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Photo-catalytic Routes for Chemicals

Langford [1] in a recent publication defined photocatalysis “as a term that combines the basic notion of a catalyst as a material that enhances the rate as a reaction approaches equilibrium without being consumed with the notion that the reaction is accelerated by photons which of course are consumed. Thus it is a hybrid concept”. Following the report by Carey et al. in 1976 [2] on the photodechlorination of polychlorinated biphenyls (PCBs), there have been a spate of publications in this area. Rajeshwar has reported in his review [3] that the number of papers in this area grew from 249 in 1975-80 to nearly 16755 in 2000-2010. The photocatalysis research area has seen three generations of development according to Langford [1]. The first generation was focussed on the understanding of semiconductor-solution interface, the second generation devoted to development of thin films doped semiconductors, dye sensitization and the third generation centred around nanostate and self organized materials as photo catalysts.

Petroleum and natural gas have been serving as the primary source of the chemicals, reagents, solvents and polymers used in various applications. However, nature has been successful in synthesizing starch from water and carbon dioxide. Most of the reactions involve electron transfer or redox chemistry. For this to take place in a facile manner, the donor and acceptor levels of the species should be energetically and symmetrically matched between substrate and the system. Nature possibly adapts this by the manipulation of the species. For example, the activation of dinitrogen by nitrogenase enzyme is achieved by the ability of the enzyme to perturb the orbitals of dinitrogen such that the LUMO of dinitrogen will become suitable for electron transfer which destabilises dinitrogen and makes it active.

6.1 PHOTOCATALYSIS

Photo-catalysis involves the excitation of electrons from the valence band or HOMO to the conduction band or LUMO on exposing the catalyst to the radiation. This leads to the formation of highly reactive electrons and holes in the conduction band and valence band respectively. Various processes involved

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in semiconductor photo-catalysis are shown in **Figure 1**. The electrons are capable of carrying out reduction reactions and holes can carry out oxidation reactions. This process can be exploited in various ways. The three main ways are: (i) For producing electricity (ii) For decomposing or removing pollutants and (iii) For the synthesis and production of useful chemicals

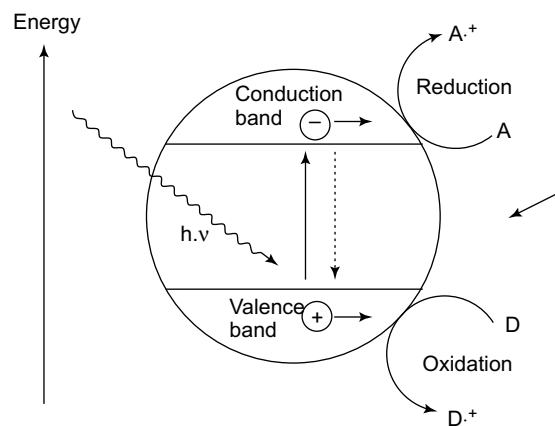


Figure 6.1 Simple representation of the process involved in photocatalysis [4,5]

6.2 PHOTOCATALYTIC CHEMICAL PRODUCTION

Photo-catalytic synthesis of compounds can be carried out utilizing the electrons and holes created. So, the reaction should be either a reduction or oxidation or a combination of both. As previously stated for a reaction to take place the potential of the energy levels of the catalyst and the reactant should be suitable for the electron transfer to take place. The photo-catalytic splitting of water has received considerable attention and the literature is extensive on this aspect and is dealt with in other chapters.

6.2.1 Photo-catalytic Oxidation

Conventional oxidizing agents used in organic synthesis like potassium dichromate, potassium permanganate, various acids and peroxides are toxic in nature. These oxidizing agents are difficult to handle and release dangerous fumes and gases during the reaction. If one can carry out oxidation reactions using solar irradiation, it will be an environment friendly process. This has led to many attempts to carry out oxidation reactions photo-catalytically [6].

6.2.2 Oxidation of Alcohols

Oxidation of alcohols to the aldehydes and ketones is an integral part of organic synthesis. There are variety of reagents used for this purpose and their

separation after the oxidation is a difficult task. Photo-catalytic oxidation by using semiconductors will be an easier method since the separation of the catalyst is not necessary. One more advantage of photo-catalytic oxidation is that the products will be free from solvent. Photo-catalytic dehydrogenation of 2-propanol has attracted general interest from the energy-storing viewpoint ($\Delta H_0 = 69.9 \text{ kJ mol}^{-1}$, $\Delta G_0 = 25.0 \text{ kJ mol}^{-1}$) There is no theoretical limit on the quantum efficiency for the photo-catalytic dehydrogenation of 2-propanol in the liquid phase, since this reaction becomes exergonic ($\Delta G < 0$) due to the spontaneous evolution of the product hydrogen.

Table 6.1 *Various photo-catalytic oxidation reactions, catalysts in mostly liquid phase and at RT (RT = Room temperature)*

<i>Reaction studied</i>	<i>Catalyst employed</i>	<i>Ref</i>
Benzylic and allylic alcohols to aldehydes, ketones	molecular iodine	[6]
Benzyl alcohol to Benzaldehyde	9-phenyl-10- methylacridinium ion	[7]
2-propanol to acetone	TiO ₂ (110)	[8]
	(Bu ₄ N) ₄ [W ₁₀ O ₃₂]	[9]
	cis-Rh ₂ Cl ₂ (CO) ₂ (dpm) ₂	[10]
	(Dioctadecyl dimethylammonium) ₄	[11]
	[W ₁₀ O ₃₂]	
	Ag/TiO ₂	[12]
	Pt dispersed on Brookite	[13]
	Trans[IrCl ₂ (SnCl ₃) ₄] ³⁻	[14]
	Chloro(tetraphenyl porphyrinato)Rh(III)	[15]
	RhCl(CO)(PPh ₃) ₂	[16]
	Pt dispersed on TiO ₂	[17]
	Chloro(tetraphenyl porphyrinato)Rh(III)	[18]
2-propanol to acetone	5wt%Pt dispersed on TiO ₂	[19]
ethanol to acetaldehyde	TiO ₂ and ultrasonication	[20]
methanol, ethanol and and n-propanol to aldehydes	Heteropoly tungstates	[21]
secondary alcohols to ketones		
Allyl alcohol to acrolein		
Propargyl alcohol to aldehyde		
Aromatic secondary alcohols	silica encapsulated Heteropoly tungstate	[22]
Benzyl alcohol	TiO ₂ (anatase)	[23]
1-Phenyl ethanol, Benzhydrol		
4-Chlorobenzhydrol		
4,4'-dichlorohydro Benzoin		
4,4'-dimethoxyhydro Benzoin		
to oxidation products		
Benzyl alcohol to benzaldehyde	[Hex ₄ N] ₄ [S ₂ Mo ₁₈ O ₆₂]	[24]
	[Bu ₄ N][S ₂ W ₁₈ O ₆₂]	
Ethanol to acetaldehyde	Pd dispersed on CdS	[25]
methanol to formaldehyde	Rutile (110)	[26]
methanol to HCHO	silica coated CdS	[27]
methanol to HCHO	cis Rh ₂ Cl ₂ (CO) ₂ (dpm) ₂	[28]

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Table 6.1 (Continued)

Reaction studied	Catalyst employed	Ref
Methanol to HCHO	[IrH(SnCl ₃) ₅] ₃	[29]
Ethanol to acetaldehyde; CH ₃ OH to HCHO	Pt dispersed on CdS	[30]
Ethanol to CH ₃ CHO	titanium tetraisopropoxide/tetraethoxide	[31]
ethanol to acetaldehyde	Pt dispersed on CdS	[32]
n-octanol to n-octanal	TiO ₂	[33]
Ethanol to acetaldehyde	CuCl ₂ in HCl	[34]
Dehydrogenation of Cyclohexanol	Chloro(tetraphenylporphyrinato Rh(III))	[35]
dehydrogenation of CH ₃ OH	cis-[Rh ₂ Cl ₂ (CO) ₂ (dpm) ₂]	[36]

The presence of surface hydroxyl groups increases the oxidation reaction and the oxygen vacancies were found to play an important role in the oxidation of 2-propanol to acetone using TiO₂. Reaction in vapour phase is limited to 623 K above which thermal desorption takes place. The list of photocatalytic oxidation reactions studied are given in Table 6.1.

The dehydrogenation of 2-propanol using cis-[Rh₂Cl₂(CO)₂(dpm)₂] gave acetone, pinacol and cyclohexanol. The yield of acetone was maximum when the wavelength was 312 nm. In Table 6.2 the data are given to substantiate this statement.

Table 6.2 Yields (in micromoles) of photocatalytic oxidation products of 2-propanol using cis [Rh₂Cl₂(CO)₂(dpm)₂] as catalyst [10]

Wave length(nm)	260	285	312	338	364	390	414	440
acetone	258	754	945	344	45.9	11.5	8.4	5.6
Pinacol	Trace	6.6	7.9	trace	0.00	0.00	0.00	0.00
Cyclohexanol	0.08	0.59	1.17	0.15	0.00	0.00	0.00	0.00

Benzylic and allylic alcohols are oxidized to aldehydes and ketones using iodine as the photo-catalyst. The oxidation of the substrates was found to be dependent on the solvent used [6]. Various products formed by the oxidation of allylic and benzylic alcohols by molecular iodine and their yields are given in Table 6.3

6.3 METHANE TO METHANOL

Methane is a major component of natural gas. Methane can be directly used as a fuel. But most of the sources are located off-shore or in remote places inland. The transportation of methane containing natural gas is difficult because of the difficulty in compression methane and it is not economically favourable. Because of this limitation, in many cases the natural gas containing methane is flared at the source. Goal gasification also produces upto 18% methane. This places a condition that the gaseous methane has to be converted to a liquid

Table 6.3 *Products and yields during the photocatalytic oxidation of allylic and benzylic alcohols using molecular iodine [6]*

<i>Substrate</i>	<i>Product</i>	<i>Irradiation time (h)</i>	<i>Yield</i>
C ₆ H ₅ CH ₂ OH	C ₆ H ₅ CHO	5	88
p-MeOC ₆ H ₄ CH ₂ OH	p-MeOC ₆ H ₄ CHO	3	92
o-MeOC ₆ H ₄ CH ₂ OH	o-MeOC ₆ H ₄ CHO	3	90
m-MeOC ₆ H ₄ CH ₂ OH	m-MeOC ₆ H ₄ CHO	3	88
2,4(MeO) ₂ C ₆ H ₃ CH ₂ OH	2,4(MeO) ₂ C ₆ H ₃ CHO	2	96
3,4,5(MeO) ₃ C ₆ H ₂ CH ₂ OH	3,4,5(MeO) ₃ C ₆ H ₂ CHO	2	85
p-ClC ₆ H ₄ CH ₂ OH	p-ClC ₆ H ₄ CHO	6	85
2,4 Cl ₂ C ₆ H ₃ CH ₂ OH	2,4 Cl ₂ C ₆ H ₃ CHO	6	85
C ₆ H ₅ CH=CHCH ₂ OH	C ₆ H ₅ CH=CHCHO	6	85
p-MeC ₆ H ₄ CHOHCH ₃	p-MeC ₆ H ₄ COCH ₃	2	94
p-NO ₂ C ₆ H ₄ CHOHCH ₃	p-NO ₂ C ₆ H ₄ COCH ₃	5	80
PClC ₆ H ₄ CHOHC ₆ H ₅	P-ClC ₆ H ₄ COC ₆ H ₅	3.5	84
p-NO ₂ C ₆ H ₄ CHOHC ₆ H ₅	p-NO ₂ C ₆ H ₄ COC ₆ H ₅	4.5	77
(p-FC ₆ H ₄) ₂ CHOH	(P-FC ₆ H ₄) ₂ CO	7	78
p-MeC ₆ H ₄ CHOHCH ₂ OH	P-MeC ₆ H ₄ COCH ₂ OH	7	78
p-ClC ₆ H ₄ CHOHCH ₂ OH	p-ClC ₆ H ₄ COCH ₂ OH	6	75
p-NO ₂ C ₆ H ₄ CHOHCH ₂ OH	p-NO ₂ C ₆ H ₄ COCH ₂ OH	8	50

which can be directly used as a fuel or used for the production of chemicals. Direct conversion of methane and carbon dioxide to oxygenated compounds is preferable route. The limited data available in literature are given in Table 6.4.

Table 6.4 *Catalysts and reaction conditions for the conversion of methane to methanol*

<i>Catalyst</i>	<i>Reaction conditions</i>	<i>Ref</i>
La/WO ₃	Hg Lamp	[37,38]
WO ₃	Visiblelight laser	[39]
WO ₃ , TiO ₂ , NiO	UV Laser	[40]
SiO ₂	Hg lamp	[41]
TiO ₂ /SiO ₂		
CdS-TiO ₂ /SiO ₂		
Cu/CdS-TiO ₂ /SiO ₂ -2		
Products are acetic acid,,ethane, acetone and CO		

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6.4 PHOTO-CATALYTIC DEHYDROGENATION REACTION

Selective oxidation of hydrocarbons by molecular oxygen (refer to Table 6.5) is an important goal for economic, environmental and scientific reasons.

Table 6.5 *Alkane Dehydrogenation Reactions*

<i>Reaction</i>	<i>Catalysts</i>	<i>Reaction conditions</i>	<i>Ref</i>
dehydrogenation of alkane	RhCl(CO)(PR ₃)	400W Hg lamp	[42]
cyclohexane to benzene	MOO _x /TiO ₂	40W fluorescent lamp	[43]

6.4.1 Conversion of Benzene to Phenol

The total production of phenolis of the order 5X10⁶ tones per year. The current process called the cumene process is a multistage process and hence has a low overall yield, energy intensive and gives rise to various undesirable side products like 2-phenylpropan-2-ol and methyl styrene. The direct formation of phenol from hydrocarbon sources like benzene will be attractive for various reasons and the attempts in this direction are given in Table 6.6.

Table 6.6 *Details of catalysts and reaction conditions for the oxidation of benzene to phenol*

<i>Reaction</i>	<i>Catalyst</i>	<i>Conditions</i>	<i>Irradiation</i>	<i>Ref</i>
			source	
Benzene to phenol, hydroquinone and catechol	TiO ₂ P-25 with Fe ³⁺ , H ₂ O ₂ Pt/TiO ₂ P25 Fluorinated TiO ₂ Polyoxometalate	liquid phase	450W Xe lamp >300nm	[44]
Benzene to Phenol Toluene, Benzaldehyde benzylalcohol, cresols	UO ₂ ²⁺	Liquid RT	Dye laser	[45]

6.4.2 Oxidation of Cyclohexane

Oxygenation of cyclohexane is an important reaction for the production of alcohols and ketones which are precursors for the synthesis of adipic acid which is an intermediate in the production of nylon. The available data are given in Table 6.7.

Table 6.7 Catalysts for the oxidation of cyclohexane in liquid phase at room temperature (RT)

Cyclohexane to cyclohexanone	Variety of tungstate like $(Et_4N)_4W_{10}O_{32}$	400 W Hg lamp	[46]
cyclohexanol			
cyclohexene to cyclohex-2-en-1-one and epoxide	Iron(III) meso-tetrakis (2,6dichlorophenyl) Porphyrin	>350nm	[47]
cyclohexane to Cyclohexanone	TiO ₂	125W Hg Lamp 350 nm	[48]

Table 6.8 Data on the oxidation of light alkanes, in mostly liquid phase or vapour phase

Reaction	Catalyst	Irradiation Source	Ref
ethane to acetaldehyde	MoO ₃ on SiO ₂	75W Hg	[49]
Propane to aldehyde and ketone	Na, K, and Rb loaded on V ₂ O ₅ on SiO ₂	300W Xenon	[50]
Isobutene to acetone	Tin oxide on SiO ₂	310nm	[51]
Propane to acetone and propanaldehyde	MoO ₃ on SiO ₂	1000W Xe lamp	[52]
	Rh on V ₂ O ₅ on SiO ₂	300 w Xe lamp	[53]

6.4.3 Oxidation of Light Alkanes to Oxygenated Products

Selective conversion to partial oxidative products is difficult due to the low chemical reactivity of light alkanes. The main interest is devoted to the dehydrogenation of n-butane to butenes and butadiene which are precursor for manufacturing synthetic rubber. The relevant data are given in Table 6.8.

6.4.4 Oxidation of cyclic hydrocarbons present in Petroleum

A selective and environment friendly photo-catalytic route for the conversion of cyclic hydrocarbons present in petroleum is desirable for various reasons like for the production fine chemicals and other industrial chemicals. Selective oxidative dehydrogenation of cycloalkane has been the subject of many studies because of the importance of refining and reforming process in petroleum

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industry. There are only a few practical processes for converting alkanes to more valuable products and some of these are given in Table 6.9.

Table 6.9 *Data on oxidation of cyclic and aromatic hydrocarbons in liquid phase and room temperature*

<i>Reaction</i>	<i>Catalyst</i>	<i>Irradiation Source</i>	<i>Ref</i>
Toluene to benzaldehyde and benzyl alcohol	UO ₂ ²⁺	275 W tungsten halogen lamp	[54]
oxidation of cumene, benzyl alcohol and benzaldehyde	TiO ₂	125 W Hg lamp	[55]
Substituted aromatics to hydroxylated aromatics	TiO ₂ , TiO ₂ /HY	125W Hg lamp	[56]
4-substituted toluenes to aryl aldehydes and ketones	TiO ₂	500W Hg lamp	[57]
Naphthalene to 2-formyl Cinnamaldehyde	TiO ₂	250 W Hg lamp	[58]
Cyclopentene to cyclopenten-2-en-1-one	Titanium stearate	Hg Lamp	[59]
Hexene-1 to acetaldehyde propionaldehyde, Butyraldehyde			

In Table 6.10, the data for the oxidation of aromatic compounds are summarized.

Table 6.10 *Yields of aromatic hydroxylated species for 45 minutes irradiation using TiO₂[55]*

<i>Substrate</i>	<i>Conversion %</i>	<i>Total yield OH derivative</i>	<i>O:m:p ratio</i>
Phenol	70	75	54.5:0.5:45.0
phenylamine	40	50	49.7:0.0:50.3
N-phenylacetamide	50	60	20.0:03.0:77.0
Nitrobenzene	50	20	29.0:34.0:37.0
Cyanobenzene	60	30	45.0:30.0:25.0
1-Phenylthanone	55	30	38.5:21.0:40.5

There are various other oxidation reactions of importance in synthetic organic chemistry which can be carried out by photocatalytic means. the important ones are oxidation of hydrocarbons, phosphines, sulfides and olefins, benzhydrol to benzophenone diphenyl sulfides to aromatic aldehydes and sulfoxides, Fluorene to Fluorenone, dihydroanthracene to anthracene, diphenyl methane to benzophenone or acetophenon, cumene to cumyl alcohol, toluene to benzaldehyde.

6.5 PHOTOCATALYTIC REDUCTIONS

6.5.1 Photocatalytic Reduction of Carbon Dioxide and Dinitrogen

These are two important reactions and have been investigated by a number of workers. These two reactions have some relevance to photo synthesis and nitrogen cycle. In view of the importance these two reactions will be dealt with separately. However for a compilation of the relevant data please refer to Magesh et al [5].

6.5.2 Photocatalytic Reduction of Carbonate

When carbon dioxide present in the atmosphere dissolves in water it is mostly present in the form of carbonates. Therefore it is appropriate to study the photo-catalytic reduction of carbonate to form various chemicals. The results involving the photo-catalytic reduction of carbonate species to organic chemicals are given in Table 6.11.

Table 6.11 *Products, catalysts, and reaction conditions for photocatalytic reduction of carbonate*

<i>Methanol</i>	MoS ₂ , ZnTe, CdSe P25 TiO ₂	125 W Hg	[60]
Methanol and methane	TiO ₂	15W lamp 365 nm	[61]
CH ₃ OH, HCHO HCOO ⁻	Cr and Mg doped TiO ₂	125 W Hg	[62]
HCOOH, HCHO CH ₃ OH	SrFeO ₃	450W Hg	[63]
Bicarbonate, acetate propionate	MnS	450W Hg	[64]

6.5.3 Photocatalytic Reduciton of other Nitrogen Containing Compounds

The reduction of nitrate is of interest as a means of mimicking reduction of nitrogen oxyanion substrates in nature and developing novel nitrogen fixation systems [66,67]

6.5.4 Photocatalytic Hydrogenation

Hydrogenation of olefins is an important reaction and has applications in Fischer-Tropsch process, preparation of edible oils and in organic synthesis. some relevant data are given in Table 6.12.

6.5.5 Reduction of Organic Nitro Compounds to Amines

The reduction of various nitro compounds to the corresponding amines plays an important role in synthetic chemistry for various drugs, dyes and polymers. Anilines are widely present in the drug and dye molecules. The reduction of nitro compounds is also environmentally significant because of the toxic effects of nitro aromatic compounds.

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Table 6.12 *Products, catalysts, and conditions for reduction of various hydrocarbons*

1-pentene	Fe(CO) ₅	Laser Irradiation	[67]
Ethylene	H ₄ Ru ₄ (CO) ₁₂	450 W Hg	[68,69]
norbornadiene	Cr(CO) ₆	1-80 atm	[70]
1-octene	cis-HMn(CO) ₄ PPh ₃	100 W Hg	[71]
alkenes	H ₄ Ru ₄ (C) ₁₂	355 nm	[72-74]
diphenylacetylene	Pt,Rh Pd on TiO ₃ 2	125 W Hg	[75]
1,5cyclooctadiene	Rh ₄ (CO) ₁₂	500W Hg	[76]

Table 6.13 *Catalysts and Conditions in the Photocatalytic formation of Hydrogen Peroxide*

Oxygen to H ₂ O ₂	Ru(II) complex	500 W Xe	[77]
	Ru(II) Complex	500W W-X lamp	[78]
	metal porphyrins	500W W-Xlamp	[79]
	TiO ₂ -fluoride	40W lamp	[80]
water to H ₂ O ₂	TiO ₂	> 400 nm	[81]

6.5.6 Photocatalytic Formation of Hydrogen Peroxide

Hydrogen peroxide plays an important role as oxidising agent in a variety of pollution control systems. It is also used in organic synthesis as Fenton's reagent. It is used as a disinfectant, as propellant and also for the production of various peroxides and production of oxyacids. Few typical examples are given in Table 6.13.

6.5.7 Other Organic Photocatalytic Reactions

There are a variety of isomerization reactions which can be carried out by photocatalytic means. Polymerization is an important industrial process and the dependence of world today on polymers is high. Various polymerization reactions have been carried out by photocatalytic means using both homogeneous and heterogeneous catalysts.

In addition to various reactions considered in this chapter, there are also other reactions like condensation, bond cleavage which can be carried out by photo-catalytic means. Though considerable effort has already been placed on photo-catalytic transformations, the production of chemicals by this route has yet to be fully realized though the feasibility has already been established. The transformation of these processes from laboratory to industrial production though may not have reached the required maturity, it is only a matter of

time, when this can occur. When it takes place the production of chemicals can become a neat process with acceptance from people with environmental concerns.

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