

How Advances in Catalysis Enable Green Chemistry?

B. Viswanathan

Abstract

In manufacturing Chemical Industry, **Green Chemistry** is the buzz word. In this presentation how the practice of catalysis enables all the arms of Green Chemistry, namely the E-factor, atom economy, Yield and Waste reduction, is illustrated. A brief consideration is given to the new concept of Photon Assisted Catalysis in the context of Green Chemistry..

1 Introduction

Catalysis and green chemistry are twin born subjects, though the realization might have taken some time period. Ever since the science of catalysis starting from the defining the term catalysis by Berzelius in 1835, the developers of the science of catalysis have been striving to make every process developed to be a so called Green Process. It is known that no subject so pervades modern chemistry as that of Catalysis. So catalysis has to be considered as the fundamental pillars of green chemistry, the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances. The design and application of new catalysts and catalytic systems are simultaneously achieving the dual goals of environmental protection and economic benefit. This aspect (Environmental Effect) is nowadays measured in terms of a parameter called **E – factor**(Environmental factor) and defined as the kg of waste product to kg of desired product. Let us look at the E factor data of four principal sectors of chemical production. The data given in Table 1. are only a measure of approximate Annual production of the product worldwide or at a single site.

Table 1. Approximate values of annual production and the E-factor as Industry sector-wise. The figures given in column 2 are only relative or indicative values not absolute (magnitude) values.

Industry segment	Volume Tons per annum	E-factor
Oil Refining	$10^6 - 10^8$	< 0.5
Bulk Chemicals	$10^4 - 10^6$	$< 1-5$
Fine Chemicals	$10^2 - 10^4$	$5 - > 50$
Pharmaceuticals	$10 = 10^3$	$25 - > 100$

Another parameter in the context of green chemistry is Atom efficiency which is defined the relative number of atoms in the reactant and product.

The catalytic reactions are efficient and green can be understood with an example shown in Fig.1.

Classical reaction shown on top gives 85-95 % yield, and 4kg of aqueous effluent per kg of product and involves 12 unit operations while the zeolite catalyzed reaction shown below yields greater than 95% with 0.035 kg aqueous effluent per Kg of product and involves only 3 unit operations.

Many of the organic reactions carried out stoichiometrically in various solvents are based on techniques that often involve high costs, inefficiencies, and harmful environmental impacts, thus necessitating developing green procedures. Catalysis is considered to be a unique and fundamental pillar of green chemistry, and one of the tools in organic synthesis and transformations for the development of a wide range of fine chemicals and functional materials. The unique feature of green catalytic processes are enhanced selectivity thereby reducing unwanted side products and this approach has been contributing to both fundamental and applied aspects of catalytic transformations. The purpose of this presentation is to demonstrate with a selected few examples how the change over to catalytic transformations and synthesis methodology has contributed to the economy of the process and also reduced the environmental effects.

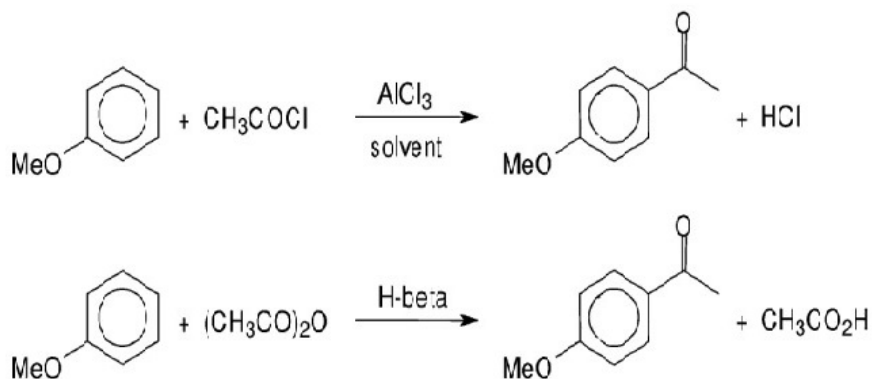


Figure 1: Examples of Catalyzed and classical Friedel Crafts reaction

2 Acid-Base Catalysis

The concept of acid-base catalysis is an old concept. Conventionally, mineral acids (HF, H₂SO₄) which can be corrosive and also promote many side and further reactions. Secondly the acidity concept has limited validity depending on the value of ionization constant. But the concept of solid acids brought many changes in these parameters thus facilitating many of the synthetic organic reactions like electrophilic substitutions(eg.Nitration) Friedel Crafts alkylation and acylation and a number of rearrangement reactions like Beckmann and Fries rearrangements. There are numerous examples of solid acid catalyzed reactions improved the process technology from various points of view (yield, selectivity, atom economy, E-factor and others) and let us consider one typical example to substantiate this statement. The conventional process for the production of caprolactum involves the reaction of cyclohexanone with hydroxylamine sulphate yielding cyclohexanone oxime which is then subjected to Beckmann rearrangement with stoichiometric amount of sulphuric acid. This process produces 4 kg ammonium sulphate per kg of the desired product. The manufacturer, Sumitomo now employs a vapour phase Beckmann rearrangement using high silica MFI zeolite. The two processes are shown pictorially in Fig.2.

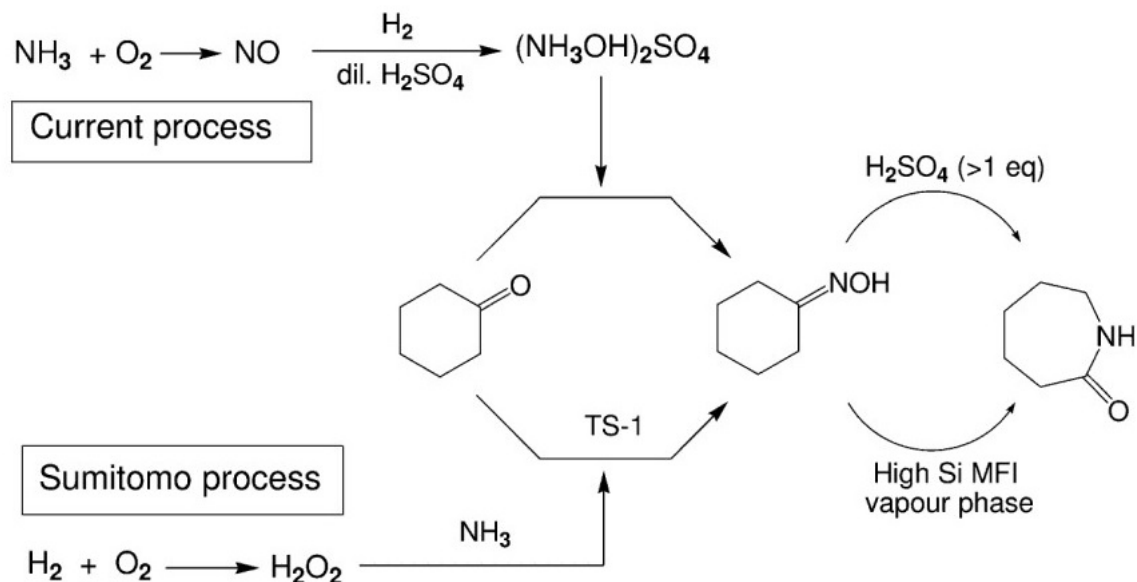


Figure 2: Sumitomo Commercial Process versus Classical Process for Caprolactum

In organic chemistry, the conversion of an acid to its ester requires one equivalent of Bronsted acid to protonate the acid function but the acids can undergo esterification reaction with catalytic amount of solid HUS-Y zeolite.

A solid base catalyst can also be obtained by functionalization of meso-porous MCM-41 with 1,5,7 Triazabicyclo(4,4,0)dec-5-ene (TBD). This base catalyst can be used for Knoevenagel condensation, Michael

additions and Robinson annulation reactions. Hydrotalcites or otherwise known as Layered Double Hydroxides (LDH) can also be employed as solid bases in organic reactions like aldol, Knoevenagel and Claisen Schmidt condensations. In general, using solid acid-base catalysts in organic chemistry is one of the major contributions of catalysis to make organic processes green. There are many examples on acid-base catalyzed organic reactions wherein the benefits of Green Chemistry have been realized.[1].

3 Other typical Organic Reactions enabled by Catalysis

3.1 Catalytic Hydrogenation

It must be noted that green chemistry postulates are nowadays employed in a variety of organic reactions like catalytic oxidation, and reduction, C-C bond formation reactions, avoiding use or excess of solvents, employing renewable raw materials, Enantio-selective transformations and risky reactions. It can be presumed that catalysis enabled almost all the aspects of organic chemistry. Catalytic hydrogenation is unquestionably the work horse of synthetic organic chemistry starting from Sabatier and it has benefited in selective hydrogenation of some specific functional group (chemo-selective) among a variety of them and also stereo-specific hydrogenation has also been achieved. Catalytic asymmetric hydrogenation has led to the Nobel price to W.S.Knowles and R. Noyori recently in 2001. Even though, catalytic hydrogenation is a mature technology, even today new applications seem to appear and benefit the society.

3.2 Catalytic Oxidation

It is probably true that catalytic alternatives are mostly and urgently required in oxidation reactions for the production of fine chemicals and some of the pharmaceuticals. these processes employs more safer reagents like molecular oxygen and hydrogen peroxide and stable free radicals generated from NaOCl as oxidant. Recently 4-hydroxy TEMPO (2,2',6,6'-tetramethyl piperidine-4-oxyl) has been used as catalyst for the production of Progesterone from stigmasterol. There are many other examples of using safer oxidant like hydrogen peroxide or NaOCl and these oxidations have been exploited in industrial production of fine chemicals.

3.3 Bio-catalysis

Bio-catalysis has many features in relation to green chemistry like mild reaction conditions (pH, temperature, physiological) environmentally acceptable catalyst (enzymes) and solvent (mostly water) and generate chemo-, stereo-, regio-selective products with high yields. In addition functional group protection and de-protection steps normally used in classical reactions are not needed. The enzyme oxidase can be used in many of the hetero-aromatics with molecular oxygen as oxidant.

3.4 Other Catalytic Methods Enabling Green Chemistry

One of the major issues in the synthetic organic chemistry is the use of solvents. It is known that solvents are major components (even to the extent of 85% in pharmaceutical industry with recovery levels around 50%) in many chemical industrial production. The choice can be water (non-toxic, non-flammable, available and less expensive and polar) especially for homogeneous catalysts since recovery and recycling of the catalysts are possible. These concepts have been mainly responsible for the process of hydro-formylation of propylene to n-butanol using water soluble Rh(I) complex catalyst a process adopted by Rohmchemie/Rhone Poulenc. In the same way alternate raw materials like bio-waste for the generation of useful chemicals, alternate procedures for C-C bond formation have also been practiced using green methods. These and other aspects wherein catalysis has enabled green chemical procedures can be accessed in reference [2].

4 Photon Assisted Catalysis

The concept of Photo-catalysis has come to be associated (since 1972 vigorously) with fuel production through the decomposition of water by semiconductors, (this effort is still on to find means to carry out this process most efficiently) in synthesis of chemicals (using molecular species or ions, but this field has to get more attention in the coming days) and extensively in de-pollution (in the form of degradation of dye molecules and hazardous chemicals both in water and air media and this effort has provided a number of solutions in pollution abatement) and these situations are pictorially shown in Figure.3. It is known that sun is a perennial source of providing energy sources, much greater magnitude than that is required by the universe and nature has taught us to store this energy in green chemistry pathway in materials and chemicals though the attempts to replicate photosynthesis in the laboratory are still large to learn, it should be stated that nature has always shown us the green chemistry in almost all chemical process that man wants to duplicate in manufacturing. In simple terms, nature has shown us the way to carry out energy conversion process by means of suitable activation by probes like photons (mainly) electrons and species that hold these energy conversion species namely molecules and ions.

In general sense and in short, photon assisted processes which are similar to nature's method of photosynthesis are mainly concerned with photons that are utilized to excite the frontier orbitals of molecules to its unoccupied vacant orbitals. In Photo-catalysis the photon energy is absorbed and an electron from an occupied band is excited to the allowed (for occupation) levels in the empty band leaving a hole in the occupied (valence) band. If the substrate is suitable, can undergo both reduction by the excited electron and the hole will involve in the oxidation of substrate in a selective way. This unique feature can be effectively utilized in energy conversion process or pollution abatement. The pollutants can be completely oxidized to carbon dioxide and water. This special feature has found its utility in degrading dyes, cleaning washrooms. in windscreens instead of wiper, and many other practical situations. This is a major area of photo-catalysis enabling Green chemistry in the universe in a big way [4] In this short write-up, these aspects are mentioned as a contribution of photo-catalysis to Green chemistry.

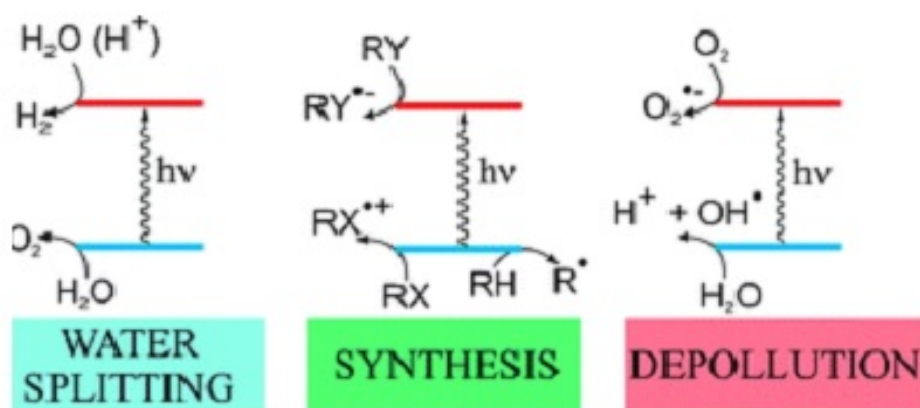


Figure 3: **The three major processes of Photo-catalysis**

The field of photo-catalysis is an emerging area of Science in the last 50 years. Many opportunities are still to be exploited in critical areas of energy and environment. A simple example is the selective conversion of cyclohexane to cyclohexanol and cyclohexanone using TiO_2 photo-catalyst. This simple photocatalytic process is shown in Figure 4

5 Conclusion

It appears that many exciting opportunities exist to revolutionise the chemical manufacturing industry by appropriate catalyst which will enable the process to be completely **Green**. It is only a matter of time.

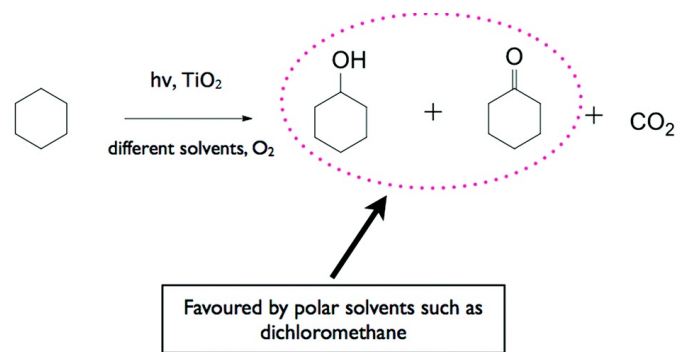


Figure 4: The Photocatalytic oxidation of cyclohexane on TiO_2 in different solvents. Polar solvents favour the desired products cyclohexanone and cyclohexanol, however, complete oxidation to CO_2 takes place in non-polar solvents.

References

- [1] R.A.Sheldon, I.Arends, and Ulf Hanefeld, *Green chemistry and Catalysis*, Wiley-VCH Verlag (2007).
- [2] R.A.Sheldon, E-factor, green chemistry and catalysis An Odyssey, *Chem. Commun.*, (2008), 3352-3355; A.Kate, Lavanya Kumar sahu, Jaya Pandey, Mohit Mishra and Prasanna Kumar Sharma, Green Catalysis for Chemical Transformations: The need for the Sustainable Development, *Current Research in Green and Sustainable Chemistry* **5**(2022)100248; P.T.Anastas, M.M.Kirchoff and T.C.Williamson, Catalysis as fundamental Pillar of Green Chemistry. *Applied Catalysis* **A271** (2001)3-13.
- [3] Davide Ravelli, Daniele Dondi, Maurizio Fagnonia and Angelo Albin, Photocatalysis. A multi-faceted concept for green chemistry, *Chem.Soc.Rev.*, (2009), 38, 1999–2011.
- [4] Huasheng Wu, Lingxiangyu Li, ORCID logo Sen Wang, Nali Zhu, ORCID logo, Zhigang Li, Lixia Zhao ORCID logo and Yawei Wanga, Recent advances of semiconductor photocatalysis for water pollutant treatment: mechanisms, materials and applications, *Phys. Chem. Chem. Phys.*, (2023), **25**, 25899.

Biodata

(This article was composed by **B.Viswanathan** who has been associated with the **National Center for Catalysis Research** at the Indian Institute of Technology, Madras where he was a faculty in the Department of Chemistry since 1970 till 2003.)