

Module 4

CO_x (Oxides of Carbon): CO₂, CO

Carbon Monoxide:

- The most Toxic Pollutant.
- Its colorless and odorless gas.
- It is lighter than the air.

Sources Of CO: Partial combustion of fossil fuel in vehicles engine is the main source of CO, B/c of uneven combustion due to uneven distribution of fuel in combustion chamber.

Effects Of CO:

CO reduces the blood ability to carry oxygen to body tissue including vital organs such as the heart, and brain.

It is most harmful to those who suffer from heart and respiratory disease.respiratory disease.

Headache, fatigue, nausea, and dizziness, convulsions

SO_x:(Oxides of Sulphur): SO₂,

Sulphur dioxide: A Major Component in the Env.

Natural sources:

- Volcanic Eruption: produced about 67% to the Env.
- Forest Fires: produced about 1%.

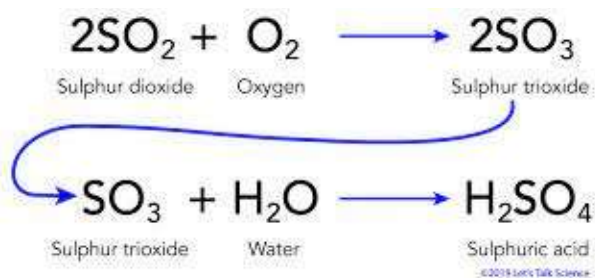
Artificial Sources: They can produce 33% SO₂

- Combustion of fossil fuel especially coal containing sulphur.
- Petroleum Refinery.
- Metallurgical Operations of Fe, Cu, Extraction.
- Cement preparations or Manufacturing.
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- Waste Water Treatment.

- In paper manufacturing.
- In food Packaging, preservations, Disinfectants, and in Bleaching.
- Lead chamber and contact process.

Effects of SO₂:

- 1) Acid Rain : Sulphuric acid is produced from the reaction of sulphur dioxide with ozone, the resulting sulphite ions then react with water vapor in the atmosphere to produce sulphuric acid vapour in the atmosphere to produce sulphuric acid.



- 2) The acid rain formed due to SO₂ can destroy plants, damage buildings, paints, change water and soil pH by making them acidic (Which is unfit for drinking and other purposes).
- 3) Industrial or sulfurous Smog:- Sulfurous type smog are formed by sulfurous & sulphuric by the combustion of fossil fuel containing large amount of sulphur. They are formed when there is a humidity, stagnant air and cold weather condition.
- 4) The smog formed can reduce visibility on road that increases accident chances. Cause irritation of eye. Lung infections.

NO_x(Oxides of Nitrogen):- There are about eight different type of oxides of nitrogen but three out of them act as pollutants which are the following;

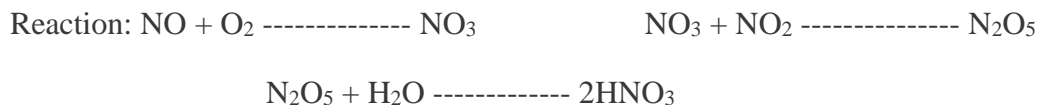
Nitric Oxide (NO): - (0.1 – 2 PPM) Nitric oxide is produced through the combination of oxygen and nitrogen in the air at very high temperatures. This can occur naturally as the result of lightning strikes but is more common in the hot cylinders of engines as they burn fuel and produced NO. Reaction: $\text{N}_2 + \text{O}_2 \longrightarrow 2\text{NO}$

Nitrogen Dioxide (NO₂): - (10.4 – 15 ppm) Nitrogen dioxide is produced through the further reaction of nitrogen oxide with oxygen in the air. This reaction is relatively fast and is increased further by the presence of heat and sunlight.

Reaction: $2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2$

Nitrous Oxide (N₂O):- (0.5 ppm) Their contribution to the environmental pollutions is very small because of lower formation of Nitrose oxide in the environment.

Effect's Of NO_x:- The NO_x can produce a secondary pollutant in the env. Known as nitric acid. They are formed when oxide of nitrogen in the atmosphere react with water vapors. 1) Acid Rain Formation Occur: (HNO₃) atmosphere react with water vapors.



Brief discussion on 12 principles of green chemistry.

The twelve principles of green chemistry that have been formulated are listed below:

1. Pollution Prevention

It is better to prevent waste than to treat or clean up waste after it is formed

2. Atom Economy

Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.

3. Less Hazardous Chemical Synthesis

Whenever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

4. Designing Safer Chemicals

Chemical products should be designed to preserve efficacy of the function while reducing toxicity.

5. Safer Solvents and Auxiliaries

The use of auxiliary substances (solvents, separation agents, etc.) should be made unnecessary whenever possible and, when used, innocuous(harmless)

6. Design for Energy Efficiency

Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.

7. Use of Renewable Feedstocks

A raw material or feedstock should be renewable rather than depleting whenever technically and economically practical.

8. Reduce Derivatives

Unnecessary derivatization (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be avoided whenever possible.

9. Catalysis

Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

10. Design for Degradation

Chemical products should be designed so that at the end of their function they do not persist in the environment and instead break down into innocuous degradation products.

11. Real-time Analysis for Pollution Prevention

Analytical methodologies need to be further developed to allow for real time in-process monitoring and control prior to the formation of hazardous substances.

12. Inherently Safer Chemistry for Accident Prevention

Substance and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires.

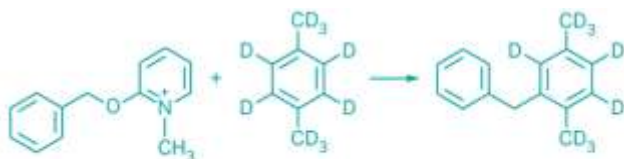
Microwave Synthesis

Components: **1. High Voltage Transformer:** The 240V supply is jumped to a few thousand volts, which is then fed to the cavity magnetron. **2. Cavity Magnetron:** A cavity magnetron is a high-powered vacuum tube that transforms the electrical energy into long-range microwave radiations (frequencies between 300MHz and 300 GHz). **3. Waveguide:** A waveguide is a hollow metallic tube that guides the waves generated at the magnetron's output toward the target material.

Heating Mechanism: Reacting materials under microwave irradiation are heated by two mechanisms, such as **dipolar interaction**, **ionic conduction** and **interfacial polarization**. As the orientation of the electric field (of electromagnetic radiation) changes over time, the polar molecules (or ions) attempt to follow the field by changing their orientation inside the material to line up along the field lines in an energetically favorable configuration (namely, with the positive side pointing in the same direction as the field lines). As these molecules change direction rapidly (millions of times per second at least), they gain energy, which increases the temperature of the material. This process is called dielectric heating.

Nature of the material decides its interaction with microwave. For example, Sulfur – transparent, Copper – reflect, Water – absorb microwaves.

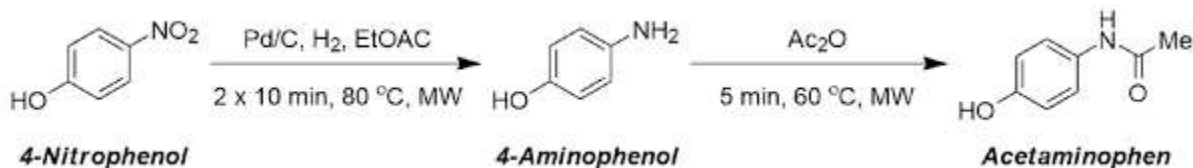
Example:



Oil bath: 10 minutes, 100 °C, 12% conversion
Microwave: 10 minutes, <100 °C, 86% conversion



Heat block: 40 hours, 15.0 °C, 86% yield, 91% ee
Microwave: 4 hours, 15.4 °C, 84% yield, 92% ee



Bio catalyzed reactions

Biocatalysis refers to the use of living (biological) systems or their parts to speed up (catalyze) chemical reactions.

Biocatalysts are derived from plants, microorganisms (yeast, bacteria, fungi) or animal tissue (Ex. Protease from pancreas).

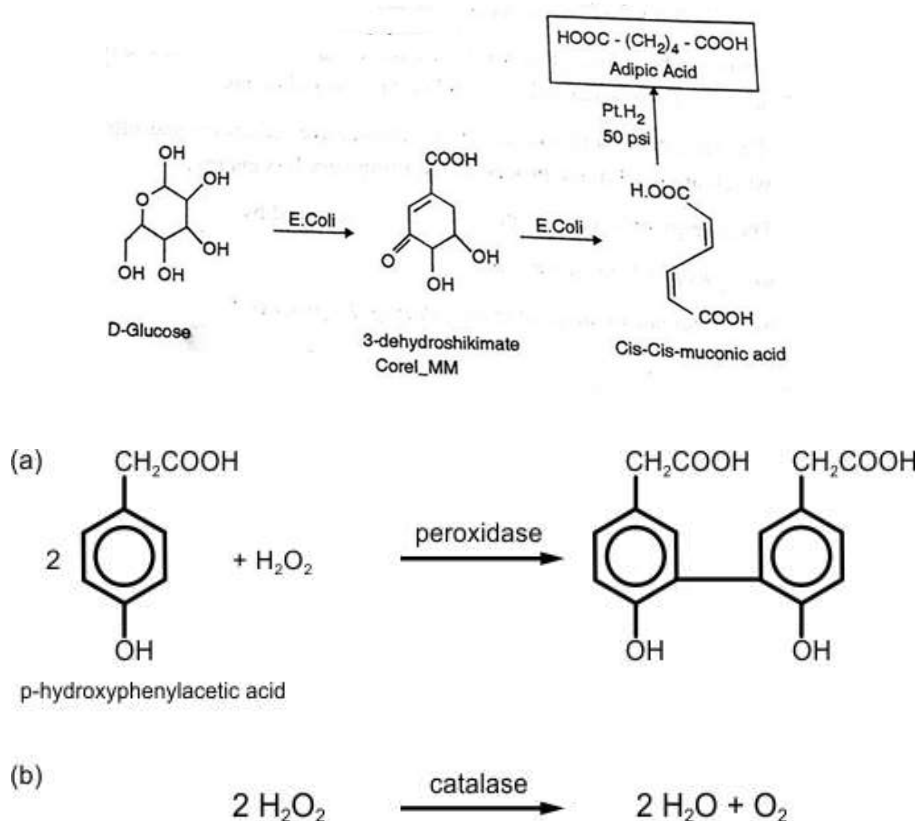
Enzymes are one of the well-known and largely used biocatalysts. Enzymes are bulky molecules (mostly proteins) which has got three-dimensional structure. Active site of the enzyme reacts with the substrate (reactant) through a mechanism similar to lock and key model.

Microbial strains are used to produce the desired enzyme in large quantities for commercial (industrial) applications following the FDA regulations.

Catalytic activity of the enzymes is affected by enzyme concentration, temperature, pH, inhibitors, substrate concentration etc.

Enzymes provide more powerful way of producing enantiomerical pure compounds through chemoselectivity, regioselectivity and stereoselectivity.

Examples



Solvent Free Reactions

Solvent less reaction is chemical reaction system in the absence of a solvent.

Advantages

Economic: Expensive solvent usage can be avoided. That in turn save money on solvent.

Simple: Laborious extraction steps, separation of product from the mother liquor, evaporation of solvent can be avoided.

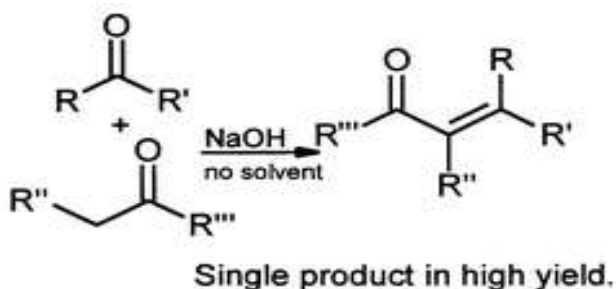
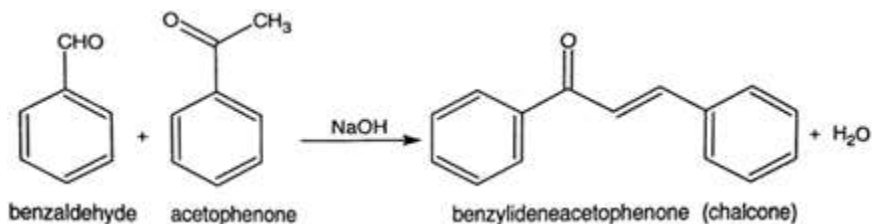
Environmental benign and safe: Eliminates the usage of carcinogenic, toxic, neurotoxin, flammable solvents.

Efficient: Rate of the solvent free reactions is usually high due more availability of reactants. Also, selectivity is better compared to conventional approach.

Conditions

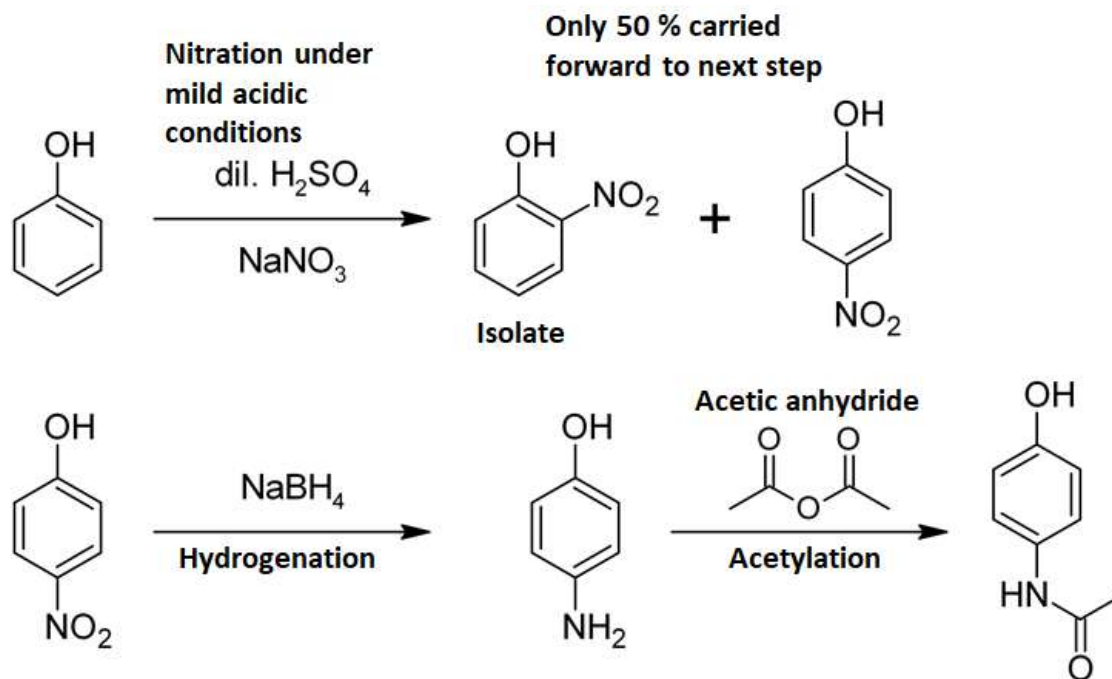
1. No reaction media to separate, purify, dispose, recycle
2. No need of specialized equipment for a laboratory scale preparation.
3. Chromatography can be avoided due to formation of sufficiently pure compounds.
4. Reactions can be performed by milling, grinding, microwave irradiation, UV light irradiation, heating etc.

Examples

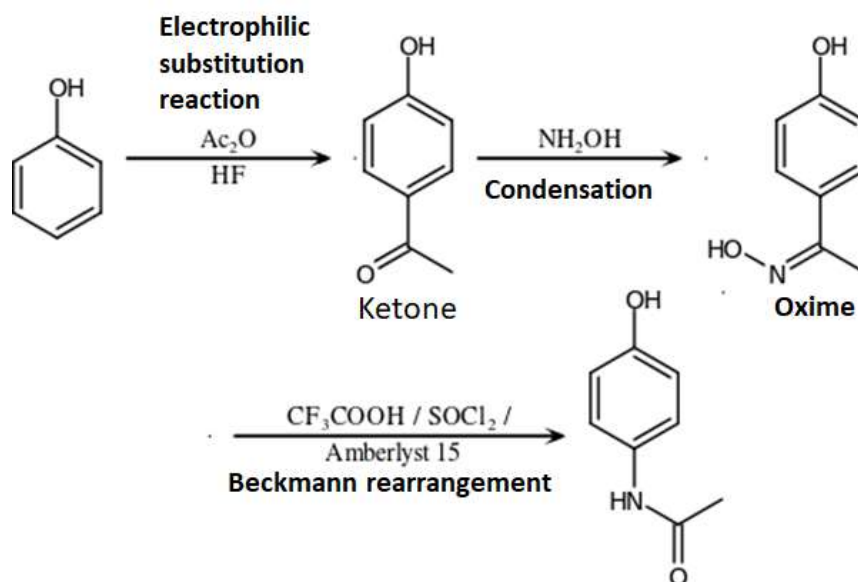


Synthesis of paracetamol by conventional and green chemistry approach

Conventional method

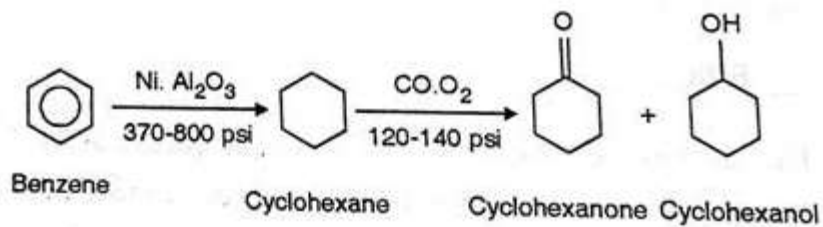


Green chemistry method



Synthesis of Adipic acid by conventional and green chemistry approach

(A) Traditional pathway : Using Benzene (Carcinogenic solvent)



(B) Greener pathway : Using glucose (absolutely safe)

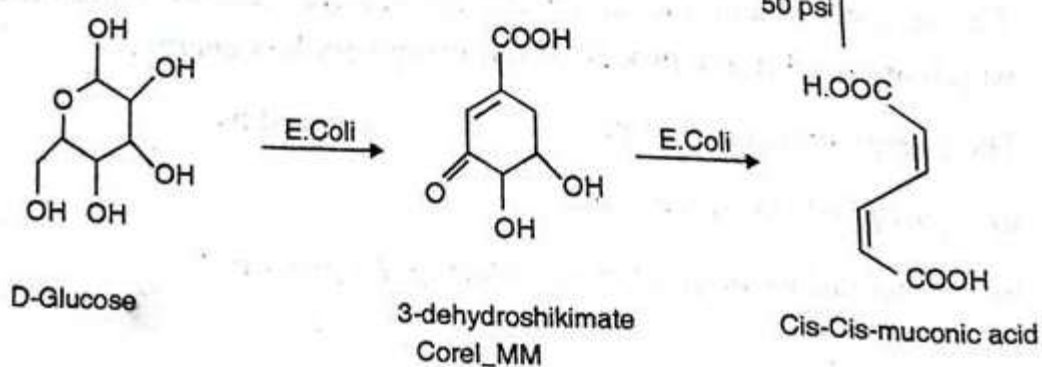


Photo electrocatalytic hydrogen production

Semiconductor (photoactive) material is used to construct the electrode (photo electrode). This photo electrode is combined with the Pt electrode to construct the photo electrocatalytic cell.

Charge carrier (electron and hole) – generation, separation, transportation are the three important steps decides the efficiency of the cell to produce hydrogen.

Light is illuminated on the photo electrode. Electrons present in the valence band (VB) of the semiconductor absorb the light energy and excite to the conduction band (CB). Immediately those electrons are separated to move on to the collector.

Electrons are collected and travel through the external circuit to the counter electrode to drive the hydrogen evolution half reaction (HER): $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$

Holes diffuse to the semiconductor surface and drive the oxygen evolution half reaction (OER):

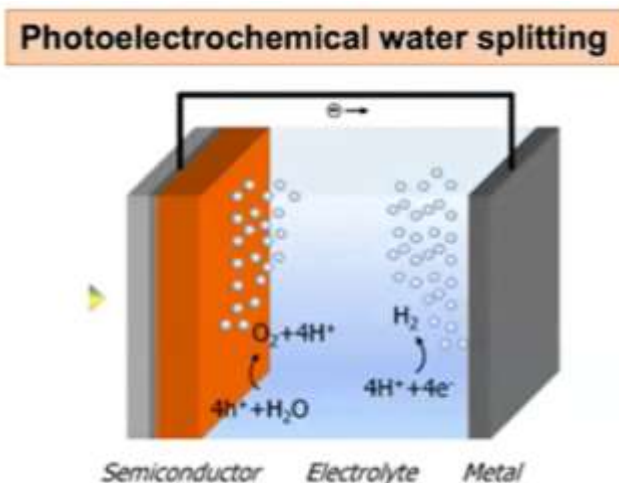
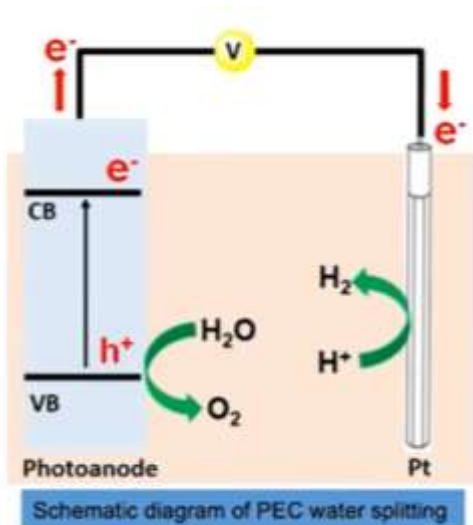
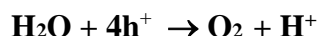


Photo catalytic hydrogen production

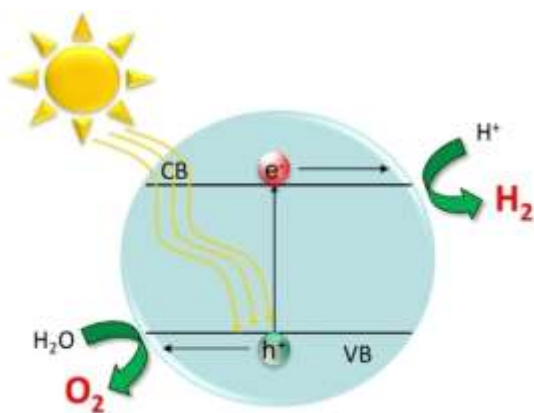
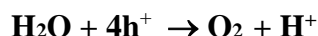
Semiconductor (photoactive) material is used in the form of powder or film (coating). And it is dispersed or submerged in the reaction medium.

Charge carrier (electron and hole) – generation, separation are the two important steps decides the efficiency of material to produce hydrogen.

Light is illuminated on the photo active semiconducting material. Electrons present in the valence band (VB) of the semiconductor absorb the light energy and excite to the conduction band (CB). Immediately those electrons are separated to move on to the surface of the material.

Electrons reach out the surface to react with protons adsorbed onto the surface to drive the hydrogen evolution reaction (HER): $2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_2$

Holes diffuse to the semiconductor surface and drive the oxygen evolution reaction (OER):

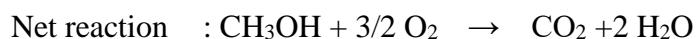
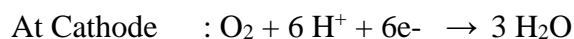


Schematic of the photocatalytic hydrogen evolution

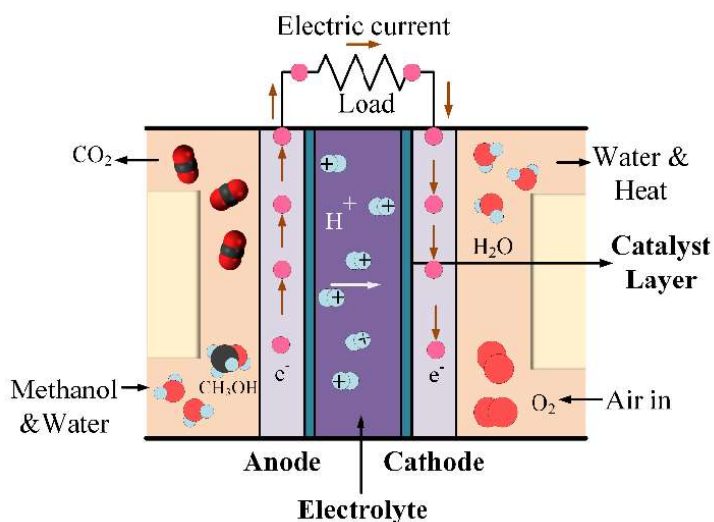
Methanol – oxygen fuel cell

It consists of two electrodes made up of platinum. In between the electrodes H_2SO_4 is placed as an electrolyte. Methanol is supplied at the anode and pure oxygen gas is supplied at the cathode. The Methanol is oxidized to CO_2 & H_2O with the Liberation of electrical energy. And the oxygen is reduced at the cathode to produce water.

The cell reactions are as follows,



The cell delivers an emf of 1.20 V.



Schematic of the methanol oxygen fuel cell

Photovoltaic cell

Photovoltaic cell is semiconductor device that convert sunlight into direct current electricity. Photovoltaic cell is based on photoelectric effect

Construction

Polycrystalline silicon wafers are made by block-cast silicon ingots into very thin wafers/slices (250-350 μm) as shown in the Figure. The wafers etched slightly to remove saw damage. Wafer is lightly p- doped to make a solar cell form wafer, surface diffusion of n-type dopant is done on the front side, this forms a p-n-junction few hundred nanometers below the surface (10^{-9}m).

Antireflecting coating of silicon nitride/ TiO_2 is then applied in a layer using plasma enhanced chemical vapour deposition (PEVCD) technique. The wafer is then metallized. The metal grid contact made by using silver past. The rear contact is made by screen printing using aluminum paste. Metal rods are then given to make ohmic contact with the silicon.

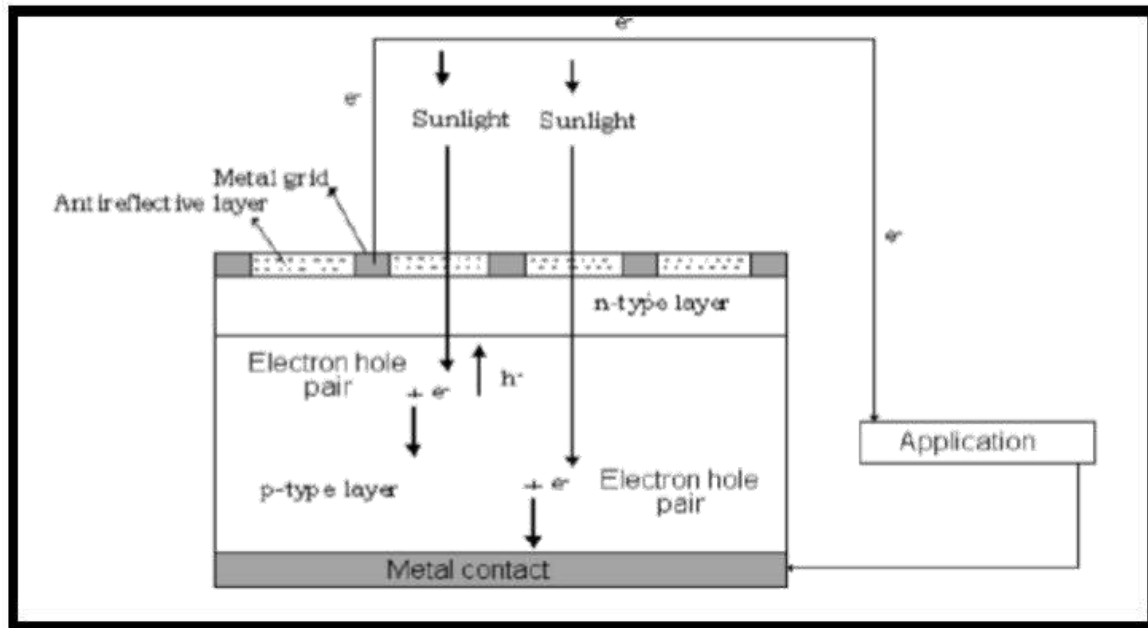
Working

Photovoltaic cells or Solar cells are the semiconductor devices which converts sunlight into direct current electricity. Sunlight consists of Electromagnetic radiation of particles called Photons ($h\nu$). The photons carry a certain amount of energy given by the Planck quantum equation,

$$E = hc / \lambda$$

Where h is Planck's constant, c is the velocity of light and λ is the wavelength of the radiation.

When light radiation falls on the p-n-junction diode, electron-hole pairs are generated by the absorption of radiation. The electron is drifted and collected at n-type end and holes are drifted and collected at the p-type end. When these two ends are electrically connected through a conductor, there is a flow of current between the two ends the external circuit. Thus, photoelectric current is produced and available for the use.



Schematic of the photovoltaic cell