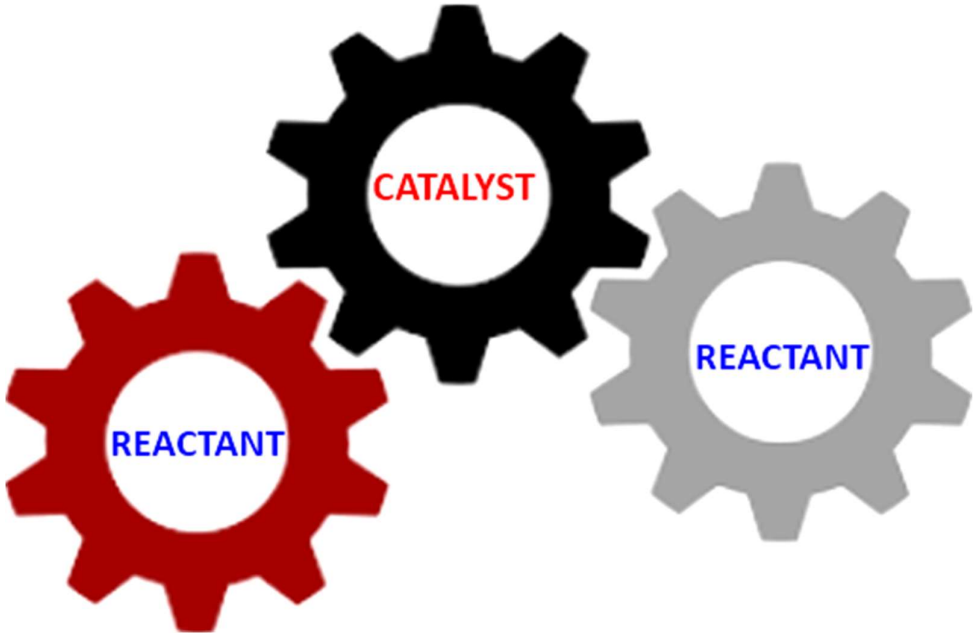
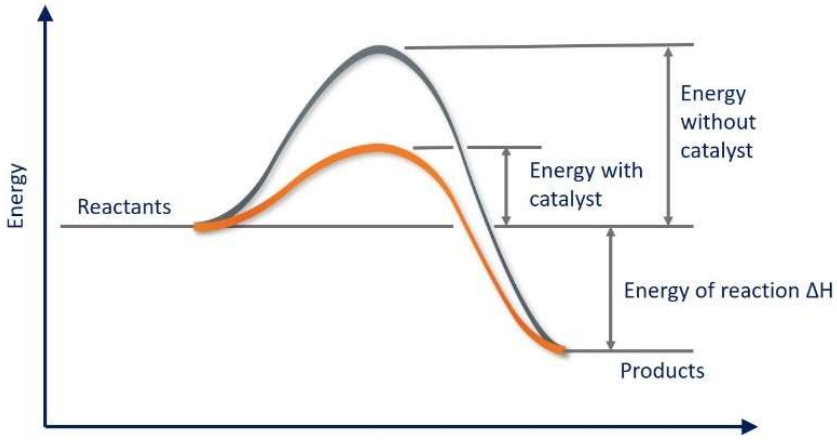
Chapter 1

Introduction



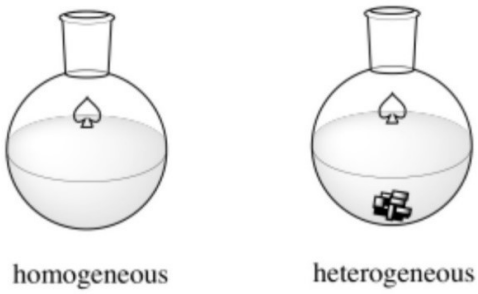
1.1 Introduction

Catalyst is a substrate which increase the rate of reaction without itself getting consumed.



Catalysts are mainly of two types: **heterogenous and homogeneous**.

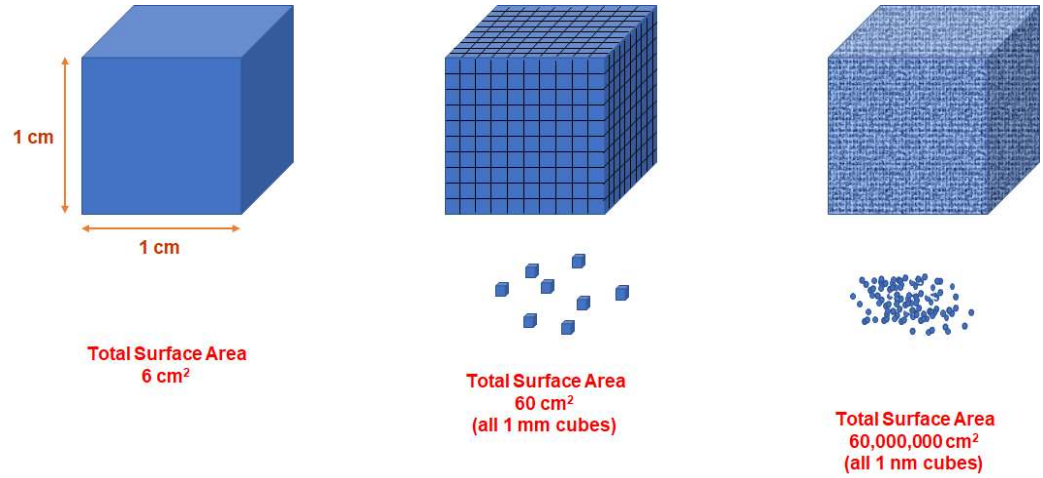
In heterogeneous the catalyst is in different phase from the reaction medium while the homogeneous the catalyst is in the same phase of the reaction medium. If we look closely, in homogenous catalysis both the reactant and catalyst are in the same phase and is more efficient as the catalyst is having high interaction with the substrate. But at the end of the reaction, it is very difficult to isolate the homogeneous catalysts.



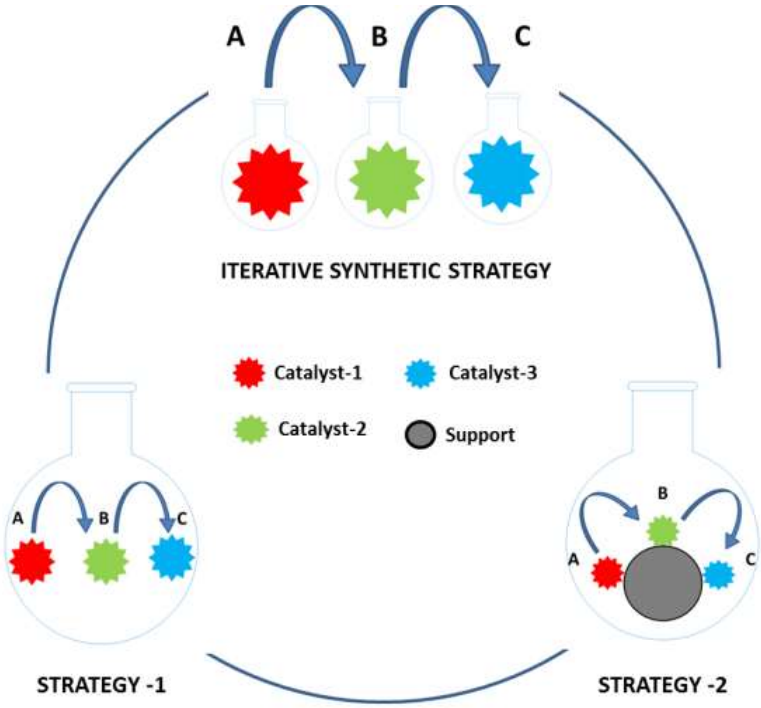
The heterogenous catalyst is having an advantage of ease of separation from the reaction medium by simple technique like filtration.

As like the homogeneous catalysts, the heterogeneous catalysts are not evenly distributed in the reaction medium and have limited catalytic sites for the substrate. The rate of reaction is directly proportional to the catalytic sites or surface area. Therefore, the surface area of the heterogenous catalysts is increased either by loading on some inert material or reducing the particle side.

When the particle size of the catalyst is reduced to nano scale, the science dealing with this is known as Nanoscience or nanotechnology. Nanoparticles are of extreme interest for the loading of the catalysts. Due to their high surface area the loading of the catalyst is found to be high as compared to the other supports. The reaction rates are high as compared to the normal catalyst as most of the catalytic sites are exposed and accessible to the substrate.



In the current era of organic synthesis, repetitive synthetic strategies are posing serious drawback. Therefore, there is a serious need to perform multi-transformations in a single reaction vessel, avoiding the isolation and purification at every stage. One such development is multi-catalysis in which multiple catalytic reactions are done in a single reaction vessel.



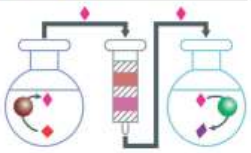
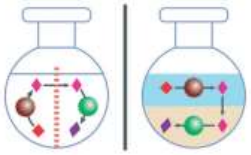
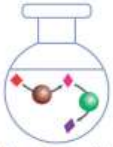
In multi catalysis system we can have two strategies: 1. there could be different catalysts in a single vessel acting conjunctionally or sequentially, 2. there could be multifunctional catalyst. Scenario 1 is not that lucrative as the isolation of the catalysts

in pure form is sometimes not possible or a laborious one. Therefore strategy 2 is the preferential condition.

Strategy 2 involves co-immobilization of the two or more catalysts on the surface of the same support, resulting in a single catalytic material exhibiting many different catalytic properties.

There are many immobilization techniques and different catalytic systems are supported on them. These includes mesoporous silicas, zeolites, bimetallic nanoparticles, various polymers, nanoflowers, “metal–organic frameworks” (MOFs), “covalent organic frameworks” (COFs), “cross-linked enzyme aggregates” (CLEAs), hydrogels, lamellar double hydroxides (LDH).[1-6]

Egon Heuson, talk about the advantages and disadvantages of multi catalytic systems. The advantages include energy saving, high yields due to synergy (thermodynamics), unique set of reaction conditions between catalysts and simple implementation. And the disadvantages include less flexibility and risk of incompatibility[7].

Process type	Advantages	Disadvantages	Process scheme
Two-pots/two-steps 2P2S	→ Flexible processes → Ease of combining catalysts → Fine and independent adjustment of reaction conditions	→ High energy consumption → Poor atom economy	
⇒ The two catalysts are used sequentially in two different reaction compartments			
Two-pots/one-step 2P1S	→ Energy saving → High yields due to synergy (thermodynamics) → Different reaction conditions for the two catalysts	→ Complex implementation → Problem of reagent circulation between compartments	
⇒ The two catalysts are in two separate compartments but are connected to each other and work in parallel			
One-pot/two-steps 1P2S	→ Energy saving → Simple implementation	→ Reaction equilibrium shift not possible → Action required during the process → Longer reaction time	
⇒ At the end of the first catalytic reaction, a second catalyst is added to the same reaction medium to perform the second catalytic step			
One-pot/one-step 1P1S	→ Energy saving → High yields due to synergy (thermodynamics) → Unique set of reaction conditions → Simple implementation	→ Less flexibility → Risk of incompatibility between catalysts	
⇒ The two catalysts are introduced into the reaction medium as the reaction is initiated and work sequentially or in parallel			
Multicatalytic materials (MCMs)	→ Advantages of 1P1S with greater synergy between the catalytic sites and greater ease of implementation	→ Disadvantages of 1P1S	

Based on the environmental protection and subsequent requirements the definition of green chemistry is as follows[8]: *Green chemistry efficiently utilizes (preferably renewable) raw materials, eliminates waste and avoids the use of toxic and/or hazardous reagents and solvents in the manufacture and application of chemical products.* Anastas has mentioned, the guiding principle is the design of environmentally benign products and processes (benign by design)[9]. This principle is reconstituted in the 12 Principles of Green Chemistry[9,10] which are as follows:

1. Waste prevention instead of remediation

2. Atom efficiency

3. Less hazardous/toxic chemicals

4. Safer products by design

5. Innocuous solvents and auxiliaries

6. Energy efficient by design

7. Preferably renewable raw materials

8. Shorter syntheses (avoid derivatization)

9. Catalytic rather than stoichiometric reagents

10. Design products for degradation

11. Analytical methodologies for pollution prevention

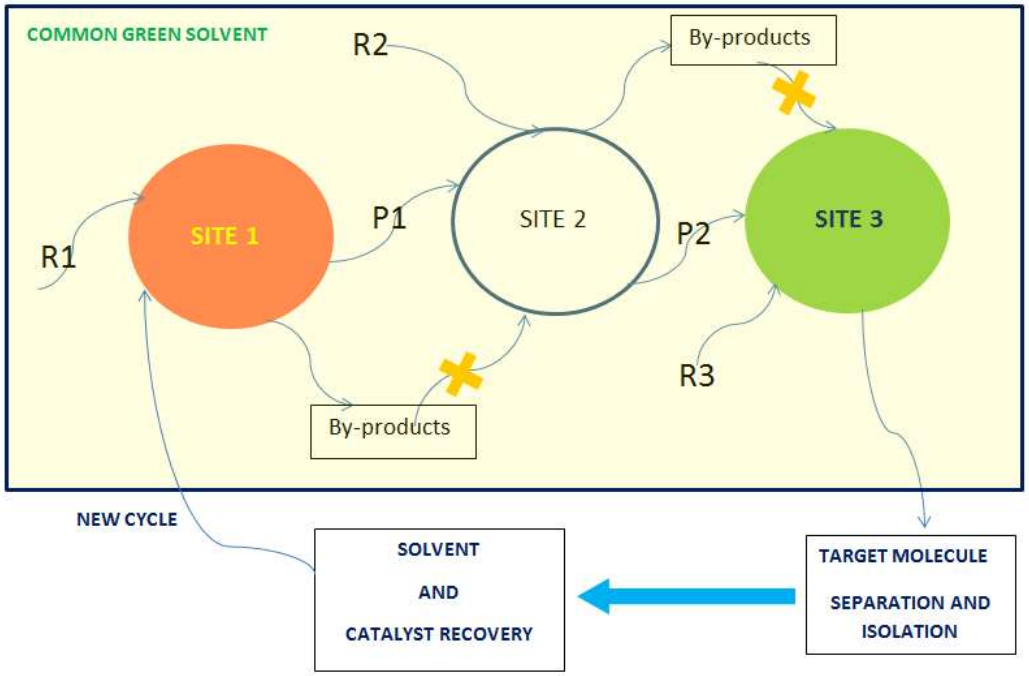
12. Inherently safer processes

Green chemistry principles are to take care of the environmental impact of both chemical products and the processes by which they are produced.

To keep these principles in mind, we have developed tandem catalytic reactions to produce target products in a single step. For the purpose parameters like solvent system, temperature, stoichiometry of the reagent used and the amount of catalytic system were optimized. We have focussed on the development of methods involved in the synthesis of fine chemicals or pharmaceutical intermediates in a domino or

tandem like catalysis processes. In a broad way these processes directly affect the atom economy and have a significant impact on the manufacturing of pharma intermediates and fine chemicals. Tandem reactions in which multiple reactions are combined into one step, in such process intermediates are not separated but allowed to transform into products or reactant for the next step. Due to these consecutive chemical processes, there is an overall saving of energy and unit operations in a chemical plant. The term tandem catalysis is broadly used in the literature that involves the sequential application of catalytic transformation with minimum or no work up or maintain the similar and mild reaction conditions. To carry out one pot tandem processes the special development of catalytic system is required by inducting multiple catalytic sites on a single support. The cooperative and synergistic action of all the catalytic centres require to carry out the tandem reaction successfully.

The development of a green one pot tandem catalytic process for the production of API, the following parameters should be taken care: (i) sufficient reaction site should be available on the surface of matrix (ii) there are chances of formation of by-products, during the different reaction steps should not interfere during the reaction or in the preceding steps (iii) there should be an immediate desorption of products from the surface and should not block the catalytic sites (iv) the product of the first step should easily available as a reactant for the second step and so on for the continuation of the tandem process (v) the selection of the solvent system for this tandem process is crucial and it should be compatible with all the reaction components, should be green in nature as well as recyclable (vi) the corrosion of the matrix and the leaching of the catalytic components should be monitored throughout the process. All these aspects can be set by process optimization. Overall, economic and ecological aspects should be considered for the development of the one pot multi-stage organic transformations on the industrial scale (Scheme I).



Scheme I: Proposed tandem multicomponent single catalytic system for a given organic transformation. R1, R2 and R3 are the different reactants. P1 and P2 are different processes.

In the current work we have the following objectives:

- Synthesis of new catalytic systems.
- Characterization of the synthesized catalytic systems.
- Evaluation of the catalytic systems with respect to different substrates and different reaction conditions.
- Application of the said catalytic system.

1.2 References

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