**Short Review Article on Catalysis for Catalysis Orientation Program 2012**

**National centre for Catalysis Research IIT Chennai**

Name of Student: - Hitesh Suresh Pawar

Ph.D (Sci) Chemistry

Institute Of Chemical Technology Matunga, Mumbai.

**Heterogeneous catalysis for organic transformations**

**Introduction**

The term catalysis (from the Greek kata-, “down,” and lyein, “loosen”) was first employed by the great Swedish chemist [Jöns Jacob Berzelius](http://www.britannica.com/EBchecked/topic/62958/Jons-Jacob-Berzelius) in 1835 to correlate a group of observations made by other chemists in the late 18th and early 19th centuries. These included the enhanced conversion of [starch](http://www.britannica.com/EBchecked/topic/563582/starch) to [sugar](http://www.britannica.com/EBchecked/topic/571880/sugar) by [acids](http://www.britannica.com/EBchecked/topic/3677/acid) first observed by Gottlieb Sigismund Constantin Kirchhoff; [Sir Humphry Davy’s](http://www.britannica.com/EBchecked/topic/152896/Sir-Humphry-Davy-Baronet) observations that [platinum](http://www.britannica.com/EBchecked/topic/464081/platinum-Pt) hastens the [combustion](http://www.britannica.com/EBchecked/topic/127367/combustion) of a variety of [gases](http://www.britannica.com/EBchecked/topic/226306/gas); the discovery of the stability of [hydrogen peroxide](http://www.britannica.com/EBchecked/topic/278760/hydrogen-peroxide) in acid solution but its decomposition in the presence of [alkali](http://www.britannica.com/EBchecked/topic/15573/alkali) and such [metals](http://www.britannica.com/EBchecked/topic/377422/metal) as [manganese](http://www.britannica.com/EBchecked/topic/361875/manganese-Mn), [silver](http://www.britannica.com/EBchecked/topic/544756/silver-Ag), platinum, and [gold](http://www.britannica.com/EBchecked/topic/237258/gold-Au); and the observation that the oxidation of [alcohol](http://www.britannica.com/EBchecked/topic/13366/alcohol) to [acetic acid](http://www.britannica.com/EBchecked/topic/3235/acetic-acid-CH3COOH) is accomplished in the presence of finely divided platinum. The agents promoting these various reactions were termed [catalysts](http://www.britannica.com/EBchecked/topic/99128/catalyst), and Berzelius postulated a special unknown catalytic force to be operating in such processes.

In 1834 the English scientist [Michael Faraday](http://www.britannica.com/EBchecked/topic/201705/Michael-Faraday) had examined the power of a platinum plate to accomplish the recombination of gaseous [hydrogen](http://www.britannica.com/EBchecked/topic/278523/hydrogen-H) and [oxygen](http://www.britannica.com/EBchecked/topic/436806/oxygen-O) (the products of [electrolysis](http://www.britannica.com/EBchecked/topic/183116/electrolysis) of [water](http://www.britannica.com/EBchecked/topic/636754/water)) and the retardation of that recombination by the presence of other gases, such as [ethylene](http://www.britannica.com/EBchecked/topic/194436/ethylene-H2CCH2) and [carbon monoxide](http://www.britannica.com/EBchecked/topic/95021/carbon-monoxide). Faraday maintained that essential for activity was a perfectly clean metallic surface (at which the retarding gases could compete with the reacting gases and so suppress activity), a concept that would later be shown to be generally important in catalysis.

Berzelius in 1986 employed the term catalysis to identify the occurring of chemical reaction by a catalytic contact. In his view catalyst was the substance to force up reactions towards forward direction of reaction product without being consumed or reacting in reaction process. The overall catalysis can be divided in to two parts viz. homogeneous and heterogeneous catalysis. The Homogeneous and heterogeneous catalyst has some barriers and advantages as per reaction types as,

|  |  |  |
| --- | --- | --- |
| **Property** | **Homogeneous** | **Heterogeneous** |
| Solubility | Soluble | Insoluble |
| Recovery | Difficult and expensive | Easy and chef |
| Thermal stability | Poor | Good |
| Activity | Excellent/good | Good/poor |
| Active side | Single | Multiple |

Table1:-Comparison of major advantage/disadvantages of homogeneous and heterogeneous catalyst.

Thus, because of some advantages of heterogeneous catalysis the researcher are directed towards the heterogeneous catalysis or by converting homogeneous catalyst in to heterogeneous catalyst by using various solid supports e.g. silica, alumina, clay etc.Thus we have focused in this review heterogeneous catalysis for various organic reactions.

**Properties Of catalyst**

* **Physical properties:** pore size, surface area, and morphology of the carrier; and the geometry and strength of the support
* **Chemical properties:** composition, structure, and nature of the carrier and the active catalytic components

**Surface Area and Pore Size Measurements**

* A standardized procedure for determining the internal surface area of a porous material with surface area greater than 1 or 2 m2/g is based on the adsorption of N2 at liquid N2 temperature onto the internal surfaces of the carrier. Each adsorbed N2 molecule occupies an area of the surface comparable to its cross-sectional area (16.2Å2). By measuring the number of N2 molecules adsorbed at monolayer coverage, one can calculate the internal surface area.
* **Pore Size measurement**

For materials with pore diameters greater than about 30Å, the mercury intrusion method is preferred. The penetration of mercury into the pores of a material is a function of applied pressure.

The Wash burn equation:   
d= -4 γCosɵ/p  
where d =pore diameter, nm  
 p =applied pressure, atm  
 θ =wetting or contact angle, between the mercury and the solid is usually 130o  
 γ=the surface tension of the mercury, 0.48 N/m

**Surface Composition of Catalysts**

* XRD and TEM measure the structure and/or chemical composition of catalysts extending below the catalytic surface. The composition of the surface is usually different from that of the bulk. It is on these surfaces that the active sites exist and where chemisorptions, chemical reaction, and desorption take place.
* The tools available for surface composition characterization are X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), ion scattering spectroscopy (ISS), and secondary-ion mass spectroscopy (SIMS).XPS is used more widely than the others for studying the surface composition and oxidation states of industrial catalysts.
* XPS refers to the technique of bombarding the surface with X-ray photons to produce the emission of characteristic electrons. These are measured as a function of electron energy. Because of the low energy of the characteristic electrons, the depth to which the analysis is madeisonly~40Å.The composition of this thin layer as a function of depth can be determined by removing or sputtering away top layers and analyzing the underlying surfaces.
* This technique can provide properties including oxidation state of the active species, interaction of a metal with an oxide carrier, and the nature of chemisorbed poisons and other impurities.
* ***Examples of Catalytic reactions***

**Heterogeneous catalysis for hydrogenation reaction:-**

Hydrogenation was the most familiar reaction in the organic chemistry for the reduction of various functional groups.Hydrogeneous reactions also has most significant role in the chemical and pharmaceuticals industry for synthesis of various chemicals, pharmaceuticals, bulk and fine chemicals etc.The reduction of alkenes, alkynes’, nitro, carbonyl etc functional groups are common reaction that can be catalysed by heterogeneous catalyst in presence of hydrogen gas. The large no of expensive and inexpensive catalyst are available for this purpose e.g. palladium, platinum, rany nickel, with different composition in presence of solid support carbon, silica alumina etc.The metals are its self active but heir selectivity can be depends on the reaction condition as well as catalyst composition with solid support because of number of active sites increases.

The number of techniques was used to deposit and anchored the active metal on the surface of support. This gives the wide range of catalyst percentage on solid support having different reactivity and selectivity towards the different type of reactions. The catalytic activity can also been decreased or increased by addition of some additives. For example Linder catalyst pd/CaCo3 is more active, selective and reactive towards hydrogenation of alkenes. The hydrogenation reaction can occurs on the surface of catalyst with different steps as shown below.

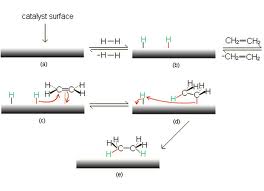


Fig 1:- Mechanism of heterogeneous catalysis for hydrogenation of alkenes.

**Continuous flow condition Hydrogenation reaction:-**

*Bimbisar Desai and C. Oliver Kappe* has explained various hydrogenation reactions including O-debenzylations, aromatic nitro group reductions and reductive dethionations were investigated under continuous flow conditions in a novel, laboratory scale hydrogenation device that combines endogenous hydrogen generation and heterogeneous Pd/C or Raney-Ni catalyst cartridges. They described the hydrogenation of various functional groups of dihydropyrimidones by heterogeneous catalysis under continuous flow condition.

* Hydrogenation of C5 Benzyl esters

|  |
| --- |
|  |

Fig 2:- Hydrogenation of C5 Benzyl esters

* Reduction of Aromatic nitro group

|  |
| --- |
|  |

Fig 3:- Reduction of Aromatic nitro group

* Reductive Dethionations

|  |
| --- |
|  |

Fig 3:- Reductive Dethionations

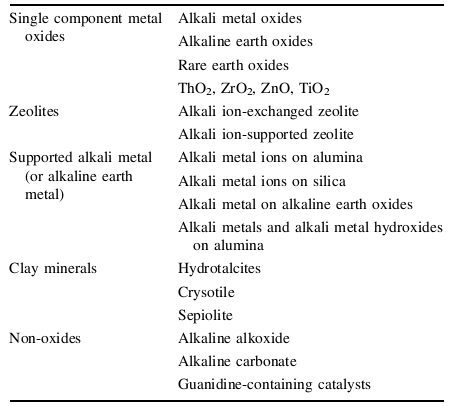
Thus in this way Bimbisar desai Oliver kappe derived continuous catalytic hydrogenation process for different functional groups of dihydropyrimidones.

* **Heterogeneous Base catalyst**

The numbers of organic reactions are carried out by using below mentioned heterogeneous base catalyst with different solid support. E.g. etherification, esterification, hydrolysis, cyclisation, condensasation, elimination, addition Dae-Won Lee reports in review various Trans etherification reaction for biodiesel synthesis by using heterogeneous base catalyst.

Following the report by Pines et al., certain metal oxides with a single component were found to act as heterogeneous basic catalysts in the absence of such alkali metals as Na and K. In the 1970s, Kokes et al. reported that hydrogen molecules were adsorbed on zinc oxide by acid-base interaction to form proton and hydride on the surface. They proved that the heterolytically dissociated hydrogen’s act asinterme- diates for alkene hydrogenation. In the same period, Hattori et al. reported that calcium oxide and magnesium oxide exhibited high activities for 1-butene isomerisation if the catalysts were pre-treated under proper conditions such as high temperature and high vacuum. The 1-butene isomerisation over calcium oxide and magnesium oxide was recognized as a base- catalyzed reaction in which the reaction was initiated by abstraction of a proton from 1-butene by the basic site on the catalyst surfaces.

Types of heterogeneous Base Catalyst

****

Since numbers of researchers are being done focused their research on heterogeneous catalysis as per their synthetic applications. The field of catalytic research becomes most prom icing and challenging for organic transformation because of wide applications of catalyst in organic synthesis.

1) Hand book of heterogeneous catalytic hydrogenation for organic synthesis.

Shigeo nishimura, john wiley and sons.

2) Continuous hydrogenation reaction using continuous flow high flow device. Bimbisar desai Oliver kappe.

3) Catalyst characterization: characterization techniques Catalysis Today 34 (1997) 307-327

4) Heterogeneous Base Catalysts for Transesterification in Biodiesel

Synthesis, Catal Surv Asia (2009) 13:63–77