which becomes active with more energetic photons (Scheme 6).

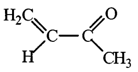
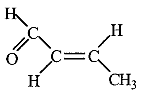
Effect of Temperature. Photooxidation ($\lambda > 400$ nm) of 1-butene in BaY has been investigated at two different temperatures (253 and 318 K).[171] After low-temperature irradiation (Table 6), the FT-IR and ^1H NMR spectra indicated that methyl vinyl ketone was the major product, while after room-temperature irradiation also crotonaldehyde was present. These two carbonylic compounds are in fact the only possible products deriving from the oxidation of 1-butene following Frei's mechanism, with methyl vinyl ketone as preferred one since it is formed from a more stable allyl radical cation. At 318 K several saturated ketones and aldehydes are also observed, even if irradiation with $\lambda > 495$ was employed. This suggests

Table 5. Photooxidation of BaY Loaded with Propylene and O_2 at Different Wavelengths at 318 K[171]

	Product distribution (%) [a]		
λ_{exc} (nm)			Saturated aldehydes
> 400	67	20	13
> 285	55	28	17

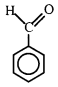
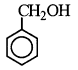
[a] It has been determined using ex-situ proton NMR spectroscopy.

Table 6. Photooxidation ($\lambda > 400$ nm) in BaY Loaded with 1-Butene under Oxygen-Saturated Conditions at Different Temperatures[171]

	Product distribution (%) [a]		
	Unsaturated compounds [b]		Saturated aldehydes and ketones
Temperature (K)	 methyl vinyl ketone	 crotonaldehyde	Propionaldehyde Acetaldehyde Butyraldehyde 2-butanone
253	95	0	5
318	42	18	40

[a] It has been determined using ex-situ proton NMR spectroscopy. [b] These products derive from the allyl hydroperoxide decomposition, as proposed in Frei's mechanism.

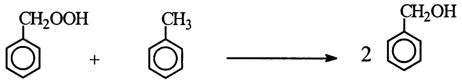
Table 7. Photooxidation (λ > 400 nm) of Toluene in Different Zeolites under Oxygen-Saturated Conditions at Room Temperature[172]

	Product distribution (%) [a]		
Zeolite			Others [b]
NaY	92	5	3
BaX	88	6	6
BaY	87	4	9
BaZSM-5	31	1	68
BaBeta	27	tr [c]	73
BaHY	56	4	40

[a] It has been determined using GC, after extraction of the products from the zeolite with CH_3CN. [b] Phenol, cresol, and condensation products. [c] Trace amounts.

that also thermal chemistry contributes to the formation of nonselective, short-chain saturated aldehydes and ketones. In particular, Larsen and co-workers proposed that these carbonylic compounds could derive from epoxide ring-opening thermal reactions.

Effect of the Parent Zeolite. Toluene/O_2 complexes loaded in some different types of zeolites have been irradiated (λ > 400 nm) at 318 K, and the reaction mixtures were analyzed combining in-situ FT-IR and ex-situ proton NMR and GC-MS (see Table 7).[172] This approach has evidenced that the level of selectivity achieved in the formation of benzaldehyde, even in the most highly selective zeolites such as NaY and BaY, is not 100%, as previously stated by Frei[163] and Larsen.[164] In fact, the selectivity in the formation of aldehyde from toluene is approximately 87% (Table 7). Benzyl alcohol is likely formed by the reaction of the parent toluene with the hydroperoxide obtained from the initial charge transfer state, according to eq 43.



(43)

Table 7 shows that a significant decrease in selectivity is obtained using BaZSM-5 and BaBeta zeolites. These have in common the presence of acid sites, which favor the formation of condensation products. Accordingly, Ramamurthy and co-workers demonstrated that the presence of small quantities of acid sites can alter the reactivity of various alkenes substrates.[175-177] In this regard, the comparison between BaY and BaHY becomes relevant: in fact, the presence of acid sites, by partial exchange of one-third of the Ba^{2+} cations with protons, causes a relevant loss of selectivity. Analogous results have been obtained with *p*-xylene as substrate.[172]

Effect of Alkene Chain Length. Larsen and co-workers[171] find out that after photooxidation of 1-pentene in BaY at room temperature a mixture of products is obtained, ethyl vinyl ketone and 2-pentenal, which are the two possible products resulting from Scheme 5, and in addition 3-penten-2-one and some saturated aldehydes are formed. On the basis of some similar, previously documented reactions,[178] the authors attribute this unexpected reactivity to a possible isomerization reaction of 1-pentene to 2-pentene in the zeolite, followed by the photooxidation of 2-pentene.

Great efforts have been done for a full comprehension of some important parameters, such as the roles of the zeolite, cations, temperature, and irradiation wavelength. Problems connected to stability and possibility of recycling the same zeolite wafer merit further attention. In particular, an effort should be made to find experimental conditions that consent the achievement of acceptable desorption rates of the oxidation products from the zeolite host. The possibility of employing these photocatalytic systems for synthetic purposes depends on enhancement of visible light absorption, which, in the described experiments, is always lower than 1%.

4. Other Wide-Band-Gap Oxides

The band gap of oxide dieletrics is significantly wider than that of semiconductor materials. Therefore, the realization of photoinduced processes requires irradiation with far-UV light and this is disadvantageous from the point of view of energy costs. Extensive investigation in the past decade, however, seems to indicate that dispersed oxide dieletrics are capable of initiating photochemical and photocatalytic transformations of adsorbed molecules under illumination also with visible light.[145,179,180]

Special attention has been devoted to sulfated zirconia. Bedilo and co-workers[178] showed that irradiation with green light ($\lambda = 546$ nm) is an efficient method of generating radical cations from benzene and some of its methyl derivatives on sulfated zirconia, in analogy to what previously obtained on a ZSM-5 zeolite.[179] Illumination was conducted at 103 K, and the formed radical cations proved to be stable at this temperature under vacuum for several hours. The concentration of radical cations increases with increasing molecular oxygen pressure. The authors attributed the ability of producing ionized benzene to the very strong acceptor sites of sulfated zirconia. Donor−acceptor complexes are key intermediates in the general mechanism proposed for the light-induced formation of radical cations (eqs 44−47):

$$D + A_S \rightleftarrows [D{\cdot}A_S] \tag{44}$$

$$[D{\cdot}A_S] \overset{h\nu}{\rightleftarrows} [D^{+}{\cdot}A_S^{-}]^{*} \tag{45}$$

$$[D^{+}{\cdot}A_S^{-}]^{*} \rightarrow D^{+} + A_S^{-} \tag{46}$$

$$D^{+} + A_S^{-} \rightarrow \text{products} \tag{47}$$

The first step (eq 44) consists of the formation of an electron donor−acceptor complex between an organic donor molecule (D) and a surface acceptor site (A_S). This complex undergoes photoexcitation (eq 45), followed by the charge separation and stabilization of the radical cation (D^+) (eq 46). Information on the chemical nature of products has not been given from authors. Oxygen shifts the absorption band to lower energies. This fact marks an important difference between these systems and those based on zeolites investigated by Frei and others.[158−177] In fact, here oxygen only strengthens acceptor sites already present on the surface of sulfated zirconia. Moreover, as this oxide does not have a zeolite supercages system, it is very unlikely that it could have a similar stabilizing effect on donor−acceptor complexes. The authors proposed that the acceptor site should contain a strong Lewis site, a strong Brønsted site, and an electron trap located close to each other.

Volodin demonstrated that illumination into intrinsic surface absorption bands of wide-band-gap oxides, such as MgO and CaO, results in a charge separation and stabilization of electron and hole centers on the surface.[180] This charge separation is a necessary way for the generation of very reactive oxygen radical anions on the surface and can be considered to be the first step of photochemical and photocatalytic transformations of various molecules on the oxide dielectrics. CaO is of particular interest because it can be illuminated with longer wavelength ($\lambda \leq 365$ nm) with respect to MgO. Stabilization of electron and hole centers under irradiation depends on the existence of definite defects on the initial oxide surface.

The photoepoxidation of propylene by molecular oxygen has been used as a probe reaction in a screening study of silica supported metal oxides;[145] the experiments were carried out by putting the samples in a closed reaction vessel of quarz, adding gaseous propylene and O_2, and irradiating with a Xe lamp. Photooxidation products were separately analyzed by GC. Silica itself is photoactive for epoxidation (1.5% conversion and 22% selectivity for epoxide),[181] and the addition of alkaline-earth metal oxides tends to increase the selectivity for propylene oxide (33% for SiO_2/CaO) while the conversion remains very low (<5%). Tentatively, the authors attribute this behavior to the electronegativity of the added element, which could affect the oxidative ability of the hole formed at the photoexcitation site.

III. Photosensitization

A. Primary Photochemical Steps

The reactivity of O_2 with most molecules is inhibited by spin restriction. However, O_2 can be converted to highly reactive species by interaction with photoexcited sensitizers. Electron-transfer reactions from the excited triplet of the sensitizer is possible and leads to the formation of superoxide radical anion ($O_2^{\bullet-}$), which, as a doublet, does not face the spin restriction of ground-state O_2. In acidic media, $O_2^{\bullet-}$ will be protonated to give $HO_2^{\bullet}$ radical. Further reduction would convert this species to the corresponding anion, protonation of which yields H_2O_2. With an appropriate catalyst, H_2O_2 can be converted to $OH^{\bullet}$ radical either by direct decomposition or through a reductive pathway. This sequence of elementary steps is rather general and is followed in several catalytic systems where O_2 activation is the key passage.

Alternatively, the molecule of O_2 can be efficiently activated by the excited triplet state of a photosensitizer through an energy-transfer process that generates singlet oxygen ($^1O_2$). This species is highly reactive, and its extensive involvement in the oxofunctionalization of unsaturated molecules is well-established. $^1O_2$ is known to react with electron-rich alkenes via a 2 + 2 addition process.[182] When the alkene contains allylic hydrogen atoms, however, the "ene reaction" is the dominant pathway.[183−186] Alkenes with more than one distinct allylic hydrogen yield several hydroperoxides.

The main processes that lead to the formation of $^1O_2$ or $O_2^{\bullet-}$ in the presence of a photosensitizer (P) and a substrate (S) are schematized by eqs 48−51 and 52 and 53, respectively. Electron-transfer sensitization induces the reductive activation of O_2 and the oxidation of the substrate (S) to a radical cation in analogy with the systems described in section II; on the other hand, the process occurs here through two consecutive steps. Both the energy transfer and the electron-transfer photoactivations of O_2 hold special interest in the oxidations of alkenes.

$$P + h\nu \rightarrow P^* \tag{48}$$

$$P^* + O_2 \rightarrow P + {}^1O_2 \tag{49}$$

$$P^* + O_2 \rightarrow P^{\bullet+} + O_2^{\bullet-} \tag{50}$$

$$P^{\bullet+} + S \rightarrow P + S^{\bullet+} \tag{51}$$

Alkenes are also known to be able to react directly with electron-deficient photosensitizers according to eq 52.[187−189] This process results in the formation of an alkene radical cation ($S^{\bullet+}$) and sensitizer radical anion ($P^{\bullet-}$), which, subsequently, may reduce O_2 to give O_2^- (eq 53).

$$P^* + S \rightarrow P^{\bullet-} + S^{\bullet+} \tag{52}$$

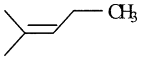
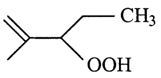
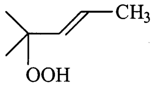
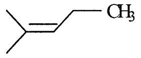
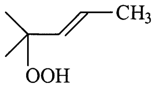
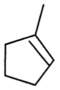
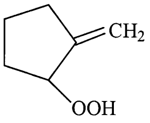
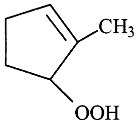
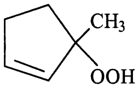
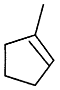
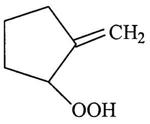
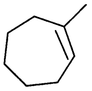
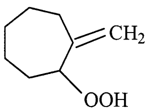
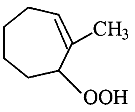
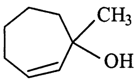
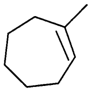
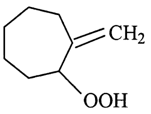
$$P^{\bullet-} + O_2 \rightarrow O_2^{\bullet-} + P \tag{53}$$

Although the photosensitized oxidation has found much synthetic applications, regio- and stereocontrol are still difficult issues,[183] since the oxidation pathways, initiated by the reactive species derived by reactions 48−53, often occur simultaneously, so reducing the selectivity of the processes. To improve the selectivity of photosensitized oxidation of alkenes a number of researchers have turned their attention to the use of organized media.

B. Oxidation of Alkenes within Zeolites

Examples of alkenes oxidations that proceed with the involvement of $^1O_2$ are the hydroperoxidation of alkenes containing allylic hydrogens. Fox and coworkers reported that $Ru(bpy)_3^{2+}$ inside zeolite Y can work as a photosensitizer to oxidize tetramethylethylene and 1-methylcyclohexene.[190] Irradiation, performed on $Ru(bpy)_3^{2+}$-exchanged zeolite slurry in methanol containing alkene, leads to the formation of $^1O_2$, which freely diffuses from the solid matrix to

Table 8. Alkene Photooxidation with Thionin-Exchanged Zeolites[193–195]

Organised Photosensitizer	Substrate	Main products (%)
Thionin		 40  60
NaY/thionin		 100
Thionin		 6  45  48
NaY/thionin		 100
Thionin		 10  47  43
NaY/thionin		 100

the solution where it reacts with the alkene with usual selectivity.

More recently, Ramamurthy and co-workers investigated the oxidation of *trans*-stilbene and *trans*-4,4′-dimethoxystilbene included within alkali-metal cation-exchanged zeolites X or Y.[191] Powder dispersions of the zeolite having adsorbed both the alkene and the electron-transfer sensitizer 9,10-dicyanoanthracene were irradiated in hexane under oxygen atmosphere. The authors found that oxidation of stilbenes included in zeolites is much more efficient than in an isotropic solvent. On the basis of quenching experiments, they concluded that this process should be initiated by an electron transfer from the stylbene to the singlet excited dye (eq 52). Following eq 53, the subsequent oxidation process involves the formation of O_2^- and leads to the formation of carbonylic derivatives.

The photoreactivity of the guest molecules is influenced by included cations.[192] In particular, while the photooxidation is efficient in Li^+- and Na^+-exchanged zeolites, it is strongly inhibited in the presence of Rb^+ and Cs^+. The proposed explanation is that these bigger cations may preclude the close contact between the dye and the substrate that is needed for efficient electron transfer.

In other articles Ramamurthy's group demonstrated that irradiation of organic dyes such as thionin, methylene blue, and methylene green caged inside X and Y zeolites may induce highly selective oxidations of alkenes.[174,193–196] Since the oxidation processes were inhibited by oxygen quencher such as β-carotene and *N*,*N*-dimethylaniline, the authors proposed that the reactive species is $^1O_2$.[193] A typical experiment consisted in exposing a slurry of dye-exchanged zeolite (300 mg) in hexane (12 mL) containing the alkene (12 μL) to visible radiation (450 W medium-pressure mercury lamp, $\lambda > 420$ nm). The produced hydroperoxides were isolated in 65–75% yield after 15–30 min irradiation.

Table 8 reports some significant examples describing the selectivity achieved with thionin-exchanged zeolites. For comparison, the results obtained with homogeneous solution irradiations carried out in acetonitrile are also shown.[197] It is to be outlined that autoxidation via radical pathway without the involvement of $^1O_2$ is known to give a different distribution of products.[190,198]

Table 8 shows that irradiation of isotropic solution of 2-methyl-2-pentene yields two hydroperoxides with no appreciable selectivity, because of the presence of two distinct allylic hydrogen atoms (first line).[193,194] On the contrary, a single hydroperoxide is preferentially obtained within NaY (second line). Table 8 also shows that only one hydroperoxide is obtained when the heterogenized thionin is photoexcited in the presence of methylcycloalkenes. Interestingly, the hydroperoxide resulting from abstraction of the methyl hydrogen that is formed in the lowest yield in solution is obtained with high selectivity within zeolite.[177] Photochemical experiments in the presence of a tetraphenylporphyrin complex, which is too large to enter the NaY voids, did not change the selectivity. This confirms that the observed regioselectivity with thionin is the result of oxidation reactions taking place within zeolite.[195]

The ratio of the produced hydroperoxides and mass balance provide evidence that the described dye-exchanged zeolites lose part of their efficiency and selectivity under prolonged irradiations.[195] First of all, the primary oxidation products may compete with the substrate in the reaction with the photogenerated $^1O_2$. In particular, the tendence of hydroperoxides to remain inside the zeolite can favor their secondary oxidation.

Side reactions originated from Bronsted acid chemistry may also reduce efficiency and selectivity of those photooxidation processes that are susceptible to cationic rearrangements. It has been found that this kind of interference can be controlled by addition of stoichiometric amounts of a base such as pyridine or diethylamine.[173,176]

Dyes were found to undergo decomposition within CsY and NaY likely via an electron-transfer pathway in which the zeolite acts as a donor.[199−202] In particular, thionin, methylene blue, and methylene green within NaY decomposed by less 25% after 15 min irradiation, whereas within CsY more than 60% of the dyes had decomposed for the same time.

The ability of zeolites to control regioselectivity is strongly related to the nature of the doping cation.[173,194] In particular, formation of the secondary hydroperoxide is favored with Li^+- and Na^+-containing zeolites with respect to heavier alkali-metal ions such as Cs^+. To obtain more insights into the role of the cation on the observed product distributions, ab initio and DFT calculations were carried out on model systems.[195] Although some predictions are not compatible with the observed regioselectivities, that work confirms fairly strong cation−alkene binding as well as additional geometric and orbitals distortions. Previous works reported that zeolites are able to bring about conformational control of aryl alkyl ketones.[203,204]

Two plausible hypotheses have been proposed to rationalize the origin of the regioselectivity within zeolites.[173,193,194] In the first model, the solid support is postulated to control the conformation of the alkene as a consequence of steric strain between alkene bulky substituents and the adsorbing solid surface. The consequent rotation of carbon−carbon bonds may place the methylene hydrogens away from the incoming $^1O_2$, preventing the formation of the tertiary hydroperoxide. According to the experimental results, reactions involving Na^+ ions are expected to yield higher selectivity than those with larger cations such as Cs^+, which may inhibit the interaction between the alkene and the surface. In the second model, the selectivity is attributed to the polarization of the alkene by the interacting cation, which could influence the electron density distribution of the olefinic π-cloud. Smaller cations such as Li^+ would be expected to polarize the alkene more effectively than larger cations. For this model too, selectivity is expected to decrease for Li^+ to Cs^+ according to the experimental data.

In addition to the problem of regioselective oxidation of alkenes, one investigation[205] considers the possibility of generating predominantly one enantiomer by assembling a supramolecular structure of an alkene, a thyazine dye and oxygen within NaY zeolite: in the presence of a chiral inductor (ephedrine hydrochloride) irradiation results in a high regioselectivity and a fair enantioselectivity (about 15% ee).

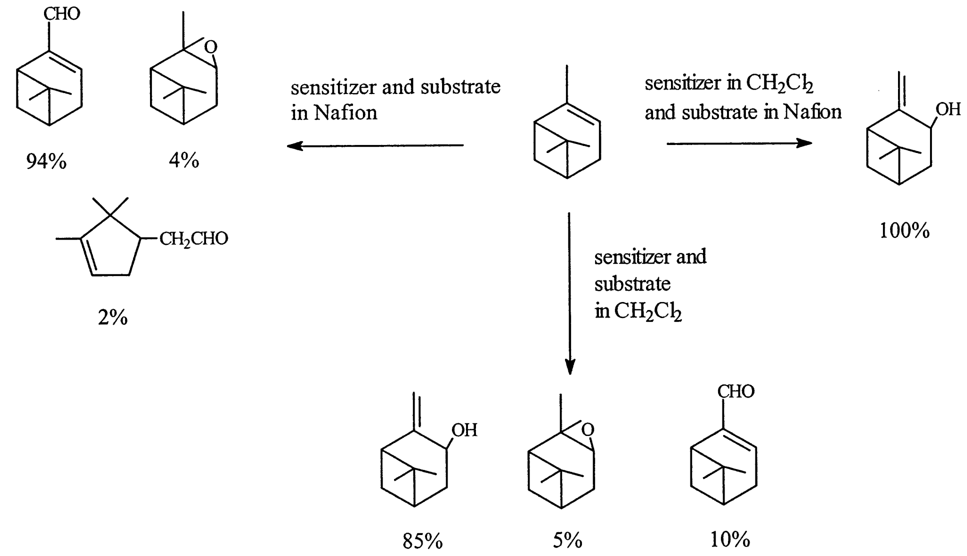
C. Oxidation of Alkenes with Multicomponent Systems

In the photochemical systems described in the previous paragraph, both the sensitizer and the substrate were localized and confined within the same restricted space of a zeolite. Tung and co-workers demonstrated that a good control of the selectivity in photooxidation processes may be achieved by isolation of the substrate within Na−ZSM-5 zeolites from the sensitizer in the surrounding solution.[206] The adsorbed substrates were *trans,trans*-1,4-diphenyl-1,3-butadiene or *trans*-stilbene or 2,3-dihydro-γ-pyran, the dissolved sensitizers were 9,10-dicyanoanthracene or hypocrellin A, and the employed solvents were isooctane or pentaerythritol trimethyl ether. Both the sensitizer and the solvent were chosen so that they could not diffuse within the channels of the zeolites because of their size. Generally, after about 4 h of photolysis ($\lambda > 400$ nm) of the zeolite powder dispersion, the conversion of the starting alkene was near 100% and the material balance was greater than 90%. Following this strategy, the authors could successfully conduct photosensitized alkene oxidation with a high degree of selectivity, which is not observed in solution.

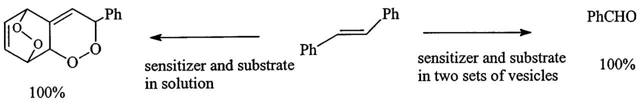
The main reason for the observed selectivity is due to the fact that the isolation of the substrate within the zeolites away from the sensitizer in the solution bulk prevents them from undergoing electron-transfer processes. On the other hand, $^1O_2$ can be generated in the solution and can diffuse into the ZSM-5 channels, where it can react with the alkene. When the substrate *trans*-stilbene is included within ZSM-5 zeolite and the sensitizer 9,10 dicyanoanthracene is dissolved in the solution, the photooxidation yields the endoperoxide as an intermediate of 1,4-cycloaddition of $^1O_2$, which would decompose to give benzaldehyde in 100% yield as final product. On the contrary, in homogeneous solution oxidation products that are typical of the electron-transfer pathway prevail.

Tung and co-worker also achieved a remarkable control of the selectivity of the photosensitized oxidation of *trans,trans*-1,4-diphenyl-1,3-butadiene, *trans*-stilbene, and α-pinene within Nafion membranes.[207] In particular, these photochemical systems give selectively either the $^1O_2$- or O_2^--mediated products depending on the status and location of the substrate

Scheme 7



Scheme 8



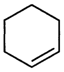
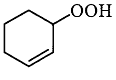
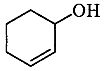
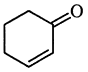
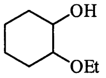
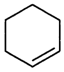
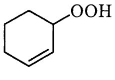
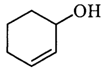
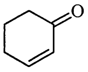
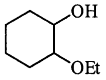
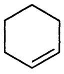
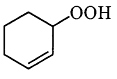
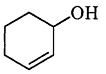
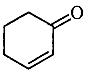
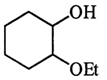
and the sensitizer molecules in the reaction media. Upon incorporation of the alkene within Nafion membranes and dissolution of the sensitizer 9,10-dicyanoanthracene in the surrounding organic solvent, the photochemical behavior is analogous to that observed within ZSM-5 zeolites: electron-transfer processes are prevented, and the $^1O_2$ produced in the solution diffuses into the Nafion clusters and reacts with the alkene. On the contrary, electron transfer from the alkene to the singlet excited state of the sensitizer is favored when the substrate and the sensitizer are incorporated within the water-swollen membranes. As a result, the photosensitized oxidation mainly gives products derived from the electron-transfer pathway. Scheme 7 reports, as an example, the results obtained in the oxidation of α-pinene sensitized by 9,10-dicyanoanthracene.

In more recent works Tung's group investigated the photosensitized oxidation of *trans*,*trans*-1,4-diphenyl-1,3-butadiene, *trans*-stilbene, *trans*-1,2-dimethoxystilbene, 1,4-diphenyl-1,3-butadiene, α-pinene, and 2,2,6,6-tetramethylpiperidine using mixed surfactant vesicle medium.[208−210] In these systems the sensitizers were a tetraphenylporphyrin complex, methylene blue, or 9,10-dicyanoanthracene. The authors incorporate the alkene in the bilayer membranes of one set of vesicles and the sensitizer in another set of vesicles and found that the $^1O_2$ produced in the sensitizer-containing vesicles diffuses into the substrate-containing vesicles and reacts with the alkene. The diffusion of $^1O_2$ is demonstrated by the observation that the quantum yields for the product formation were significantly higher in D_2O than in H_2O dispersions. As shown in Scheme 8, the photosensitized oxidation of *trans*-stilbene using tetraphenylporphyrin in vesicles leads to the quantitative formation of the 1,2-cycloaddition products of $^1O_2$. On the contrary, only the products of $^1O_2$ 1,4-cycloaddition products to the diene were observed in homogeneous solutions. This result indicates that the organized semirigid environment in vesicles may prevent conformation changes of the alkene to adapt the necessary geometry for 1,4-cycloaddition.

Some other efforts have been made in the last years to check on the possibility to induce photooxidation of organic substrates by molecular oxygen with modified Nafion membranes. Methylene blue-sensitized photooxidation of anthracene was investigated by Niu and co-workers,[211] who found that the photochemical efficiency was higher than that observed in ethanol solution. Lee and co-worker [212] have succeeded in generating singlet oxygen in Nafion powders by photoexcited 2-acetonaphthone.

We have recently investigated a composite photocatalyst in which both palladium(II) *meso*-tetrakis-(*N*-methyl-4-pyridyl)porphyrin(PdTMPyP^{4+}) and Fe^{III}-TDCPP were heterogenized on the same Nafion membrane.[213] The first complex, which is mainly fixed at the surface of the polymer matrix, undergoes a pronounced enhancement of the lifetime of its triplet excited state compared to that of the porphyrin in solution phase. The role of the palladium porphyrin is that of inducing the photoactivation of O_2 with visible light ($\lambda > 500$ nm), generating $^1O_2$ via energy transfer from its triplet state. As a consequence, the $^1O_2$-mediated oxidation of cyclohexene to the corresponding allylic hydroperoxide can be achieved with a selectivity higher than 90%. The iron porphyrin, which can penetrate more deeply inside the anionic cavities of Nafion, works as a catalyst for O_2-mediated autoxidation processes that are initiated by the photogenerated hydroperoxides (see section II.B). Table 9 shows that, in contrast with the behavior observed in homogeneous solution (see total turnover), these processes continue in the dark for many hours giving cyclohex-2-en-1-ol and *trans*-cyclohexane-1,2-diol monoethyl ether as main oxidation products. The presence of this ether, indirectly, reveals the formation of great amount of cyclohexene epoxide, which undergoes ring opening because of the strong acidic environment inside Nafion. The good photo-

Table 9. Photoinduced Catalytic Oxygenation of Cyclohexene by the Composite System PdTMPyP^{4+}/FeTDCPP^{+}/Nafion[a] [213]

Organised photocatalytic system	Substrate	Product distribution (%)				Total turnover [b]
PdTMPyP^{4+}/FeTDCPP^{+} /Nafion + $h\nu$		 71	 13	 9	 7	340
PdTMPyP^{4+}/FeTDCPP^{+} /Nafion + $h\nu$ dark		 14	 36	 4	 46	4700
PdTMPyP^{4+}/FeTDCPP^{+} Solution + $h\nu$ dark		 38	 11	 6	 45	360

[a] Product yields after 3 h of photoirradiation at $\lambda > 500$ nm in the presence of 760 Torr of O_2. In some cases irradiation was followed by 95 h of thermal catalysis in the dark. [b] Moles of oxidized alkenes/mol of FeTDCPP^{+} which was present at the beginning of the process.

catalytic efficiency of the oxidation process is demonstrated by an overall quantum yield of 1.1, as well as by a turnover value of 4.7×10^3 with respect to the iron porphyrin. Cyclooctene undergoes oxygenation too. In contrast to the case of cyclohexene, cyclooctene epoxide can be accumulated in a significant amount. Concerning the stability of the system, the metalloporphyrins undergo about 1% degradation during the process, while the Nafion matrix can be utilized several times without observable modification.

Recent studies have demonstrated that the nonemissive platinum(II) quaterpyridine complex $[Pt(QP)](CF_3SO_3)_2$ shows strong photoluminescence at room temperature as a consequence of incorporation into Nafion membranes.[214] Likely the rigid matrix inhibits the deactivation processes of the photoexcited complex via molecular distortion. Another major effect of Nafion is to stabilize the complex toward photochemical decomposition. In fact, the heterogeneous photosensitizer could be used for many cycles (10 h of irradiation) without any loss of activity. $[Pt(QP)](CF_3SO_3)_2$ incorporated in Nafion membrane was employed as photosensitizer to generate $^1O_2$, which diffuses into the solution where several alkenes were oxidized. For example, *trans*-stilbene was converted to benzaldehyde with 100% yield, calculated on the basis of the consumption of the substrate.

IV. Conclusions

In the previous discussion we have provided evidence that photocatalysis with organized systems is a widely applicable method for achieving oxofunctionalization of hydrocarbons with O_2, in mild temperature and pressure conditions. Starting with the very basic principles that govern the primary photochemical steps, we proceeded to examine the subsequent activation processes of both the substrate and O_2. Finally, we showed that organized assemblies may also drive subsequent thermal reactions. In particular, heterogeneous or microheterogeneous environments, whose detailed characterization requires a wide range of interdisciplinary chemical investigations, may control both efficiency and selectivity of oxidation processes. An important aspect to outline is that, in a number of cases, the described photocatalysts may be removed from the reaction vessel by simple filtration and reused for photocatalytic experiments without significant loss of activity.

Photoexcited metal oxides are of great interest in oxidative catalysis. The necessity to optimize the performance of widely employed semiconductors such as TiO_2 has stimulated researchers on its modifications. In particular, doping with metal species, surface derivatization, and use of nanostructured systems are successful strategies to obtain modified TiO_2 with predictable properties. Photocatalytic efficiencies that are comparable to that of TiO_2 may be achieved with heterogeneous photocatalysts on the basis of the use of polyoxotungstates, which may present the important advantage of not causing any mineralization of the substrate. The photochemical reactivity of some metal oxides may be also influenced by their degree of dispersion on light transparent inorganic supports, which can induce the occurrence of reaction pathways that are not otherwise observed.

The results reviewed clearly demonstrate unique aspects of host−guest photocatalysis in the solid state as well as in solution phase. Several matrices may control the photochemical and photophysical behavior of a guest molecule: zeolites; organic polymer cyclodextrines; micelles. This effect can be attributed primarily to restrictions of the diffusional mobility of substrates and reaction intermediates. Interestingly, common organic photosensitizers offer regio- and stereocontrol of the oxidation process when they are caged within zeolites, especially when they include alkali-metal cations. Among the interactions of molecules inside zeolites, very high electrostatic fields and field gradients in the internal pores are of particular interest since they make possible to induce alkene oxygenation with very low energy photons.

Control of the access of sensitizer and substrate into different solid supports has been advantageously employed to enhance the selectivity of either $^1O_2$- or O_2^--mediated processes; this depends on the status and location of the reactants in the reaction media. A number of the described multicomponent systems that are characterized by a cooperative reactivity can be considered models of natural enzymes, which in living organisms catalyze the selective oxidation of hydrocarbons.

As a final remark, we point out that the use of light rather than a chemical reagent and of a robust and reusable catalyst makes photochemical excitation an ideal means for efficient and large scale utilization of solar energy in applied synthesis. In fact, photocatalysis allows one to realize shorter and more selective reaction sequences, to use less expensive feedstock, and to minimize waste. This is of particular interest in the production of intermediates for pharmaceutical and agricultural industry, where low amounts of high added value products are often prepared through multistep procedures, with the production of a large amount of byproducts and waste.

V. Acknowledgment

This work is also the result of stimulating discussions we had with our teacher and colleague Prof. Vittorio Carassiti, who passed away recently. For his unceasing guidance and encouragement we remember him with gratitude and affection.

Note Added After ASAP Posting

Reference 145 was incorrectly cited on page N in a version of this paper posted ASAP on August 31, 2002. This reference is now removed in this corrected version posted October 9, 2002.

VI. References

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