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Photocatalytic routes for chemicals

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1. Introduction

Petroleum and natural gas serve as the primary source of most of the chemicals, reagents solvents and polymers used in various applications. These compounds are obtained by employing various organic transformations (1). The dependence on fossil fuel source can be reduced if one can evolve alternate strategies and raw material inventory as a feed stock for chemicals.

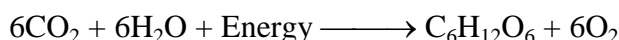
The primary source of life on earth is the sun. Most of the living systems on earth depend on photosynthesis since it is the source of food, fuel and oxygen. The process of photosynthesis occurs not only in plants but also in algae and certain bacteria (2).

Natural photosynthesis has evolved over a period of three billion years. It involves molecules combining with suitable macromolecules to carry out reactions with required efficiencies. Nature has been successful in synthesizing starch from water and CO₂. If mankind can synthesize molecules using sunlight as the energy source, it will solve energy and environment related problems. The molecules or compounds include not only molecules like hydrogen from water but also the synthesis of other industrially important chemicals as well (3). It is also the desire to reduce carbondioxide levels using photoelectrochemical means. There are plants which can convert CO₂ to hydrocarbons.

Most of the reactions involve electron transfer or redox chemistry. For this to take place, the donor and acceptor levels of the species should be energetically and symmetrically matched to each other. Nature appears to adapt to this situation by appropriate manipulation of the species. This can be understood in the example of activation of dinitrogen by the enzyme nitrogenase. This is due to the ability of the nitrogenase to perturb the orbitals of dinitrogen such that the LUMO of N₂ will become suitable for electron transfer which subsequently destabilizes N₂ and makes it reactive.

1.1 Photosynthesis

Photosynthesis can be represented by the equation:



The process of photosynthesis is driven by light induced generation of sufficiently stabilized cation-anion radical pairs in multiple protein complexes located in and around an organized membrane called thylakoid membrane. Photosynthesis system contains photosystem I (PS I) and photosystem II (PS II) which are incorporated in suitable positions in a thylakoid membrane. These two photosystems are so well aligned and operating in series to carry out the transfer of hydrogen from water to CO₂ to produce carbohydrates. Cleavage of water to molecular oxygen takes place in PS II where plastoquinone (PQ) gets converted to plastohydroquinone or plastoquinol (PQH₂). Thus PS II can be called as light driven plastoquinone oxidoreductase. The reduction of plastoquinone A (PQ) to plastohydroquinone A (PQH₂) is shown in Fig.1.

The formed PQH₂ diffuses through the thylakoid membrane and gets reoxidised to PQ by the cytochrome complex and gets transferred back to PS II. The cytochrome b₆f complex which is now in reduced form reduces the plastocyanin. The cytochrome b₆f complex thus serves as very important bridge for transfer of hydrogen from PS II to PS I. The reduced plastocyanin diffuses to the PS I where it reduces the NADP⁺ to NADPH. The NADPH then serves as the hydrogen source for the CO₂ reduction. Fig. 2 shows the structure and process involved in the cytochrome b₆f complex.

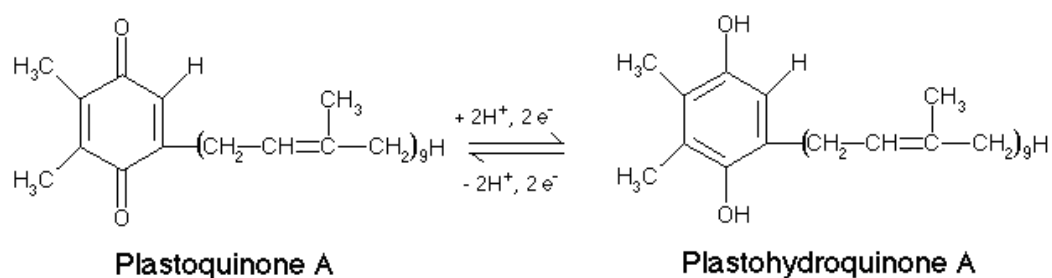


Figure 1. Reduction of plastoquinone A to plastohydroquinone A (Figure taken from ref. 4).

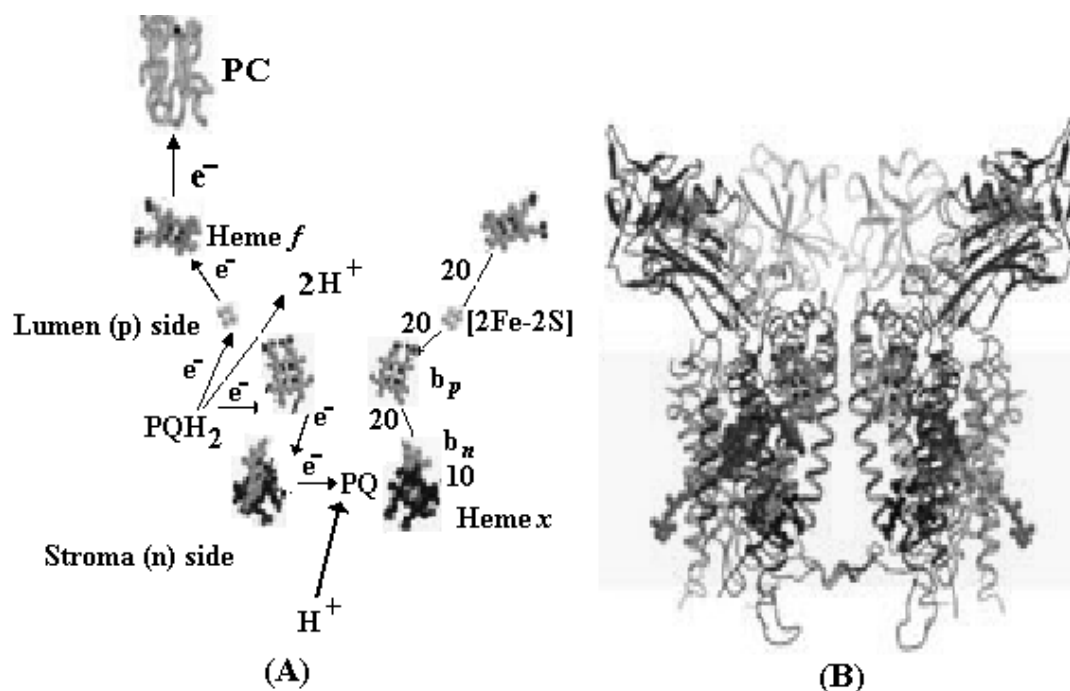


Figure 2. (A) Redox groups and electron/proton transfer pathways in the cytochrome b_6f complex (B) Structure of cytochrome b_6f complex (Figure taken from ref. 5)

The anisotropic incorporation of PS I, PS II and cytochrome b_6f complex into the thylakoid membrane are important for energy conversion. The photosynthesis route shows the complex redox process involved in the various steps. All these processes are achieved only because of the various reduction potentials evolved by the complex protein based complexes present in the system.

2. Photoelectrochemistry

Photoelectrochemistry involves compounds having an energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The condition for a compound to be able to get

activated by light is that the energy gap between LUMO and HOMO should be equal to that of the energy of the light used. Those compounds which satisfy the condition mentioned above are called photocatalysts. The reactions carried out by the photocatalysts are classified into two categories namely homogeneous and heterogeneous photocatalysis.

2.1. Photocatalysis

Photocatalysis 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 in semiconductor photocatalysis are shown in fig.3. The electrons are capable of carrying out reduction reactions and holes can carry out oxidation reactions.

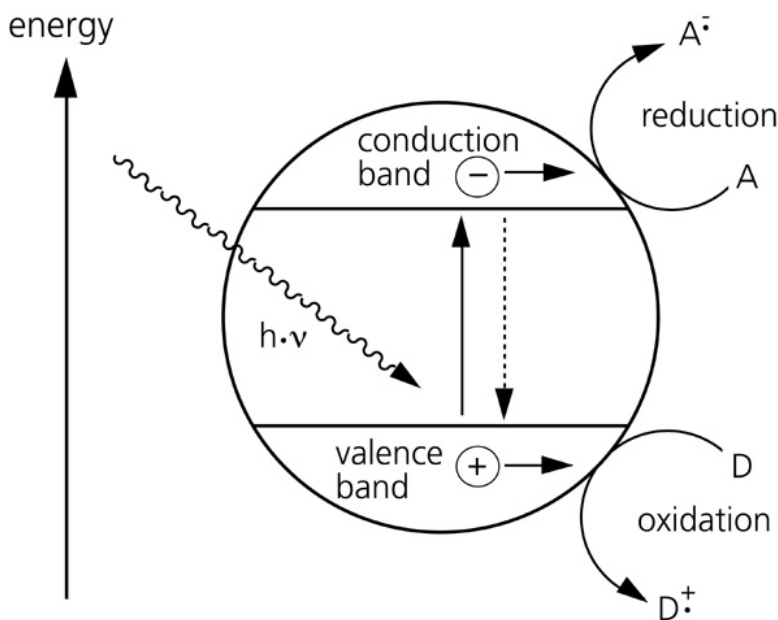


Figure 3. Process involved in semiconductor photocatalysis (Fig. taken from ref. 6).

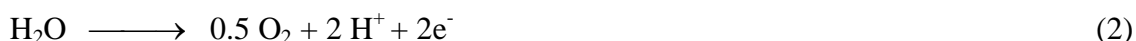
These electrons and holes can be exploited by a variety of means. The various ways of exploiting them are

- (i) for producing electricity
- (ii) for decomposing or removing pollutants
- (iii) for the synthesis and production of useful chemicals

2.1.2. Importance of position of energy levels

The ability of a photocatalyst to carry out a particular reaction depends on the position of the energy levels of the catalyst as well as the substrate. For a

compound to carry out the reduction reaction, the potential of conduction band or LUMO should be more negative than that of the potential required for the reduction reaction. For a compound to be able to carry out the oxidation reaction the potential of the valence band or the HOMO should be more positive than the potential required for the oxidation reaction. Let us consider the reaction of the photocatalytic splitting of water as an example. The following are the two reactions involved.



The oxidation reaction leading to oxygen evolution mentioned in equation (2) will take place at a potential +1.23 V where as the reduction reaction leading to the hydrogen evolution will take place at 0.00 V. The reduction reaction mentioned in equation (1) will happen only if potential of conduction band of photocatalyst is more negative than 0.00 V. Likewise the oxidation reaction mentioned in equation (2) will happen only if potential of valence band of photocatalyst is more positive than +1.23 V.

Accordingly, depending on the positions of CB and VB, the systems can be classified by OR (both reactions possible), O type (only oxidation is feasible) R type (reduction reaction alone takes place) and X type (neither reaction can occur).

2.1.3. Choice of the photocatalyst

Fig. 4 shows the band position and bandgap of various semiconductor photocatalysts. Among them, WO_3 and Fe_2O_3 cannot carry out the photosplitting of water since their conduction band potentials are less negative than the hydrogen evolution potential. All the given catalysts can carryout the oxygen evolution reaction. But out of them, only a few were studied for water splitting reaction because of other problems like photocorrosion, cost, higher bandgap and stability.

Another important parameter to be taken into account while choosing the photocatalyst is the percentage of ionic character of the cation-anion bond. A system which has higher percentage ionic character ($> 40\%$) will have higher band gap and will not be able to absorb light in the visible region. A catalyst which has a percentage ionic character between 20-30% with suitable positions of the valence and conduction band potentials with respect to the reaction under consideration will be successful for carrying out the reaction (7).

It is important to mention that the commercial success of a photocatalyst depends on its ability to function by utilizing the visible light. This is because of the composition of sunlight which has 46 % visible radiation, 47 % IR

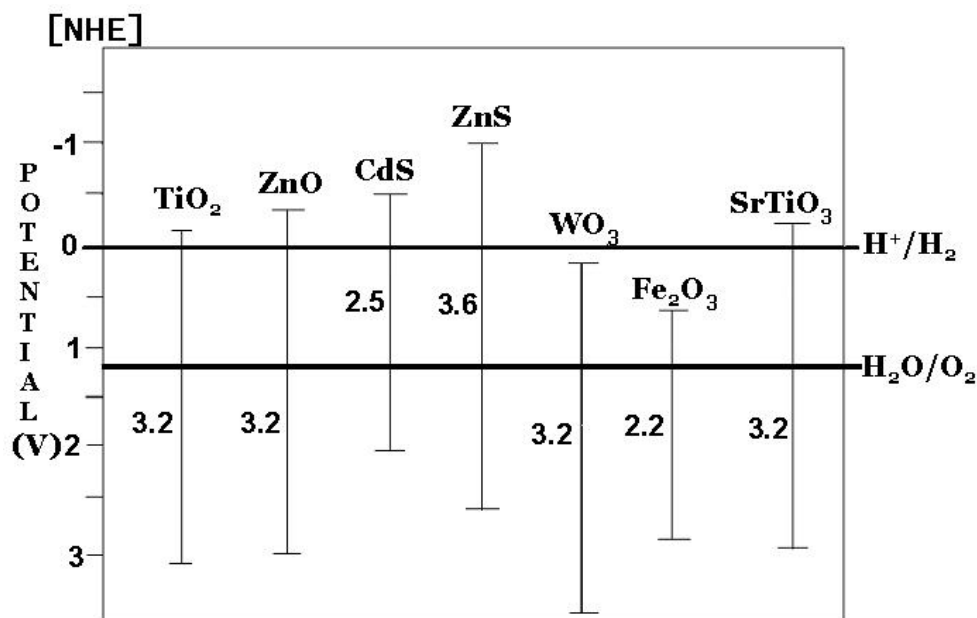


Figure 4. Band positions of various semiconductor photocatalysts.

radiation and only 7 % UV radiation (8). But TiO₂ which is the most efficient and stable photocatalyst available can function only by using the UV light. So, research has been focused on finding a photocatalyst or modifying the available catalysts so that they can function by absorbing light in the visible region.

3. Photocatalytic chemical production

Photocatalytic synthesis of compounds can be carried out by 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 photocatalytic splitting of water has received considerable attention and the literature is extensive on this aspect. Hence this will not be taken up in this presentation.

3.1. Photocatalytic 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 reactions. 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 photocatalytically (9).

Photocatalytic oxidation has been widely used for process like the decontamination of water and air. However, the application of photocatalytic oxidation for the synthesis of compounds of commercial importance alone will be considered in this section. Photocatalytic oxidation was carried out as early as 1964 where oxidation of 2-propanol to acetone was carried out using ZnO and TiO₂ (10).

3.1.1. Oxidation of alcohols

Oxidation of various alcohols to their aldehydes and ketones is an integral part of organic synthesis. There are various reagents used for this purpose and their separation after the oxidation is a difficult task. Photocatalytic oxidation by using semiconductors will be an easier method since the task of separation of the catalyst is not there (11). One more advantage of photocatalytic oxidation is that the products will be free from solvent.

Photocatalytic dehydrogenation of 2-propanol has attracted general interests 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 photocatalytic dehydrogenation of 2-propanol in the liquid phase, since this reaction becomes exergonic ($\Delta G < 0$) due to the spontaneous evolution of product hydrogen (12).

Table 1. Various photocatalytic oxidation reactions, catalysts and reaction conditions.

Reaction studied	Catalyst used	Reaction conditions	Ref
Various benzylic and allylic alcohols to acetones and ketones	Molecular iodine	Liquid phase Room temperature	9
Benzyl alcohol to benzaldehyde	9-phenyl-10-methylacridinium ion	Liquid phase Room temperature	11
2-propanol to acetone	TiO ₂ (110)	Vapor phase 350 K	13
	(Bu ₄ N) ₄ [W ₁₀ O ₃₂] (Tetrabutyl ammonium decatungstate)	Liquid phase Room temperature	14
	Cis-[Rh ₂ Cl ₂ (CO) ₂ (dpm) ₂] dpm-bis(diphenylphosphino) methane	Liquid phase Room temperature	15
Reaction studied	Catalyst used	Reaction conditions	Ref
2-propanol to acetone	(Dioctadecyldimethylammonium) ₄ [W ₁₀ O ₃₂]	Liquid phase Room temperature	16
	Ag dispersed on TiO ₂	Liquid phase Room temperature	17
	Pt dispersed on brookite TiO ₂	Liquid phase Room temperature	18
	Trans-[IrCl ₂ (SnCl ₃) ₄] ³⁻	Liquid phase Room temperature	19

Table 1. Continued

	Chloro(tetraphenylporphyrinato) rhodium(III)	Liquid phase Room temperature	20
	[RhCl(CO)(PPh ₃) ₂]	Liquid phase Room temperature	21
	Pt dispersed on TiO ₂	Liquid phase Room temperature	22
	Chloro(tetraphenylporphyrinato) rhodium(III)	Liquid phase Room temperature	23
2-propanol to acetone Ethanol to acetaldehyde	5 wt % Pt dispersed on TiO ₂	Liquid phase Room temperature	24
2-propanol to acetone Ethanol to acetaldehyde	TiO ₂ + Ultrasonication	Liquid phase Room temperature	25
Methanol, ethanol and n-propanol to aldehydes. Secondary alcohols to ketones. Allyl alcohol to acrolein Propargyl alcohol to propargyl aldehyde	Heteropolytungstates (PW ₁₂ ³⁻ , SiW ₁₂ ⁴⁻ , FeW ₁₂ ⁵⁻ , H ₂ W ₁₂ ⁶⁻)	Liquid phase Room temperature	26
Aromatic secondary alcohols (ArCH(OH)R) where Ar- Aromatic R-aliphatic	Silica encapsulated H ₃ PW ₁₂ O ₄₀	Liquid phase Room temperature	27
Benzylalcohol, 1-Phenylethanol Benzhydrol, 4-Chlorobenzhydrol, Hydrobenzoin, 4,4'-dichlorohydro benzoin and 4,4'-Dimethoxyhydro benzoin to various oxidation products	TiO ₂ (anatase)	Liquid phase Room temperature	28
Reaction studied	Catalyst used	Reaction conditions	Ref
Benzyl alcohol to benzaldehyde	[Hex ₄ N] ₄ [S ₂ Mo ₁₈ O ₆₂] [Bu ₄ N] ₄ [S ₂ W ₁₈ O ₆₂]	Liquid phase Room temperature	29
Ethanol to acetaldehyde	Pd dispersed on CdS	Liquid phase 323 K	30
Methanol to formaldehyde	Rutile phase of TiO ₂ (110)	Liquid phase Room temperature	31
Methanol to formaldehyde	Silica coated CdS	Liquid phase Room temperature	32

Table 1. Continued

Methanol to formaldehyde	Cis-Rh ₂ Cl ₂ (CO) ₂ (dpm) ₂ Pd ₂ Cl ₂ (dpm) ₂	Liquid phase Room temperature	33
Methanol to formaldehyde	[IrH(SnCl ₃) ₅] ³⁻	Liquid phase	34
Ethanol to acetaldehyde Methanol to HCHO	Pt dispersed on CdS	Liquid phase Room temperature	35
Ethanol to acetaldehyde	Titanium tetraisopropoxide, Titanium tetraethoxide	Hg lamp Liquid phase Room temperature	36
Ethanol to acetaldehyde	Pt dispersed over CdS	Liquid phase Room temperature	37
n-Octanol to n-Octanal	TiO ₂	Liquid phase Room temperature	38
Ethanol to acetaldehyde	CuCl ₂ in HCl	Liquid phase Room temperature	39
Dehydrogenation of cyclohexanol	Chloro(tetraphenyl porphyrinato) Rh(III) complex	500 W lamp	40
Dehydrogenation of methanol	cis-[Rh ₂ Cl ₂ (CO) ₂ (dpm) ₂]	400 W Hg lamp	41

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 vapor phase is limited upto 350 K above which thermal desorption takes place (13). A list of photocatalytic oxidation reactions studied so far are given in Table 1.

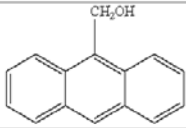
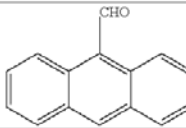
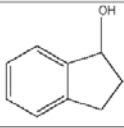
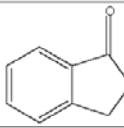
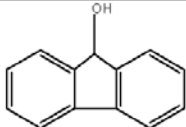
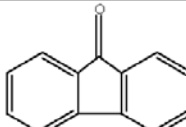
The dehydrogenation of 2-propanol using cis-[Rh₂Cl₂(CO)₂(dpm)₂] was found to give acetone, pinacol and cyclohexanol where the yield of acetone was found to be maximum at 312 nm. In Table 2 the yield of various products at different wavelengths of irradiation are given (15).

Table 2. Yields of photocatalytic oxidation products of 2-propanol using cis-[Rh₂Cl₂(CO)₂(dpm)₂] as catalyst (Ref. 15).

Wavelength (nm)	260	286	312	338	364	390	414	440
Acetone yield (μmol)	258	754	945	344	45.9	11.5	8.4	5.6
Pinacol yield (μmol)	Trace	6.6	7.9	Trace	0.00	0.00	0.00	0.00
Cyclohexanol yield (μmol)	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 photocatalyst. The oxidation of the substrates was found to be dependent on the solvent used (9). Various products formed by the oxidation of allylic and benzylic alcohols by molecular iodine and their yields are given in Table 3.

Table 3. Products and yields during the photocatalytic oxidation of allylic and benzylic alcohols using molecular iodine (Ref. 9).

Substrate	Product	Irradiation time (h)	Yield
$C_6H_5CH_2OH$	C_6H_5CHO	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	95
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
		4	75
		2.5	95
		3	90
$C_6H_5CH=CHCH_2OH$	$C_6H_5CH=CHCHO$	6	85
p-MeC ₆ H ₄ CHOHCH ₃	p-MeC ₆ H ₄ COCH ₃	2	94
Substrate	Product	Irradiation time (h)	Yield
p-NO ₂ C ₆ H ₄ CHOHCH ₃	p-NO ₂ C ₆ H ₄ COCH ₃	5	80
p-ClC 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	6	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

3.1.2. Methane to methanol

Methane forms a major part of the natural gas. Methane can be used directly as the fuel. But most of the wells are located off-shore or in remote places in the land. The transportation of methane containing natural gas is a difficult because of the difficulty in compressing methane and it is not economically favourable. Because of this limitation, in many cases the natural gas containing methane is burned (flaring) at the oil wells. This leads to an enormous loss of energy. Methane is also produced as a by-product of coal gasification, either in a stand-alone process or as part of the direct or indirect liquefaction of coal. Depending on the gasifier design and operating conditions, up to 18% of the total gaseous product may be methane.

One of the solutions to this problem lies in converting methane to methanol or anyother liquid products which can be transported easily. Methanol may be used directly as a fuel or may be converted to other valuable products like other transportation fuels, fuel additives, or chemicals. At present, the direct oxidation of methane to methanol suffers from low methane conversion and poor methanol selectivity. A process for the direct oxidation of methane to methanol, in high yield and with high selectivity, is desirable (42).

Conversion and utilization of CO₂ as well as CH₄ are important in the field of C1 chemistry. However, there is no practical technique for such conversion. Direct synthesis of oxygenated compounds from CO₂ and CH₄ has been studied to a limited extent. Photocatalytic conversion may be a promising method for direct conversion CH₄ and CO₂ together to oxygenated compounds. Synthesis of oxygenates over the coupled semiconductor Cu/CdS–TiO₂/SiO₂ from gaseous CH₄ and CO₂ by UV irradiation at low temperature was reported by Shi et al (46). The limited data available in literature are summarized in Table 4.

Table 4. Various catalysts and reactions conditions for the conversion of methane to methanol.

Catalyst	Reaction conditions	Ref.
La/WO ₃	Hg lamp	42, 43
WO ₃	Visible light laser	44
WO ₃ , TiO ₂ (rutile) and NiO	UV laser	45
Methane + CO ₂ giving CH ₃ COOH, CH ₃ CH ₃ , CH ₃ COCH ₃ , CO Catalysts: (i) SiO ₂ (ii) TiO ₂ /SiO ₂ (iii) CdS–TiO ₂ /SiO ₂ (iv) Cu/CdS–TiO ₂ /SiO ₂	473 K 125 W Hg lamp	46

3.1.3. Photocatalytic dehydrogenation reactions

Selective oxidation of hydrocarbons by O₂ (Table 5) is an important goal for economic, environmental, and scientific reasons (47, 48, 49, 50)

3.1.4. Benzene to phenol

Phenol is considered as one of the most important industrial chemicals due to its wide usage as a disinfectant, a precursor to phenolic resins, a reagent in chemical analysis, and a preservative. In order to meet this high demand, phenol is being produced over 5 X 10⁶ ton/yr globally. The current manufacturing process of phenol starts from benzene and consists of three steps (so-called cumene process): benzene alkylation to cumene (isopropylbenzene), cumene oxidation to cumene hydroperoxide, and decomposition of the latter to phenol and acetone. However, this multistage process has a low overall yield (less than 5%), requires high energy, and accompanies the generation of undesirable by-products such as acetophenone, 2-phenylpropan-2-ol, and α -methylstyrene. The development of alternative synthetic processes of phenol that are more efficient and environmentally benign is highly desirable. The ability to make phenol from hydrocarbons like benzene by photocatalytic means will be desirable for economic and environmental points of view (53). The attempts in this direction are summarized in Table 6.

Table 5. Various dehydrogenation reactions, catalysts and conditions.

Reaction	Catalyst	Reaction conditions	Ref.
Dehydrogenation of alkane	RhCl(CO)(PR ₃) where PR ₃ = PMe ₃ , PPh ₃ , PEtPh ₂ , PEt ₂ Ph, PEt ₃	400 W Hg lamp	51
Cyclohexane to benzene	MoO _x /TiO ₂	40 W fluorescent lamp	52

Table 6. Catalysts and reaction conditions in the oxidation of benzene to phenol.

Reaction	Catalyst	Reaction conditions	Irradiation source	Ref.
Benzene to phenol, hydroquinone and catechol	1. TiO ₂ -P 25 in presence of Fe ³⁺ and H ₂ O ₂ 2. Pt dispersed TiO ₂ - P25 3. Surface fluorinated TiO ₂ 4. Polyoxometalate	Liquid phase	450 W Xe lamp ($\lambda > 300$ nm using cutoff filter)	53
Benzene to phenol Toluene to benzaldehyde, benzylalcohol and cresols	UO ₂ ²⁺	Liquid phase Room temperature	Flash lamp pumped dye laser	54

3.1.5. Oxidation of cyclohexane

Conversion of cyclohexane to benzene is of industrial significance because of the variety of applications of benzene compared to only a few applications of cyclohexane. Cyclohexane has been widely used in the synthesis of nylon-66 (55). Cyclohexane oxygenation is an important commercial reaction, as the resultant products, alcohol and ketone, are precursors in the syntheses of adipic acid, which is in turn an intermediate in the production of nylon (56). The available data are given in Table 7.

Table 7. Catalysts and products for the oxidation of cyclohexane carried out in liquid phase at room temperature.

Reaction	Catalyst used	Irradiation source	Ref.
Cyclohexane to cyclohexanone, cyclohexanol	$(n\text{Bu}_4\text{N})_4\text{W}_{10}\text{O}_{32}$, $(\text{Et}_4\text{N})_4\text{W}_{10}\text{O}_{32}$, $(\text{Et}_3\text{NH})_4\text{W}_{10}\text{O}_{32}$, $(\text{Me}_4\text{N})_4\text{W}_{10}\text{O}_{32}$, $(\text{NH}_4)_4\text{W}_{10}\text{O}_{32}$, and $\text{Na}_4\text{W}_{10}\text{O}_{32}$ dispersed on SiO_2	400 W Hg lamp	56
Cyclohexane to cyclohexanone and cyclohexanol Cyclododecane to cyclododecanol	$(n\text{-Bu}_4)_4\text{W}_{10}\text{O}_{32}$	400 W Hg lamp $\lambda > 300$ nm	57
1. Cyclohexene to cyclohex-2-en-1-one and epoxide 2. Cyclooctene to epoxides	Iron(III) <i>meso</i> -tetrakis (2,6dichlorophenyl)porphyrin	$\lambda > 350$ nm	58
Cyclohexane to cyclohexanone	TiO_2	125 W Hg lamp $\lambda = 350$ nm	59

3.1.6. Oxidation of light alkanes to oxygenated products

Gas-phase selective oxidation of light alkanes is important for the usage of natural gas and liquefied petroleum gas. However, selective conversion to partial oxidative products is difficult due to the low chemical reactivity of light alkanes. One of the candidates for the selective oxidation is photooxidation of hydrocarbons over heterogeneous photocatalysts (60). The catalytic dehydrogenation of lower paraffins, olefins and alkylaromatic hydrocarbons has the highest throughputs in the chemical industry. The main interest is devoted to the dehydrogenation of *n*-butane to butenes and butadiene, which are precursor molecules for manufacturing synthetic rubber (61). The relevant data are given in Table 8.

3.1.7. Oxidation of cyclic hydrocarbons present in petroleum

There are various cyclic and aromatic hydrocarbons present in petroleum. Petroleum contributes in a major way for the fine chemicals and other chemical

Table 8. Reaction products, catalyst and conditions for the oxidation of various lighter alkanes.

Reaction	Catalyst used	Reaction conditions	Irradiation source	Ref.
Ethane to acetaldehyde	MoO ₃ dispersed on SiO ₂	Liquid phase 463 K	75 W Hg lamp	60
Propane to CH ₃ CHO, CH ₃ CH ₂ CHO, CH ₃ COCH ₃	Na, K and Rb loaded on V ₂ O ₅ dispersed over SiO ₂	Gas phase 323 K	300 W Xe lamp	62
Isobutene to acetone	Tin oxide immobilized on silica	Liquid phase Room temperature	$\lambda > 310$ nm	63
Propane to acetone and propanaldehyde	MoO ₃ dispersed on SiO ₂	Liquid phase Room temperature	1000 W Xe lamp $\lambda > 280$ nm	64
Propane to acetone and propionaldehyde	Rb dispersed on V ₂ O ₅ supported on SiO ₂	Vapor phase 333 K	300 W Xe lamp $\lambda > 300$ nm	65

Table 9. Products and catalysts for the oxidation of cyclic and aromatic hydrocarbons carried out in the liquid phase at room temperature.

Reaction	Catalyst used	Irradiation source	Ref.
1. Toluene to benzaldehyde and benzyl alcohol 2. Oxidation of cumene. benzyl alcohol and benzaldehyde	UO ₂ ²⁺	275 W Tungsten-Halogen lamp	47
Substituted aromatic compounds to hydroxylated aromatics	Polycrystalline TiO ₂	125 W Hg lamp	67
4-substituted toluenes Substituent = H, CH ₃ , C ₂ H ₅ , i-C ₃ H ₇ , t-C ₄ H ₉ to substitute aryl aldehydes ketones and acids	TiO ₂ , TiO ₂ /HY ₁₅ zeolite and TiO ₂ /HY ₂₀ zeolite composites	125 W Hg lamp $\lambda > 330$ nm	68
Naphthalene to 2-formyl cinnamaldehyde	TiO ₂	500 W Hg lamp	69
Cyclopentene to cyclopenten-2-en-1-one, cyclopentenylhydroperoxide, 6-oxabicyclo[3.1.0]hexane, Penta-1,4-dial	TiO ₂	250 W Hg lamp	70
Hexene-1 to acetaldehyde, propionaldehyde, butyraldehyde	Titanium stearate (liquid)	Hg lamp	71

industry. The compounds which are used are mainly the oxidation products of these aromatic and cyclic compounds. Therefore, a highly selective and environment friendly photocatalytic route for the conversion of these hydrocarbons to oxygenated compounds is desirable. Catalytic selective oxidative dehydrogenation (ODH) of cycloalkane has been the subject of many

studies due to the importance of refining and reforming process in the petroleum industry, but there are very few practical processes for converting alkanes (refer to Table 9) directly to more valuable products (66).

In the Table 10, the corresponding data for the oxidation of aromatic compounds are given.

Table 10. Average yields in hydroxylated species, *o:m:p* average ratios (during the first 45 min of irradiation) for various substituted aromatic compounds using TiO₂ (Ref. 67).

Substrate	Conversion (%)	Total yield of OH derivatives	<i>o:m:p</i> ratio
Phenol	~70	~75	54.5 : 00.5 : 45.0
Phenylamine	~40	~50	49.7 : 00.0 : 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-phenylethanone	~55	~30	38.5 : 21.0 : 40.5

3.1.8. Other oxidation reactions

There are various other oxidation reactions of importance in synthetic organic chemistry which can be carried out by photocatalytic means and are listed in Tables 11 and 12.

3.2. Photocatalytic reductions

3.2.1. Reduction of CO₂

The reaction which is closest in resemblance to that of the natural photosynthesis is the reduction of CO₂ by photocatalytic means. This reaction is even called as artificial photosynthesis. The ability to synthesize chemicals by reducing CO₂ not only helps as a great source of energy but also helps in reducing CO₂ in the atmosphere which is known for its green house effect.

During the past decade there has been considerable interest in the development of artificial photosynthetic systems which convert light energy into chemicals and fuel (80, 81). Many studies devoted on the light-induced splitting of H₂O into H₂ and O₂. The photochemical activation and reduction of carbon dioxide is the other major goal of artificial photosynthesis (82). Reduction of CO₂ to formate (83-85), formaldehyde (86), carbon monoxide (87) and methane (88-91) has been reported using homogeneous catalysis (83, 91), a semiconductor particulate system (85) and an enzyme-catalysed coupled system.

CO₂ has been reduced to a variety of chemicals of synthetic importance and usage in fine chemicals and other industries. The products of CO₂

Table 11. Catalysts and reaction conditions for various photocatalytic oxidation reactions carried out in liquid phase at room temperature.

Reaction	Catalyst used	Irradiation source	Ref
Aldimines to nitrones	TiO ₂	6 W Hg lamp $\lambda > 350$ nm	72
Oxidation of various hydrocarbons, phosphines, sulfides and olefins	Bis-iron(III)- μ -oxo Pacman Porphyrin	Visible light $\lambda = 425$ nm	73
Oxidation reaction of PhX(CH ₂) ₄ OH	TiO ₂	24 W Hg lamp 350 ± 10 nm	74
1. Tetraphenylethylene to dioxetane of tetraphenylethylene 2. Oxidation of substituted stilbenes to alcohols	9-mesityl-10-methylacridinium ion	500 W Xe lamp + $\lambda > 430$ nm cutoff filter	75
Oxidation of triphenylphosphine, tri- <i>p</i> -tolylarsine, triphenylstibine, and triphenylbismuthine.	TiO ₂	400 W $\lambda = 350$ nm	76
Benzhydrol to benzophenone	TiO ₂	250 W Hg lamp $\lambda > 350$ nm	77
1. Decarboxylation of phenylacetic acid and phenyloxyacetic acid to toluene and anisole respectively 2. Arylthioacetic acid to sulphinylacetic acid	TiO ₂	125 W Hg lamp $\lambda > 350$ nm	78
Diphenylsulfides to aromatic aldehydes and sulfoxides	TiO ₂	$\lambda > 350$ nm	79

Table 12. Products, Turn over number (TON) and selectivity of the photocatalytic oxidation of various hydrocarbons using Bis-iron(III)- μ -oxo Pacman Porphyrin (Ref. 73).

Substrate	Product	TON	Selectivity (%)
Fluorene	Fluorenone	284 ± 34	100
Dihydroanthracene	Anthracene	235 ± 37	100
Diphenylmethane	Benzophenone	160 ± 25	100
Diphenylmethane	Acetophenone	143 ± 10	55
Cumene	Cumyl alcohol	116 ± 14	45
Toluene	Benzaldehyde	76 ± 11	100

reduction can also be used as a fuel directly. A considerable amount of CO has been found in all the reduction reactions of CO₂. The relevant data are given in Tables 13 and 14.

Table 13. Products, catalysts and reaction conditions for the photocatalytic reduction of CO₂.

Product	Catalyst	Irradiation source	Ref.
Formate and formaldehyde	Pt-CdS-RuO ₂	250 W Xe lamp	92
Formate	1. Pd/RuO ₂ /TiO ₂ 2. Pd/TiO ₂ 3. TiO ₂	450 W Xe lamp	93
CO	1. [Ru{bpyC ₃ bpyRe(CO) ₃ Cl} ₃] ²⁺ 2. [(dmb) ₂ Ru(bpyC ₃ bpy)Re(CO) ₃ Cl] ²⁺	Hg lamp λ > 500 nm	94
CH ₄ , CH ₃ OH	Ti containing porous silica	100 W Hg lamp 323 K	95
Acetic acid, Methanol	TiO ₂	4.5 kW Xe lamp 1-25 atm pressure 293 K	96
Formate and CO	TiO ₂ embedded on SiO ₂ matrix	500 W Hg lamp	97
Methanol	Cu dispersed over TiO ₂	Hg lamp λ = 254 or 365 nm	98
Product	Catalyst	Irradiation source	Ref.
CO	[Re(bpy)(CO) ₃ {P(OEt) ₃ }] ⁺ bpy = 2,2'-bipyridine	500 W Hg lamp	99
CO	[fac-Re(bpy)(CO) ₃ Cl] (bpy = 2,2'-bipyridine)	500 W Hg lamp 25 atm pressure	100
Ethyl alcohol	1. SiC 2. Pd/ZnSe 3. Pd/Pt/ZnSe 4. Pd/Rh/ZnSe	500 W Xe lamp	101
Formate and CO	ZrO ₂	500 W Hg lamp 673 K	102
CO	[Re(4,4'-X ₂ -bipyridine)(CO) ₃ PR ₃] ⁺ (X= CH ₃ , H, CF ₃ ; PR ₃ = Phosphorus Ligands)	500 W Hg lamp λ = 365 nm	103
HCOOH, CH ₃ OH	Ag coated TiO ₂ embedded in Nafion	990 W Xe lamp	104
CH ₃ OH	Cu dispersed over TiO ₂	Hg lamp λ = 350 nm	105, 106
Formic acid, formaldehyde and methanol	RuO ₂ dispersed over TiO ₂ Nb dispersed over TiO ₂ V ₂ O ₅ doped TiO ₂ Cr doped TiO ₂	75 W Hg lamp 318 K	107

Table 13. Continued

Methanol, formaldehyde	Cu/TiO ₂	500 W Xe lamp 313 K	108
CO, carbonate	[Re(I)(CO) ₃ (bpy)(py)] ⁺ (bpy-2,2'-bipyridine ; py-pyridine) Encapsulated on NaY zeolite and Al-MCM41 molecular sieves	300 W Xe lamp $\lambda > 350$ nm	109
CO	1. [Ru(bpy) ₃] ²⁺ immobilized on cation exchange polymer 2. [Co(bpy) ₂] ²⁺	Xe lamp	110
Formic acid, formaldehyde and methanol	1. Rh dispersed over TiO ₂ 2. W doped TiO ₂	500 W Xe lamp	111
CO, methane	Pt, Ru, Rh, Ag and Cu dispersed over TiO ₂ , CdS, SiC and SrTiO ₃	Not given	112
CO and formate	TiO ₂	500 W Hg lamp Cutoff filter for $\lambda > 300$ nm	113
Methane	TiO ₂ pellets	Three 1.5 W Hg lamps	114
Methane, ethylene	Cu loaded TiO ₂	450 W Xe lamp	115
Methane and acetic acid	Pd, Rh, Pt, Au, Cu and Ru deposited over TiO ₂	500 W Hg lamp ($\lambda > 310$ nm)	116
Product	Catalyst	Irradiation source	Ref.
Methane	TiO ₂ (anatase)	$\lambda = 350$ nm	117
CO	[fac-Re(bpy)(CO) ₃ (4-Xpy)] ⁺ [bpy = 2,2'-bipyridine, py= pyridine, X = tert-Bu, Me, H, MeCO, CN]	500 W Hg lamp + Cutoff filter for $\lambda = 350$ nm	118
HCOOH, HCHO, CH ₃ OH, C ₂ H ₅ OH, CH ₃ CHO	Cu, Pd, Fe and Pt dispersed over SiC	500 W Xe lamp	119
CH ₄ , CH ₃ OH, CO	TiO ₂ anchored on Vycor® glass	75 W Hg lamp (Filter for $\lambda > 280$ nm) 274 K and 323 K	120, 121
Methanol	Cu ⁰ , CuO, Cu ₂ O dispersed over TiO ₂	Six 10 W Hg lamps	122
CO	MgO	500W Hg lamp	123
Formate and CO	CdS surface modified with thiol compounds	500 W Hg lamp + $\lambda > 300$ nm cutoff filter	124
Formic acid	TiO ₂	Xe lamp 64 atm pressure	125
Formic acid	TiO ₂	990 W Xe lamp 89 atm pressure 308 K	126

Table 13. Continued

CH ₄ , CH ₃ OH	Ti- β Zeolite	100 W Hg lamp ($\lambda > 250$ nm) 323 K	127
Methane and methanol	TiO ₂ incorporated on MCM-41 and MCM-48	Hg lamp ($\lambda > 280$ nm) 328 K	128
Methanol, methane	Pt/TiO ₂ anchored on Y-zeolite	75 W Hg lamp ($\lambda > 280$ nm) 328 K	129
Methane	Degussa P25 TiO ₂	Xe lamp 28 atm pressure	130
CH ₄ and CH ₃ OH	TiO ₂ supported on ZSM-5 and Y-Zeolite	75 W Hg lamp (Filter to give light of $\lambda > 280$ nm) 273-323 K	131
CO	Ru(II)(bipy) ₃ Re(CO) ₃ (bipy)Cl	250 W Tungsten halogen lamp	132
Formate	ZnS	Hg lamp ($\lambda = 280$ nm)	133
Formate	[Re(bipy)(CO) ₃ (PPh ₃)] ⁺	500 W Hg lamp	134
CO	Rh dispersed over TiO ₂	500 W Hg lamp	135
Product	Catalyst	Irradiation source	Ref.
Formic acid and formaldehyde	Hydroxo-oxobis(8-quinolyloxo)vanadium(V)	100 Quartz-iodine lamp	136
Formic acid	Cobalt(II) phthalocyanine and Zinc (II) phthalocyanine adsorbed on Nafion membrane	500 W Tungsten Halogen lamp	137
Formate, formaldehyde and methanol	ZnS and CdS supported over SiO ₂	150 W Hg lamp	138
CO	ZrO ₂	500 W Hg lamp	139
Methanol, formaldehyde and formic acid	Pt loaded K ₂ Ti ₆ O ₁₃ combined with Cu/ZnO	Sunlight, Xe lamp and Hg lamp	140
Formic acid and formaldehyde	n-Bi ₂ S ₃ and n-CdS	100 W quartz-iodine lamp 350-1000 nm	141
Methane	Dititanodecatungstophosphate (K ₇ [PTi ₂ W ₁₀ O ₄₀]6H ₂ O)	500 W Hg lamp	142
Methanol	TiO ₂ and Cu dispersed over TiO ₂	254 nm	143
Methane, formaldehyde, formic acid, methanol and	Pt dispersed on K ₂ Ti ₆ O ₁₃ combined with Fe-Cu-K dispersed on Y-Zeolite	150 W Hg lamp	144

Table 13. Continued

ethanol			
Formate and CO	Cobalt and Iron phthalocyanin	300 W Xe lamp	145
Methanol and methane	TiO ₂ supported on Y-zeolite, MCM-41 and MCM-48	Hg lamp ($\lambda > 280$ nm) 328 K	146
Formic acid, formaldehyde, methanol, glyoxalic acid, acetaldehyde and acetic acid	CdS, ZnO, SiC, BaTiO ₃ and SrTiO ₃	Hg lamp	147
Formate and CO	ZnS	500 W Hg lamp ($\lambda > 290$ nm using filter)	148
CO	[6,61-Bi(5,7-dimethyl-1,4,8,11-tetraazacyclotetradecane)]dinickel(II) Triflate	460 W Hg lamp ($\lambda > 390$ nm using filter)	149
CH ₄ , CH ₃ OH and CO	TiO ₂ containing mesoporous silica	100 W Hg lamp 323 K	150
CO	Ru(bpy) ₂ (bpy-L ₁₀ M) ⁴⁺ (bpy = 2,2'-bipyridine, bpy-L ₁₀ = 1-(2,2'-bipyridin-6-ylmethyl)-1,4,8,11-tetraazacyclotetradecane, M = H ₂ , Ni)	Not mentioned	151

Table 14. Products formed by the photocatalytic reduction of CO₂ using metal dispersed TiO₂ (Ref. 116).

Catalyst	Amount of products formed (10 ⁻⁸ mol)				
	CH ₄	C ₂ H ₆	CH ₃ OH	HCOOH	CH ₃ COOH
TiO ₂	0.7	0.1	<1	<0.5	<1
Pd-TiO ₂	24.7	1.4	<1	<0.5	<1
Rh-TiO ₂	10	0.9	<1	<0.5	5.0
Pt-TiO ₂	5.0	<0.1	<1	<0.5	<1
Au-TiO ₂	3.3	0.6	<1	<0.5	<2.8
Cu-TiO ₂	1.9	0.2	<1	0.6	4.1
Ru-TiO ₂	0.6	<0.1	<1	<0.5	2.0

3.2.2. Photocatalytic reduction of carbonate

When CO₂ present in the atmosphere dissolves in water it is mostly present in the formation of carbonate. Therefore it is appropriate to study the photocatalytic reduction of carbonate to form various chemicals. The results involving the photocatalytic reduction of carbonate species to organic chemicals are given in Table 15.

Table 15. Products, catalyst and reaction conditions for photocatalytic reduction of carbonate.

Product(s)	Catalyst	Reaction conditions	Ref.
Methanol	MoS ₂ , ZnTe or CdSe, Degussa P25-TiO ₂	125 W Hg lamp	152
Methanol and methane	TiO ₂	15 W lamp ($\lambda = 365$ nm)	153
CH ₃ OH, HCHO, HCOO ⁻	Cr and Mg doped TiO ₂	125 W Hg lamp	154
HCOOH, HCHO, CH ₃ OH	SrFeO ₃	450 W Hg lamp or sunlight	155
Bicarbonate, acetate and propionate	MnS	450 W Hg lamp	156

3.2.3. Photocatalytic reduction of N₂ to NH₃

Reduction of dinitrogen to ammonia is of great industrial significance. This is because of the wide usage of ammonia in various industries. Ammonia is used in industries like fertilizer, fine chemical synthesis, nylon industries and in the production of nitric acid.

Photocatalytic synthesis of ammonia using sunlight as the source of energy and atmospheric nitrogen will be an environment friendly process. This process becomes even more important because of the high temperature and pressure conditions required in the only industrial ammonia production process – Haber’s process. The reaction requires conditions like 400 °C and 200 atmospheric pressure. The data pertaining to the photocatalytic reduction of N₂ to ammonia are given in Table 16.

Ranjit et al studied the photocatalytic reduction of N₂ to NH₃ using Ru, Rh, Pt and Pd dispersed over TiO₂. The activity with different metal dispersed on TiO₂ follows the order Ru > Rh > Pd > Pt. This is in correlation with the electron affinity values. Metals having higher electron affinity trap the electrons effectively reducing recombination. Also the metal-hydrogen bond strength follows the same order with Ru having the highest strength. A metal capable of holding hydrogen reduces hydrogen evolution so that the adsorbed hydrogen can react with nitrogen (163).

3.2.4. Photocatalytic reduction of other nitrogen containing compounds

In recent years, intensive agricultural activities, especially excessive use of man-made nitrogenous substances made the removal of nitrate ions from drinking water more attractive. High concentration of nitrate ions in drinking water is deleterious to human beings, because they can be converted into carcinogenic nitrosamine and other *N*-nitroso compounds during nitrate degradation process. These nitroso compounds lead to so-called “blue baby

Table 16. Catalysts and conditions for the reduction of dinitrogen to ammonia.

Catalyst	Reaction conditions	Ref.
TiO ₂ , SrTiO ₃ , CdS, GaP	100 W Hg lamp	157
[WH ₄ (dpmp) ₄] and [WH ₄ (trifos)(PPh ₃)] Where dpmp = Ph ₂ PCH ₃ , Trifos = Ph ₂ PCH ₂ CH ₂ P(Ph)CH ₂ CH ₂ PPh ₂	30 W Hg lamp	158
Mesoporous tantalum oxide(Ta ₂ O ₅) and Fe ³⁺ doped Ta ₂ O ₅	450 W lamp	159
Fe ₂ Ti ₂ O ₇	(λ > 320 nm) and (λ > 455 nm)	160, 161
Pt dispersed over CdS combined with [Ru(HEDTA)N ₂] ⁺ , [Ru(HEDTA)] ₂ N ₂ ²⁻	250 W Xe lamp (λ=505 nm)	162
Ru, Rh, Pd, Pt dispersed over TiO ₂	150 W Xe lamp	163
Pt and RuO ₂ dispersed over CdS in presence of various acetato complexes [Ru(EDTA)N ₂] ²⁻	250 W Xe lamp (λ = 505 nm using filter)	164
Fe, Ru and Os dispersed over TiO ₂	400 W Hg lamp	165
Fe(III) and Ti(IV) hydrous oxides	100 W Tungsten lamp (IR and UV light filtered off)	166
Ce and V dispersed TiO ₂	400 W Hg lamp	167
Ferric oxide intercalated on montmorillonite clay	125 W Hg lamp	168
Ru ^{II} (bipy) ₃ ²⁺ adsorbed on Pt/TiO ₂ /RuO ₂ surface in presence of Ru(II)- EDTA complex and ascorbic acid	250 W Xe lamp (λ = 510nm using filter)	169
Pt/CdS/RuO ₂ or Pt /CdS-Ag ₂ S/RuO ₂ in a solution of K[Ru(EDTA-H)Cl] ₂ H ₂ O	250 W Xe lamp (λ = 505 nm using filter)	170
Vanadium (III) substituted hydrous ferric oxide	400 W Hg lamp	171
Hydrous oxides of samarium(III) and europium(III)	400 W Hg lamp	172
Chromium oxide-TiO ₂	160 W lamp	173

Photocatalytic reduction of N₂ to ammonia was carried out with Pt and RuO₂ dispersed over CdS in the presence of various acetate complexes which are given below.

1. [Ru(EDTA)N₂]²⁻ (EDTA = ethylenediaminetetraacetato ion),
2. [Ru(HEDTA)N₂]⁺ (HEDTA= N-hydroxyethylethylenediamine-N,N',N'-triacetato ion),
3. [Ru(PDTA)N₂]²⁻ (PDTA = 1,3-propylenediaminetetraacetato ion),
4. [Ru(CDTA)N₂]²⁻ (CDTA = cyclohexanediaminetetraacetato ion),
5. [Ru(H₂DTPA)N₂]²⁻ (H₂DTPA = dianion dimethylenetriaminepentaacetic acid)
6. [Ru(HIMDA)N₂]⁺ (HIMDA, N-hydroxyethyliminodiacetato ion).

The catalytic activity for N₂ reduction with variation in the above complexes follows the order 1 > 2 > 3 > 4 > 5 > 6 (164).

syndrome - a condition in which blood's capacity for oxygen transport is reduced, resulting in bluish skin discoloration in infants” (174). 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 (175, 176). The relevant data are given in Table 17.

Table 17. Products, catalyst and conditions for the reduction of nitrate, nitrite to NH₃.

Reaction	Catalyst	Reaction conditions	Ref.
Nitrate to nitrite and ammonium ion	TiO ₂ , MgTiO ₃ -TiO ₂ Cu/TiO ₂ Cu/MgTiO ₃ -TiO ₂	125 W Hg lamp	174
Nitrate to nitrite	Molybdenum-Flavin system	250 W Tungsten lamp	177
Nitrate to NH ₃	TiO ₂	150 W Hg lamp	178
Nitrate to nitrite, N ₂ and NH ₃	Co, Ag, Pt, Cu, Ni dispersed over KTaO ₃ , K ₃ Ta ₃ Si ₂ O ₁₃ , BaTa ₂ O ₆ , NaTaO ₃	450 W Hg lamp	179
Nitrite and nitrate to ammonia	Fe ³⁺ , Co ³⁺ , Co ²⁺ , Mg ²⁺ doped TiO ₂	450 W Xe lamp	180
Nitrite and nitrate to ammonia	TiO ₂	450 W Xe lamp	181
Nitrite and nitrate to ammonia	Ru, Rh, Pt, Pd dispersed over TiO ₂	450 W Xe lamp	182
Reaction	Catalyst	Reaction conditions	Ref.
Nitrite and nitrate to NH ₃	Ru dispersed over TiO ₂	450 W Xe lamp	183
Nitrite and nitrate to NH ₃	ZnS	450 W Xe lamp	184
Nitrite to NH ₃	CdS	450 W Xe lamp	185
Nitrite to NH ₃	TiO ₂ (Degussa-P25), TiO ₂ /Pt, H ₄ Nb ₆ O ₁₇ , H ₄ Nb ₆ O ₁₇ /Pt, TiO ₂ pillared H ₄ Nb ₆ O ₁₇ , H ₄ Nb ₆ O ₁₇ /(Pt, TiO ₂)	100 W Hg lamp (λ > 290 nm)	186
Nitrate to NH ₃	CdS	150 W Hg/Xe lamp	187
NO ₂ to nitrous acid	TiO ₂ aerosol	4 fluorescent lamp (maximum intensity at λ = 365 nm)	188
Nitrate to nitrite, N ₂ and NH ₃	CdS pillared in between layered H ₂ Ti ₄ O ₉ and layered H ₄ Nb ₆ O ₁₇	100 W Hg lamp	189
Nitrate to nitrite and NH ₃	Ni-Cu/TiO ₂	125 W Hg lamp	190

3.2.5. Photocatalytic hydrogenation

Hydrogenation of olefins is an important reaction and has applications in Fischer-Tropsch process, preparation of edible oils and in organic synthesis. The results reported in literature are given in Table 18.

Table 18. Products, catalysts and conditions for the reduction of various hydrocarbons.

Reaction	Catalyst	Reaction conditions	Ref.
Hydrogenation of 1-pentene	Fe(CO) ₅	Laser irradiation 351 nm – XeF 308 nm – XeCl 337 nm – N ₂	191
Hydrogenation of ethylene	H ₄ Ru ₄ (CO) ₁₂	450 W Hg lamp ($\lambda > 310$ nm or $\lambda = 366 \pm 20$ nm using filters)	192, 193
Hydrogenation of norbornadiene	Chromium hexacarbonyl	1-80 atmosphere pressure	194
Hydrogenation of 1-octene	cis-HMn(CO) ₄ PPh ₃	100 W Hg lamp	195
Hydrogenation of olefins	(η^5 -C ₅ H ₅) ₂ TiR ₂ (R = CH ₃ ; CH ₂ C ₆ H ₅ ; C ₆ H ₅)	150 W lamp	196
Reaction	Catalyst	Reaction conditions	Ref.
Hydrogenation of alkenes	H ₄ Ru ₄ (CO) ₁₂ and H ₄ Ru ₄ (CO) ₁₃	$\lambda = 355$ nm	197
Hydrogenation of olefins	RhH(CO)(PPh ₃) ₃ , RhCl(PPh ₃) ₃ and IrCl(CO)(PPh ₃) ₃	XeCl excimer laser	198
Hydrogenation of diphenylacetylene	Pt, Rh, Ni, Pd dispersed over TiO ₂	125 W Hg lamp	199
Hydrogenation of 1,5-cyclooctadiene	Rh ₄ (CO) ₁₂	500 W Hg lamp	200

3.2.6. Reduction of organic nitro compounds to amines

The reduction of various nitro compounds to the corresponding amines plays an important role in synthetic chemistry of various drugs, dyes and polymers. Anilines are very 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 (201). (refer Table 19).

3.2.7. Other reduction reactions

There are various other reduction reactions which have been carried out by photocatalytic means. A summary is given in Table 20.

Table 19. Reactions, catalysts and conditions in the reduction of nitro aromatics.

Reaction studied	Catalyst used	Reaction conditions	Ref
Nitrobenzene to aniline	Ag deposited on TiO ₂	400 W Hg lamp ($\lambda > 300$ nm)	201
Reduction of nitrosobenzene, nitrobenzene, 2-nitrosotoluene, 2,3,5,6-tetramethylnitrosobenzene, 3,5-di-bromo-4-nitrosobenzenesulfonate (sodium salt), 2,4,6-tri- <i>t</i> -butylnitrosobenzene, and 2-methyl-2-nitrosopropane	TiO ₂	Metal halide lamp	202
Reduction of nitro organics like 2-Nitropropane, 2-methyl-2-nitropropane, nitrobenzene, 4-nitrotoluene, 3-nitrotoluene, 4-nitrobenzotrile, 3-nitrobenzotrile to corresponding amines	Degussa P25 TiO ₂	150 W Xe lamp	203, 204
p-chloronitrobenzene to p-chloroaniline	TiO ₂	100 W Hg lamp	205
Reduction of nitrobenzene to C ₆ H ₅ N(O)=NC ₆ H ₅ (32 %), C ₆ H ₅ N=NC ₆ H ₅ (21 %), C ₆ H ₅ NH ₂ (15 %), C ₆ H ₅ N(H)C ₆ H ₉ (32 %)	TiO ₂ , WO ₃ , CdS	Xe/Hg lamp ($\lambda > 350$ nm using filter)	206
4-nitrophenol to 4-aminophenol	TiO ₂	500 W Hg lamp ($\lambda > 350$ nm)	207

Table 20. Various photocatalytic reduction reactions, catalysts and reaction conditions.

Reaction studied	Catalyst used	Reaction conditions	Ref.
Bis(2-dipyridyl)disulfide to 2-mercaptopyridine	Ag dispersed over TiO ₂	400 W Hg lamp ($\lambda > 300$ nm)	208
Reduction of methyl viologen (A redox reagent used in organic synthesis)	H ⁺ /K ₄ Nb ₆ O ₁₇ and CdS/K ₄ Nb ₆ O ₁₇ K ₄ Nb ₆ O ₁₇ is a layered compound	500 W Xe lamp ($\lambda > 420$ nm using filter)	209
Methyl viologen reduction	Ruthenium (II) Poly (Pyridyl) Complexes	300 W Xe lamp	210
Reduction of acetophenone	meso-Tetraphenyl porphyrinatocobalt(II)	180 W halogen lamp ($\lambda > 430$ nm using cutoff filter)	211
Aryl azide monolayers to aryl amine monolayers	CdS quantum dots	400 W lamp with various cutoff filters	212
bis(2-dipyridyl)disulfide to 2-mercaptopyridine	Au and Ag dispersed over TiO ₂	$\lambda > 300$ nm	213, 214
Reduction of racemic-[Co(acac) ₃] (Hacac = pentane-2,4-dione)	Helical ruthenium(II) complexes	500 W Xe lamp ($\lambda > 400$ nm) 298 K	215

3.3. Production of hydrogen peroxide

Hydrogen peroxide (H_2O_2) plays an important role as oxidizing agent in a variety of pollution control systems (216, 217). It is also used in organic synthesis as Fenton's reagent. It is used as a disinfectant, as propellant and also for production of various peroxides and production of oxyacids. The results reported in literature are given in Table 21.

Table 21. Catalysts and conditions in the photocatalytic production of H_2O_2 .

Reaction	Catalyst used	Conditions	Ref.
O_2 to H_2O_2	tris(2,2'-bipyridine) ruthenium(II) complex	500 W Xe lamp ($\lambda > 420$ nm using cutoff filter)	216
Water to H_2O_2	TiO_2	Liquid phase Room temperature $\lambda > 400$ nm	218
O_2 to H_2O_2	Ruthenium(II) complex $[\text{Ru}(\text{bpy})_3]^{2+}$ incorporated into Nafion and cellulose	500 W Tungsten-Halogen lamp	219
O_2 to H_2O_2	Metal porphyrins and Fe(II), Co(II) and Zn(II)-phthalocyanins adsorbed on Nafion	500 W Tungsten-Halogen lamp	220
O_2 to H_2O_2	TiO_2 -Fluoride system	40 W lamp	221

3.4. Photocatalytic isomerization

There are wide varieties of isomerization reactions (refer Table 22) which can be carried out by photocatalytic means.

3.5. Photocatalytic polymerization

Polymerization is a very important industrial process and the dependence of today's world on polymers is extremely high. Various polymerization reactions have been carried out by photocatalytic means using both homogeneous and heterogeneous catalysts. Photocatalysts have been mostly able to initiate free radical polymerization by using the excited electrons. (refer Table 23).

3.6. Other photocatalytic reactions involving larger molecules

In addition to various reactions classified earlier there are other reactions like condensation, bond cleavage, etc., which can be carried out by photocatalytic means. Details on some of the reactions are given in Table 24.

Table 22. Various isomerization reactions, catalysts and reaction conditions.

Reaction	Catalyst	Reaction condition	Ref.
Cis-trans isomerization of 1-(3,5-di- <i>tert</i> butylstyryl)pyrene	anthracene, 9-methylanthracene and 9,10-dichloroanthracene	150 W Xe lamp	222
Cis-trans isomerization of Z-8-(3,5-ditert-butylstyryl)fluoranthene Z,E-1,6-bisstyryl- 1,3,5-cycloheptatriene	1. Acridine as catalyst and camphorquinone as sensitizer 2. C ₆₀ as catalyst	150 W Xe lamp	223
Norbornadiene to quadricyclene isomerization	[Cu ₂ L ₂ (μ -NBD)], [Cu ₂ L' ₂ (μ -NBD)], [Cu ₂ L'' ₂ (μ -NBD)], [Cu ₂ L''' ₂ (μ -NBD)], [where L = 2-methyl-8-oxoquinolinato, L' = 2-methyl-5,7-dichloro-8-oxoquinolinato, L'' = 4-oxoacridinato, L''' = 2-(2-oxo-3,5-di- <i>tert</i> -butyl phenyl)benzotriazole]	500 W Hg lamp	224
Reaction	Catalyst	Reaction condition	Ref.
Cis-trans isomerization of stilbene	Diphenyldiselenide	Hg lamp ($\lambda = 436$ nm)	225
1-pentene to 2-pentene	Fe(CO) ₅	Laser irradiation 351 nm – XeF 308 nm – XeCl 337 nm – N ₂	226
Maleic acid – Fumaric acid isomerization	TiO ₂	4 W fluorescent lamp	227
1. 4,4-dimethyl-1-pentene to 4,4-dimethyl-2-pentene 2. 1-octene to 2-octene	Platinum(II) bis(acetylacetonato) in presence of silanes	Sixteen 8 W lamps	228
Isomerization of cyclohexene and methyl cyclohexene	Copper(I) trifluoromethane sulphonate	$\lambda = 254$ nm	229
1-pentene to 2-pentene	Ru ₃ (CO) ₁₂	310 or 350 nm	230
Cis-2-butene to trans-2-butene	TS-1 Zeolite	75 W Hg lamp ($\lambda > 280$ nm) 275 K	231
Cis-trans isomerization of β -carotene and canthaxanthin	CdS or ZnO	250 W Xe lamp ($\lambda > 350$ nm using filter)	232
Isomerization of cis-2-butene	Zr-Si binary oxides	Hg lamp ($\lambda > 250$ nm) 295 K	233

Table 23. Photocatalytic polymerization reactions, catalysts and reaction conditions.

Reaction	Catalyst	Reaction conditions	Ref.
Acrylate polymerization	Fe doped TiO ₂	100 W Hg lamp	234
Polymerization of methylmethacrylate	Chromium thiophene carboxylate	125 W Hg lamp ($\lambda = 440$ nm) 303 K	235
Polymerization of N-phenyl-p-phenylenediamine	Tris(2,2'-bipyridyl)ruthenium complex	500 W Xe lamp	236, 237
Reaction	Catalyst	Reaction conditions	Ref.
Polymerization of phenylacetylene	W(CO) ₆ and W(CO) ₆ -TiCl ₄	Nd ³⁺ :YAG pulsed laser (Quanta-Ray) operating at 532, 355 and 266 nm	238
Polymerization of phenylacetylene	W(CO) ₆ -CH ₃ I system	Nd ³⁺ :YAG pulsed laser (Quanta-Ray) operating at 532, 355 and 266 nm	239
Ring-Opening Polymerization of 1,1,3,3-Tetramethyl-1,3-disilacyclobutane	Pt(acac) ₂	Sixteen 8 W lamps	240
Polymerization of methylmethacrylate	Eosin(dye) sensitized CdS	308-313 K	241, 242

Table 24. Various photocatalytic reactions, catalysts and reaction conditions.

Reaction	Catalyst	Reaction conditions	Ref.
Dihydropyrazine from ethylenediamine and propylene glycol	TiO ₂ -P 25 and ZnO supported on H-ZSM5, HY, H β and HM zeolites	250 W Hg lamp	243
Synthesis of piperazine from N-(2,3-dihydroxypropyl) ethylenediamine	TiO ₂ , ZnO and CdS supported on H-ZSM5, HY, H β zeolites	250 W Hg lamp	244
Tertiary alkyl amines from NH ₃ and alcohol	Pt dispersed over TiO ₂	$\lambda > 300$ nm	245
Azobenzene to indazole, 1,2,4-triphenyl-1,2,4-triazolidines	Pt dispersed TiO ₂	500 W Hg lamp	246
Synthesis of urea from CO ₂ and NO ₃ ⁻	TiO ₂ and Cu modified TiO ₂	120 W Hg lamp ($\lambda > 300$ nm using filter)	247
N \equiv N bond cleavage of azobenzene	Pt dispersed TiO ₂	400 W Hg lamp ($\lambda > 300$ nm using filter)	248

Table 24. Continued

Reaction	Catalyst	Reaction conditions	Ref.
Conversion of NAD ⁺ to NADH and dehydrogenation of cinnamyl alcohol	TiO ₂	Fluorescent lamp 298K	249
Conversion of NAD ⁺ to NADH	CdS and TiO ₂	150W Xe lamp (λ > 400nm)	250
(i) Various organic acids + NH ₃ to give various amino acids (ii) Photo-Knoop reaction	Ru(bpy) ₃ ²⁺ , Zinc tetraphenyl porphyrin, dyes and CdS	500W Xe lamp	251
Photocatalytic processing of soyabean oil	Molecular iodine	100 W lamp	252
[4 + 4] photocycloreversion to give anthracene and [2 + 2] photocycloaddition	CdS	λ > 450 nm	253
(i) Cleavage of anthracene dimer (ii) Cis-trans isomerization of stilbene (iii) hexamethyl(dewar)benzene to hexamethylbenzene	CdS	840 W Xe lamp	254
Synthesis of L-pipecolic acid from L-lysine	Pt dispersed over TiO ₂	Hg lamp	255
	Pt, Rh and Pd dispersed over TiO ₂	400 W Hg lamp	256
Reduction of nicotinamide coenzymes (NMN ⁺ , NAD ⁺ , NADP ⁺) to NMNH, NADH and NADPH	TiO ₂	125 W Hg lamp (λ = 365 nm)	257
Addition of pyrrolidenes to butenolides to form pyrrolidizine alkaloid	Benzophenone	120W Hg lamp (λ = 350 nm)	258

4. Summary

In summary, it may be stated that

The potential of photocatalytic routes for the production of chemicals has yet to be fully realized though the feasibility has been established. This transformation of these processes from laboratory carryout to industrial production though may not have reached the required maturity; it is only matter of time, when this can occur. When it takes place, the production of chemicals can become a neater process with acceptance from environmental concerns.

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