

1. General introduction

1.1 Catalyst and catalysis: general review

Catalysis is an extremely important phenomenon for our economy. Without it, life today would be quite different from the reality we see around us. As an example, car fitted with catalytic converters to reduce the pollutants (such as NO) exhausted from the vehicle. Without technological advancement, our cities would be more polluted than they currently are. Catalysis is vital technology in today's world. Approximately 90% of all our chemicals and material are produced using catalysis at one stage or another. Many developed countries are net exporters of such chemicals and thus rely on catalysis for the health of their economies. According to the industry standard Unified Modeling Language (UML), catalysis is a next generation approach for the systematic business-driven development of component-based systems. In development and application since 1992, it has been used by Fortune 500 companies in fields including finance, telecommunication, insurance, manufacturing, embedded systems, process control, flight simulation, travel and transportation, and systems management. Catalysis is a non-proprietary method, in many projects, supported by tools and related products and services from several companies. The original developers of Catalysis are Desmond D'Souza and Alan Wills, who co-authored the first catalysis book. On the other hand, catalysis is *an acceleration of the rate of a process or reaction, brought about by a catalyst, usually present in small-managed quantities and unaffected at the end of the reaction. A catalyst permits reactions or processes to take place more effectively or under milder conditions than would otherwise be possible (Thomas 1997).*

Catalysis is not a new phenomenon, although its wide-scale application by humanity only begun in this century. A more systematic study of the phenomenon began early

in the 19th century. Studies of this process began to accelerate, with the number of notable scientists being involved. The discovery of catalytic reaction in the early part of the nineteenth century coincides with the emergence of chemistry as a rational science. Davy began experiments in 1815 on a catalytic combustion with Pt gauzes. J.J. Berzelius, who in 1836 first introduced the terms ‘catalysis’ which means ‘decomposition or dissolution’ in Greek, describing as a compound, which increases the rate of a chemical reaction, but which is not consumed by the reaction. A common misunderstanding is that catalysis “makes the reaction happen”: that the reaction would not otherwise proceed without the presence of the catalyst. This definition allows for the possibility that the small amounts of the catalyst are lost in the reaction or that the catalytic activity is slowly lost.

A catalyst does not appear in the stoichiometric equation for an overall reaction, but it is nevertheless directly involved in the conversion and appears both in individual mechanistic steps, and in the kinetic rate law.

However, the catalyst affects only the rate of the reaction; it changes neither the thermodynamics of the reaction nor the equilibrium composition. During the latter half of the nineteenth century, the theory of chemistry progressed considerably, and by the end of the century, the kinetic theory of gases and basic chemical kinetics have been formulated. In 1911, Ostwald’s redefined catalyst as a substance, which changed the speed of a chemical reaction, thus dispelling the intangible “catalytic force” of Berzelius (Pearce and Patterson 1981). From Ostwald’s view for a complete definition is as *a catalyst is a substance that increases the rate at which a chemical reaction approaches equilibrium without itself becoming permanently involved in the reaction or consumed in the process* (Thomas 1997).

By current definition of catalysis; it is a process whereby a reaction occurs faster than the uncatalyzed reaction.

A catalyst accelerates a chemical reaction. It does by forming bond with the reacting molecules. After reaction, the product, detaches from the catalyst, and the catalyst is unaltered for the next reaction. In fact, a catalytic activity is cyclic which the catalyst participates and is recovered in its original form at the end of the cycle. Figure 1.1 shows the catalytic activity between two molecules A and B to give product P.

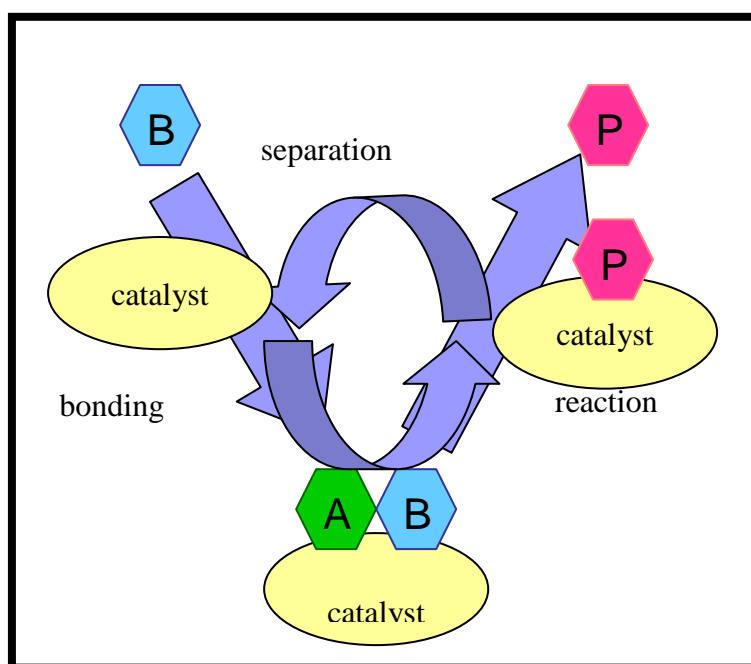


Figure 1.1: Catalytic reaction of A and B become product; P

. The cycle starts with the chemical bonding of molecules A and B to the catalyst. Then a reaction begins within this complex to give a product P, which is also bound to the catalyst. In the final step, P separates from the catalyst, thus leaving the reaction cycle in its original state. Figure 1.2 shows the potential energy diagram of a heterogeneous catalytic reaction, with gaseous reactants and products and a solid catalyst. This diagram indicates the comparison of potential energy between non-catalytic and catalytic reaction. For the non-catalytic reaction, the figure is simply a

familiar way to represent the Arrhenius equation: the reaction proceeds when A and B collide with sufficient energy to overcome the activation barrier in Figure 1.2. The change in Gibbs free energy between reactants A and B, and the product P is ΔG . The formation of the complex is exothermic, and free energy is subsequently Product P is separated from the catalyst in an endothermic step.

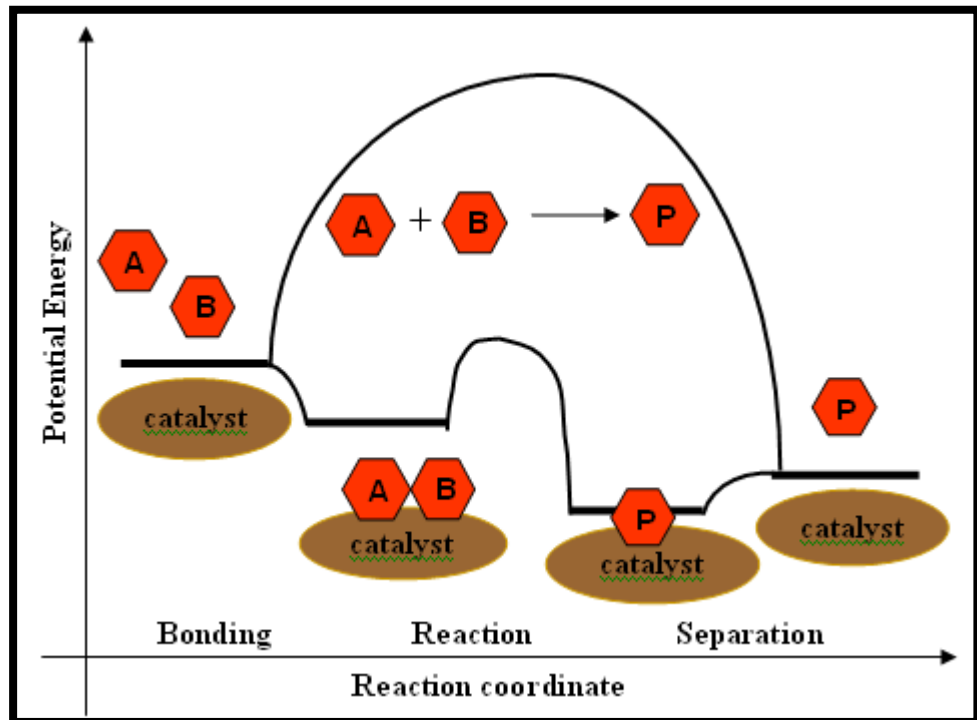


Figure 1.2: Potential energy diagram of a heterogeneous catalytic reaction with gaseous reactants, products and solid catalysts.

The energy diagram of Figure.1.2 illustrates several important points:

- The catalyst offers an alternative path of reaction, which is obviously more complex, but energetically more favorable.
- The activation energy of the catalytic reaction is significantly smaller than an uncatalyzed reaction. Hence, rate of the catalytic reaction is larger
- The overall change in free energy for the catalytic reaction equals that of the uncatalyzed reaction. Hence, the catalyst does not affect the equilibrium constant for the overall reaction of $A + B$ to P . Thus, if the reaction is

thermodynamically unfavorable, a catalyst cannot change this situation. A catalyst changes the kinetics but not the thermodynamics.

- The catalyst accelerates both forward and the reverse reaction to the same extent. In other words, if the catalyst accelerates the formation of the product P from A and B, it will do the same for the decomposition of P into A and B.

There are also cases in which the combination of catalyst with reactants or products will not be successful:

- If the bonding between reactants and catalyst is too weak, there will be hardly any conversion of A and B into product.
- Conversely if the bond between the catalyst and one of the reactants, say A, is too strong, the catalyst will be mostly occupied with species A, and B is not available to form the product. If both A and B form strong bonds with the catalyst, the intermediate situation with A and B on the catalyst is too stable and a reaction becomes unlikely. In Figure 1.2, potential energy to form product P is too low, causing the activation energy to form P to be high. The catalyst is said to be poisoned by (one of) the reactants.

In the same way, the product P may be strongly bound to the catalyst for separation to occur. In this case, the product has poisoned the catalyst.

According to UK Science Research Council (Hartley 1985), a system is said to be 'catalyzed' when the rate of change from state I to state II is increased by contact with a specific material agent which is not a component of the system in either state, and when the magnitude of the effect is such as to correspond to one or more of the following descriptions:

- a. Measurable change from state I to state II occurs only in the presence of the agent;
- b. Enhanced rate of change is found with the same sample of agent in repeated experiments using fresh reactants; and
- c. Quantity of matter changed is many times greater than that of the agent.

The catalyst can increase the rate of chemical reaction because of its capability to decrease the free energy of activation of a given reaction in comparison to the same uncatalyzed reaction. Reactant molecules and transition states are immobilised on the catalyst surface with the consequence of spatio-temporal decoupling of the elementary step reactions and the intermediate gain in energy through chemisorption. An elementary step in a catalytic reaction is by first approximation identical with the making or breaking of a chemical bond between two atoms.

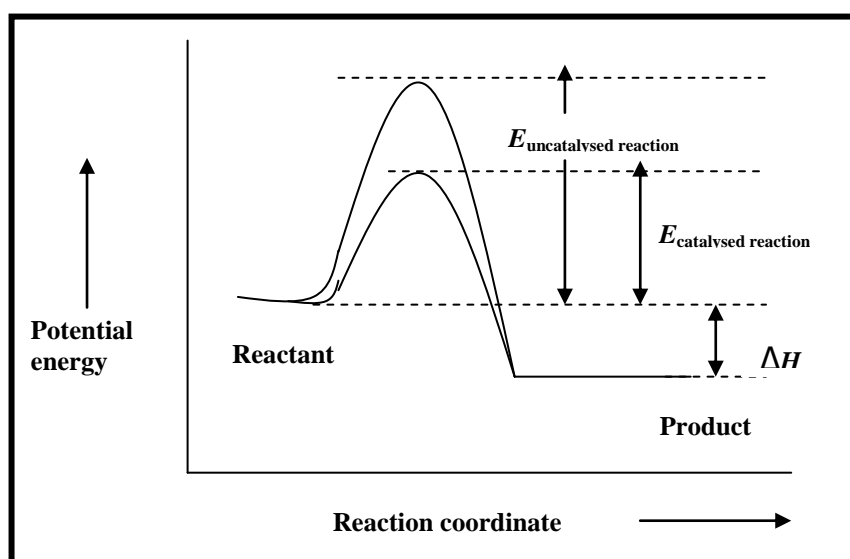


Figure 1.3: Potential energy profile for an exothermic reaction showing the lower E_a of catalysed reaction

Figure 1.3 shows that activation energy (E_a) of a catalyzed reaction is lower than that of the same uncatalyzed reaction. A catalyst can increase the rate of reaction but it

cannot initiate a reaction. It should be also stressed that the action of a catalyst changes the path of minimum potential energy through the respective hyper surface. Thus, the distribution of products will be different with or without a catalyst. In addition, a catalyst can also decelerate a reaction path to the advantage of another path. The action of catalyst onto a complex reaction mixture is therefore quite unpredictable and may vary significantly with minute changes in the chemical nature of the catalyst or external reaction conditions.

The definition of catalyst and catalysis imply that several changes can occur to the course of chemical reaction. In any case, catalysis is purely a kinetic phenomenon and operates only at a distance from thermodynamic equilibrium.

The action of catalyst can be used to:

- 1) Lower the activation energy barrier (E_a)
- 2) Attain reaction product at a faster rate
- 3) Decrease the reaction temperature at a given rate of reaction
- 4) Obtain a metastable product instead of a thermodynamically preferred product.
- 5) Maintain an equilibrium constant, K_p , and by accelerating both forward and reverse reaction.
- 6) Change the product distribution between several metastable products

The principal theme in catalysis is the desire to control the rate of chemical reactions. For any planned operation, it is essential to understand the mechanism of the control. One important point to note is that the catalyst affects only the rate of reaction; it changes neither the thermodynamic of the reaction nor the equilibrium composition (Stoltze 1999).

The phenomenon of catalysis has been extensively studied since the early decades of the 19th century but it was applied unconsciously for a much longer period before then. Table 1.1 shows a historic perspective in catalysis. However, since the mid-1980s, several other major themes have emerged in applied catalysis. Some of these reflect the growing commitment of protecting the natural environment while others represent the logical extension of pure research. Furthermore, others have arisen from a desire to produce foodstuffs and useful products from precursors that are plentiful (Thomas 1997).

Table 1.1: Past perspective in catalysis (Thomas, 1997)

Year	Discoverer	Catalytic process
1814	Kirchoff	Catalysed hydrolysis of starch by acids
1817	Humphry Davy	Introduction of hot platinum into a mixture of air and coal gas led to the metal becoming white hot
1824	Henry	Ethylene inhibited the reaction between hydrogen and oxygen on platinum
1834	Michael Faraday	Recombination of gaseous hydrogen and oxygen on platinum that had produced by electrolysis of water
1845	Grove	Decomposition water vapour into hydrogen and oxygen on hot platinum
1871	Deacon Process	Oxidation of hydrochloric acid to chlorine
1877	Lemoine	Decomposition of hydriodic acid to hydrogen and iodine on platinum sponge at 623 K
1879	Bertholet	Acid-catalysed esterification of organic acids and hydrolysis of esters
1901	Wilhelm Normann	Catalytic hydrogenation of oleic acid to stearic acid
1909	Fritz Haber	Synthesis of ammonia from hydrogen and nitrogen in the presence of a reduced magnetite catalyst using a high-pressure apparatus
1923	BASF	Synthetic methanol plant
1923	Fischer-Tropsch	Convert syn-gas to hydrocarbons and alcohols using cobalt and iron catalyst
1937	Union Carbide	Silver-catalysed oxidation of ethylene to ethylene oxide
1930s	Houdry, Lewis, Gilleland	Catalytic cracking
1930s	Ipatieff, Pines	Oligomerisation of gaseous alkenes with silicone-phosphoric acid
1960	Rabo <i>et al.</i>	Isomerising hydrocarbons using zeolite catalysts
1964	Plank, Rosinsky	Zeolites as cracking catalyst

1.1.1 The Behavior of the Catalyst

Catalysis is very crucial to the chemical industry and the number of catalysts used in the industry is about 25,000. Today, almost 90% of all chemicals produced have been in contact with a catalyst somewhere in their synthesis process. Industrial catalysts are typically complex in composition and structure.

In order to produce a good catalyst, it is dependent on four factors listed below:

- ◆ Surface area and crystallite size
- ◆ Catalyst shape and size
- ◆ Role of support
- ◆ Role of promoters

1.1.1.1 Surface Area and Crystallite Size

Surface area and crystallite size play a major role in certain types of catalysts. By assuming that the crystallites in supported catalysts are spherical or that some other simple shape and surface area are available; relationship between size, number and the total surface area of the crystallite are easily derived as below:

Spherical crystallites	Cubic crystallites
$N = 6M/\rho\pi d^3$	$N = M/\rho d^3$
$SA = 3M/\rho d$	$SA = 6M/\rho d$

where N = number of crystallites in catalyst containing mass M of active site

ρ = density of active phase

d = diameter or side of crystallites

SA = total surface area of crystallites

Crystallite of the active phases in most industrial catalyst are in a range of 50 Å to 500 Å. Manufacturing methods are available for producing such fine dispersion but

is not thermodynamically stable. High surface energy is accompanied by high surface area in very fine particles. Therefore, a method must be derived to reduce the surface energy. This can be achieved if small crystallites combine into larger ones. This happens when the operating conditions affected the rate of the process, which is called *sintering*. Sintering refers to distortions to the pore structure arising from thermal effects such that excesses in temperature or other consequent chemical interactions cause a softening, restructuring or even melting of the solid phases.

1.1.1.2 Catalyst shape and size

Catalysts come in a multitude of forms, varying from atoms and molecules to large structures such as zeolites or enzymes. In addition, they may be employed in various surroundings: in liquids, gases, or at the surface of the solids. In industry, catalysts can be manufactured in different sizes and shapes where particularly depending on the design requirements in process and the type reactor used. Figure 1.4 and table 1.2 shows some of the common shapes in which catalysts are fabricated for requirement in reactor processes. Typical dimensions of catalysts used in large fixed bed reactors are in the range 3 mm to 20 mm.

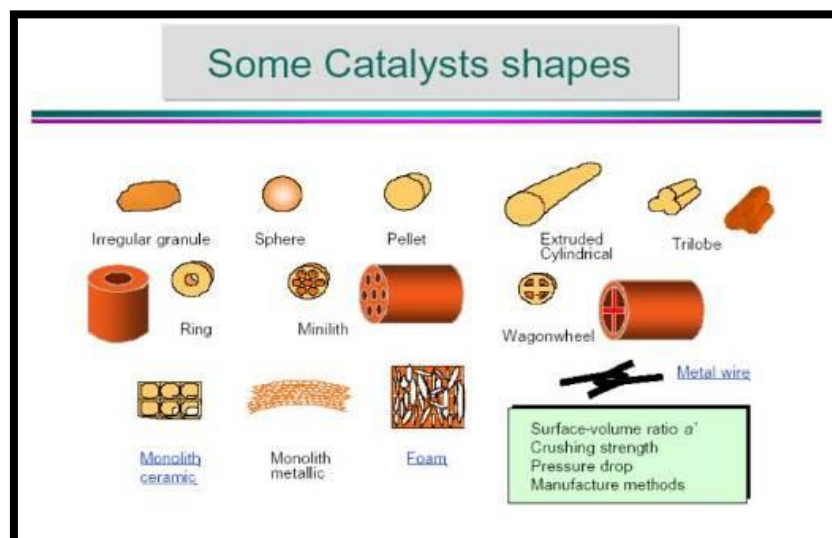


Figure 1.4: Examples of commercial catalysts shapes.

Table 1.2: Common type of catalyst in industry

Shape	Typical Catalysts	Remarks
Spheres	Several hydrosulphurisation and ammonia plant methanation catalysts. Certain impregnated precious metal catalysts (alumina spheres)	Low manufacturing costs. Some granulated material can be weak, and cementing agents are frequently used to increase strength. Packed beds of spheres produce relatively high-pressure drop.
Irregular granules	Ammonia synthesis catalyst (fused oxides), silver catalyst for formaldehyde production from methanol.	Uncommon catalyst shape. Consequences of restricted methods of manufacturing. Used for low surface area catalysts such as bulk metal.
Pellets	Low and high temperature carbon monoxide shift catalyst. Many hydrogenation catalysts used in manufacture of organic fine chemicals.	Highly regular shape with good strength. This shape is the most common one to be produced even though the cost is very expensive.
Extrudate	Very large quantities of hydrosulphurisation catalyst are produced in the form of extrudate	Low bulk density and low pressure drop. Often poor strength. Some formulations can be extruded which are difficult to form pellets. Production costs are less than pelleting.
Rings	Steam reforming of hydrocarbons (primary and secondary). Ethylene oxide catalyst and other applications where pressure drop is an important.	Impregnation of perforated rings can produce very high strength catalysts. Low-pressure drop are often used in tubular reactors. Manufactured by pressing or extrusion. Pressed rings have superior physical properties, but costly to produce.

Under normal operating conditions, the effective activity of many catalysts is to some extent controlled by mass-transfer effect (either pore diffusion, or film diffusion limitations). Not only size, but also shape affects external surface area and pressure drop characteristics. For instance, the comparison between a cylindrical pellet with a ring of similar length and outside diameter. A ring containing for about 80 % of the volume of catalyst material contained in the pellet has for about 120 % of the pellet's external surface area, yet produces a significantly reduced pressure drop (e.g. 50 % less) in a reactor.

1.1.1.3 The role of support

Most heterogeneous catalysts are sintered to some extent, metal catalysts being the most susceptible one. The support in catalyst is normally neutral, such as alumina, activated carbon or silica. A catalyst that is supported by a porous neutral metal

material is typically laid on a bed through which the liquid or gas may flow. Its catalyst support generally consists of an inert metal material in the form of graded porous granules or irregular polysurface pellets with high adhesion properties, which are called as “*supported metal catalysts*”.

For the supported metal catalysts, it shows much higher resistance to sintering. This effect has been interpreted in terms of both steric factors and simple energetics. On the other hand, to make an effective support, it should be dispersed on the metal surface. In catalysis, the support can act as a physical “spacer” between the metal crystallites (deposited in the pores via impregnation). Besides that, the function of the support material is to give the final catalyst shape and mechanical strength of the catalyst. Therefore, sintering of the metal crystallites can be eluded if there is adequate support inside the catalyst. This model has the appeal of simplicity, and it can be made semi-quantitative by application of geometric considerations.

The other approach depends on an interaction between the metal and the support. In industrial, the most widely used support material is alumina (Al_2O_3). It is because alumina is available in high purity at a moderate cost, with various polymorphs and hydrated forms, porosity and pore structures. The surface area for alumina is in the range $\sim 1 \text{ m}^2\text{g}^{-1}$ to more than $200 \text{ m}^2\text{g}^{-1}$.

The most common types of aluminas are α - Al_2O_3 and γ - Al_2O_3 . α - Al_2O_3 is produced by heating γ - Al_2O_3 in any of the hydrous oxides at above 1273 K. It has hexagonally close-packed oxide ions with aluminium ions in octahedral interstices (corundum structure). It is chemically inert and has a low surface area about $15 \text{ m}^2\text{g}^{-1}$ or less. This support is used for impregnated catalysts that operate under arduous conditions such as natural gas steam reforming or some selective oxidations catalysts. The γ - Al_2O_3 is obtained when aluminum hydrous oxide dehydrated in high temperature. It has high surface area. This support is widely used in catalyst manufacture as support

material for both impregnated and precipitated catalysts. The particle size of γ - Al_2O_3 is very small $\sim 50 \text{ \AA}$ (Thomas 1997).

1.1.1.4 The role of promoter

The patent literature contains many references where additives are described as promoters, and their use in industrial catalyst is widespread. Many catalysts are not so effective on their own, but its used in conjunction with other kinds of promoters. Promoter is a substance which, though not itself a catalyst, improves the effectiveness of the catalyst – promoters may act chemically or physically (Ferguson 2008). The role of promoters can be divided into two classes, *chemical promoter* or *structural promoter*. A *chemical promoter* is to improve the effectiveness of the catalyst by altering the electron distribution at the surface. Whilst, structural promoter is employed to improve the mechanical properties and prevent sintering (Ferguson 2008). In heterogeneous catalysis, the activity of a catalyst is greatly influenced by the surface structure. Promoters simply enhance the catalytic activity. However, after nearly 100 years of study in the area, the precise way by which they do is still a subject of debate.

1.2 Organization of Catalysis

Catalysis is essentially a chemical phenomenon. The ability of a substance to act as a catalyst in a specified system depends on its chemical nature. Catalysts can be divided into two groups, *homogeneous and heterogeneous*, depending on to whether the reactants and products share the same phase as the catalyst. In a catalytic reaction, five essential steps are recognized to affect not only the rates but also the nature of the reaction. The five essential steps may represent the catalytic actions as listed in the following:

- i) Diffusion to the catalytic site (reactant)
- ii) Bond formation at the catalytic site (reactant)
- iii) Reaction of the catalyst- reactant complex
- iv) Bond rupture at the catalytic site (product)
- v) Diffusion away from the catalytic site (product)

In homogeneous catalysis concept, steps (ii)-(iv) represent the formation and decay of the reactive intermediate. While for heterogeneous catalysis, these steps represent surface adsorption and desorption of the surface intermediates.

1.2.1 Homogeneous Catalysis

Homogeneous catalysis is a catalytic process where the catalyst is in the same phase as the reactants and products. In homogeneous catalysis, the catalyst is a molecule which facilitates the reaction. The reactant(s) coordinate to the catalyst (or *vice versa*), transform to product(s), which are then released from the catalyst.

The following list the example of processes using homogeneous catalysts:

- (a) Hydrolysis of esters with acids (liquid-liquid),
- (b) Oxidation of sulphur dioxide (SO_2) with nitrogen dioxide (NO_2) (gas-gas),
- (c) Decomposition of the potassium chlorate (KClO_3) with manganese dioxide (MnO_2) (solid-solid).

Homogeneous catalysis occurs through complexation and rearrangement between molecules. As a result, the reaction can be specific with high yields of desired products. This process is difficult to operate commercially especially with liquid phase processes due to operation restrictions on temperature and pressure, making

chemical process equipment setup complicated. Furthermore, the separation process is difficult because the catalyst is in the same phase as the reactants and products.

1.2.2 Heterogeneous Catalysis

Heterogeneous catalysis occurs when the catalyst is in a different state from the reactants, with the catalyst usually being solid and the reactants often being gaseous. In heterogeneous catalysis, the reactants diffuse to the catalyst surface and adsorb onto it, via the formation of chemical bonds. After reaction, the products desorb from the surface and diffuse. Understanding the transport phenomena and surface chemistry such as dispersion is important. If diffusion rates are not taken into account, the reaction rates for various reactions on surfaces depend solely on the rate constants and reactant concentrations. For solid heterogeneous catalysts, the surface area of the catalyst is critical since it determines the availability of catalytic sites. Surface areas can be large, for example some mesoporous silicates have areas of 1000 m²/g. The most common approach to maximizing surface area is by the use of catalyst supports, which are the materials over which the catalysts are embedded upon. Large-scale example of industrial processes in heterogeneous catalyst system is tabulated in Table 1.3.

Table 1.3: Examples of heterogeneous catalyst system in industry[http://en.wikipedia.org/wiki/Heterogeneous_catalysis]

<i>Process</i>	<i>Reactants, product(s)</i>	<i>Catalyst</i>	<i>Comment</i>
<i>Sulfuric acid synthesis (Contact process)</i>	$\text{SO}_2 + \text{O}_2, \text{SO}_3$	vanadium oxides	hydration of SO_3 gives H_2SO_4
<i>Ammonia synthesis (Haber-Bosch process)</i>	$\text{N}_2 + \text{H}_2, \text{NH}_3$	iron oxides on alumina	consumes 1% of world's industrial energy budget
<i>Nitric acid synthesis (Ostwald process)</i>	$\text{NH}_3 + \text{O}_2, \text{HNO}_3$	unsupported Pt- Rh gauze	direct routes from N_2 are uneconomical
<i>Hydrogen production by Steam reforming</i>	$\text{CH}_4 + \text{H}_2\text{O}, \text{H}_2 + \text{CO}_2$	Nickel or K_2O	Greener routes to H_2 formation by water splitting
<i>Ethylene oxide synthesis</i>	$\text{C}_2\text{H}_4 + \text{O}_2, \text{C}_2\text{H}_4\text{O}$	silver on alumina, with many promoters	poorly applicable to other alkenes
<i>Hydrogen cyanide synthesis (Andrussov oxidation)</i>	$\text{NH}_3 + \text{O}_2 + \text{CH}_4, \text{HCN}$	Pt-Rh	Related ammoxidation process converts hydrocarbons to nitrile
<i>Olefin polymerization Ziegler- Natta polymerization</i>	propylene, polypropylene	TiCl_3 on MgCl_2	many variations exist, including some homogeneous examples
<i>Desulfurization of petroleum (hydrodesulfurization)</i>	$\text{H}_2 + \text{R}_2\text{S}$ (idealized organosulfur impurity), $\text{RH} + \text{H}_2\text{S}$	Mo-Co on alumina	produces low-sulfur hydrocarbons, sulfur recovered via Claus process

In these systems, catalysis occurs through diffusion and absorption/adsorption of reactant molecules on the surface of catalyst. These systems allow easy separation of the feed and product streams from the catalyst. Further advantages of the application of heterogeneous catalysis processes are the understanding and control of the process technology (chemical engineering of reactors and process conditions in wide variations), the re-usability of the catalyst through regeneration or at least through recovery of the active component, and a better control of waste and toxic components.

The major advantages/disadvantages of heterogeneous versus homogeneous catalyst are summarized in Table 1.4. As a general picture, the main differences are the fact that in the case of homogeneous catalyst, every single catalytic entity can act as a single active sites. It makes the homogeneous catalysts intrinsically more active and selective than traditional heterogeneous catalyst.

Table 1.4: Comparison of advantages/disadvantages in homogeneous and heterogeneous catalyst systems (<http://www.eolss.net-sampleAllChapter.aspx>)

Property	Homogeneous	Heterogeneous
Catalyst recovery	Difficult and expensive	Easy and cheap
Thermal stability	Poor	Good
Selectivity	Excellent/good-single active site	Good/poor-multiple active sites

1.3 Properties of Catalyst

A good catalyst must fulfill three main criterias i.e.; activity, selectivity and lifetime.

The details of these criterias are discussed in the following sections.

1.3.1 Catalytic activity

Catalytic activity is the ability of a catalyst to transform the reactants to the desired products. It can be expressed on several units: e.g. g (product) per g (catalyst) per hour, g (product) per cm³ (catalyst) per hour, or mole (product) per mole (catalyst) per hour. For the purpose of discussion, it is defined in terms of activation energy.

In principle, the rate of any gas-solid or liquid-solid catalysed reaction can be expressed as the product of the apparent rate coefficient k and a pressure- (or concentration-) dependent term:

$$\text{rate} = kf(pi) \quad (\text{eq. 1.1})$$

where, pi is the partial pressure of the reactant i . The rate coefficient for the overall catalytic reaction may incorporate the rate coefficients of many of the elementary reaction steps that precede the rate-determining step.

For several reasons, this rate coefficient will change as the prevailing conditions of the reaction (temperature, pressure, surface concentrations, etc.) vary, and therefore, it is operationally convenient to use the Arrhenius equation:

$$k = A' \exp(-E'/RT) \quad (\text{eq. 1.2})$$

where A' is a temperature-independent pre-exponential factor and E' is the apparent activation energy of the catalytic reaction. E' cannot be expected to be the true activation energy, even if the catalyst structure remains unchanged with varying

temperature, because the concentration of reactant at the catalyst surface will be temperature-dependant.

In addition, the concept of turnover frequency or turnover number is generally used in catalytic activity. TOF or turnover frequency can be expressed as the number of times n that the overall catalytic reaction takes place per catalytic site per unit time for a fixed set of reaction conditions (temperature, pressure or concentration, reactant ratio, extent of reaction).

In other words,

$$\text{TOF} = \frac{\text{the amount of products (mol)}}{\text{the amount of catalyst active sites X time (h)}}$$

or

$$\text{TOF} = \frac{1}{S} \frac{dn}{dt} \quad (\text{eq. 1.3})$$

where S is the number of active sites.

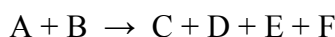
In heterogeneous catalysis, there are difficulties indeterming the number of active sites in certain catalyst. Therefore, TOF is used to measure the catalytic activity. There are also numerous examples in surface science studies where the notion on a flat surface of a metal every atom exposed should be active. However, the role of steps, kinks and defects recently unraveled by theory and experiments. For instance, ammonia synthesis or in NO activation is a clear proof that to the understanding of number of active sites is limited. It is thus justified to retreat the activity definition based on activity normalized to volume or weight of catalyst.

In other definition, activity is the rate of conversion. Rate of conversion is given as the number of moles converted or produced per unit weight and unit time. A

sequence of activities in family of catalyst can also be expressed in terms of moles per unit time and unit surface area. Generally, the surface area of the active phase determines catalytic activity. The nature of the pore structure is also important in influencing the catalytic performance. Many selective oxidation catalysts require particular well-defined pore size distribution for optimum activity and selectivity (Pearce & Patterson).

1.3.2 Selectivity

A good catalyst must possess both high activity and long term stability. But the most important attribution is its selectivity, S , which reflects its ability to convert directly the reactant(s) along one specific pathway (Thomas 1997). In catalysis definition, *selectivity* is the amount of a given reaction produced related in common unit (moles) to the amount of starting material converted. Usually, it can be expressed in percentage (%). When the reaction of reactants A and B produce C, D, E, F (Scheme 1), respectively, the selectivity S is calculated as illustrated in Scheme 2.



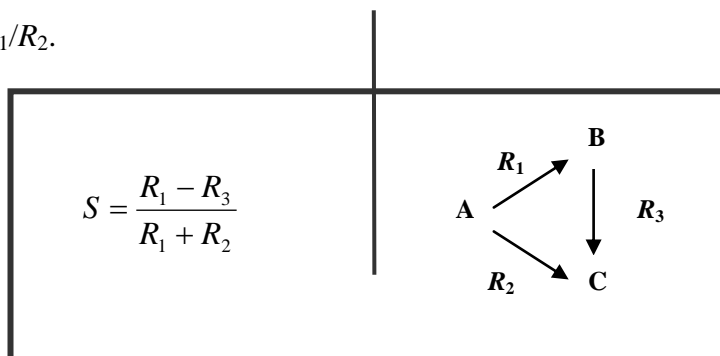
$$\% \text{ Selectivity of } C = \frac{[C]}{[C] + [D] + [E] + [F]} \times 100\%$$

Scheme 1.1: Reaction of A and B to produce C, D, E, F and the selectivity of C. [C], [D], [E], [F] is the concentration of C, D, E, F.

Selectivity can change with the degree of conversion when the product(s) undergo further transformation. Primary reaction selectivity can only be obtained from measurement at a low conversion where there are several reaction components and/or product, basis of which selectivity is expressed must be stated (Pearce & Patterson). It can happen when a reactant A can be transformed to either B or C at

rates R_1 and R_2 (Scheme 1.1), respectively, the selectivity S is calculated as shown in Scheme 1.1.

It is also sometimes convenient, when R_3 is zero, to define another index of selectivity, $p = R_1/R_2$.



Scheme 1.2: Transformation of A to B and C and selectivity

Besides selectivity, the conversion and yield are the most important parameter in a catalytic reaction. The conversion can be defined as *the amount of a given reaction component transformed into products related to the initial quantity of the same component*. It is usually expressed in percentage (%). Whilst, the yield is *the amount of a given reaction product related to the amount of a starting component and expressed by percentage (%)* where there are several reaction components and/or products, the basis of which yield is expressed must be stated.

The formula for selectivity, conversion and yield are:

$$\text{Yield} = \text{selectivity} \times \text{conversion}$$

1.3.3 Lifetime

The span of time in which a catalyst maintains a sufficient level of activity and/or selectivity is defined as the *lifetime* of a catalyst. The activity and selectivity of heterogeneous catalysts may change during the course of conversion. Seldom has the

catalytic activity increased over time due to either chemical or physical reasons, or a combination thereof. Both, activity and selectivity of most heterogeneous catalysts will also decrease after some time. From the viewpoint of process economics, the simplest approach would consider the total product made over the period of active catalyst life as well as associated shutdown periods to charge and discharge catalyst. However, the rates at which activity and selectivity (and hence overall productivity) change during the catalyst life are also important.

Figure 1.5 below illustrates two contrasting patterns of catalyst behavior. Catalyst 1 shows a high initial productivity but a short life before the catalyst performance deteriorates to the point where a decision is made to shut down the reactor and to recharge the reactor with fresh catalyst. In contrast, catalyst 2 shows a lower initial productivity, but a slow decline and much longer life before a replacement is required.

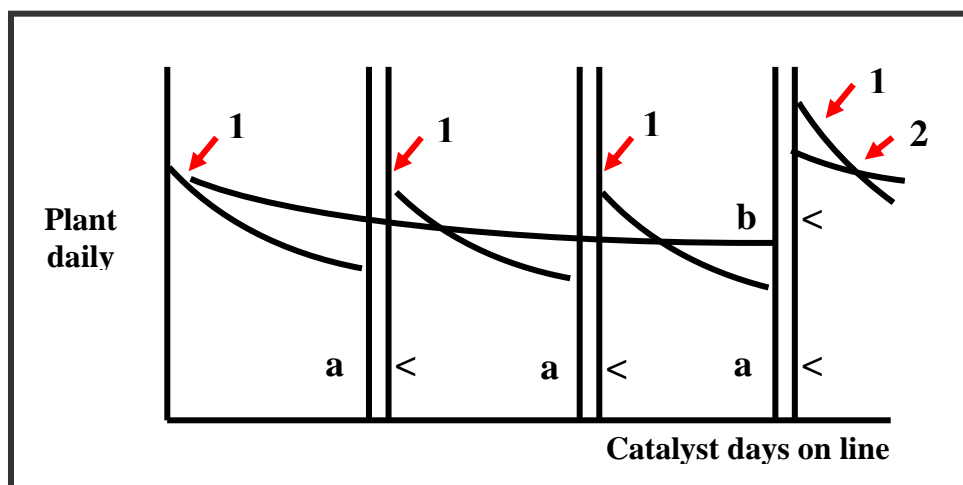


Figure 1.5: Contrasting patterns of catalyst decay, $a > < a$, catalyst 1 discharged and new catalyst charged in; $b > < b$, catalyst 2 discharged and new charged in.

The total integrated production over an extended period (usually assessed on an annual basis) for the two cases will depend on the balance of initial activity, rate of decline, number of catalysts changes and duration of off-line time at each catalyst change. From the perspective of plant operating process, catalyst 2 shows a preferred

pattern of behavior. A long on-line period without a dramatic performance change allows operating condition to be “fine-tuned” to achieve optimum production economics. Whilst, catalyst 1 shows the optimum conditions which differs considerably between early and last stage of the catalyst life. These variations and frequent operation interruptions (for shutdown and start-up) make optimum plant operation difficult to achieve.

The lifetime of a catalyst can vary from process to process, ranging from minutes to several years. With any given chemical application conditions, it is important that the exploitation of the maximum catalyst lifetime is to operate the catalyst under steady conditions as long as possible.

Catalysts lose activity and selectivity in many ways. Some catalysts undergo physical changes during normal operation such as a catalytically active phase may transform into a deactive phase. The deactivation process is always connected with the growth of solid phases with detrimental functions of the catalyst. Catalysts undergo sintering, which is the coalescence of particles to give larger particles, accompanied by loss of surface area. Sintering is normally happen on the most commercial supported catalyst. The actual rate and extent of sintering depends on a number of factors, including the metal concerned, the metal content, initial crystallite size, the nature of support material, operating conditions, and the method of catalyst manufacture (Pearce and Patterson 1981). Many catalysts have lifespans extending over many years (see Table 1.4). In every instance of operation patterns, catalysts has high growth probability of solid phases has to be avoided. Hot spots on reactors, irregularities in the feed composition due to the flow patterns, and interruptions of operation are the main causes of catalyst deactivation. These factors should be considered in designing and operating measures.

Table 1.4: Typical lifetime of some industrial heterogeneous catalysts

Process	Catalyst	Physical form	Typical life (years)
Ammonia synthesis	Fe/Al ₂ O ₃ /CaO/K ₂ O	Granules	5-10
Methanition (ammonia and hydrogen plants)	Ni/Al ₂ O ₃ /CaO	Pellets	5-10
Low temperature carbon monoxide shift	Cu/ Al ₂ O ₃ /ZnO	Pellets	2-6
Hydrosulphurisation	Co + Mo sulphides on Al ₂ O ₃	Extrudate	2-4
Natural gas steam reforming	Ni on ceramic support	Rings	2-4
Ethylene selective oxidation`	Ag/ Al ₂ O ₃	Rings	1-4
Partial oxidation of methanol to formaldehyde	Unsupported Ag	Granules/crystals	0.3-1
Ammonia oxidation	Platinum alloy	Gauze	0.1-0.5
Catalytic hydrocarbon reforming	Pt/ Al ₂ O ₃ /Cl ⁻	Spheres	0.01-0.5
Catalytic cracking	Synthetic zeolites	Fine particles	Very short

1.4 Oxidation Reaction

The selective oxidation reaction can be classified into three groups, i.e;

- 1) Dehydrogenation reaction.
- 2) Dehydrogenation and oxygen insertion reaction.
- 3) Catalytic oxidation

1.4.1 Dehydrogenation reaction

Dehydrogenation reaction is a reaction in which a hydrocarbon molecule is converted into a more unsaturated hydrocarbon by breaking C-H bonds and forming C=C bonds while the basic carbon skeletons of the hydrocarbon molecules remain intact. In the absence of oxidants, hydrogen is a byproduct. In such cases, the reactions are at high temperatures (above 773 K) because the thermodynamic equilibrium normally favors the reactants at low temperatures. At these high temperatures, undesired coking takes place and water is needed to reduce coking. The most common dehydrogenation processes are conducted in oxygen as this oxidant produces water as byproduct. The formation of water in the oxidative dehydrogenation (ODH) provides the thermodynamic driving force for the reaction. Thus, the reaction can be conducted at a lower temperature under oxygen, and deactivation due to coking is less severe. In these dehydrogenation reactions, the carbon skeletons of the hydrocarbon molecules remain intact (Kung and M.C. 1997).

Oxidative dehydrogenation of low alkanes over heterogeneous catalysis is an exothermic process. The perspective reaction is not subjected to the same thermodynamic limitations as the conventional, endothermic dehydrogenation process. Many vanadium oxide-based catalysts, molybdate-based catalysts as well as rare-earth element-based catalysts are reasonably effective for low alkane activation. However, their selectivity to the corresponding alkanes is generally low, especially at higher reaction temperature, which is necessary for high conversions (Lin, 2001)

1.4.2 Dehydrogenation and oxygen insertion reactions

In the reactions of dehydrogenation and oxygen insertion, oxygen is needed as an oxidant both for incorporation into the hydrocarbon molecules and the formation of water in the dehydrogenation steps. The general features of these reactions are that of C-H bonds being broken and C-O bonds are formed. Exceptions of these features are the oxidation of olefins to epoxides, in which no C-H bonds are broken; and the ammoxidation reactions of propene to acrylonitrile, in which C-N bonds are formed. In the attempts to correlate the changes in catalytic activity and selectivity with the properties of the metal oxide, a large variety of chemical factors have been investigated such as the presence of cation vacancies, the nature of the metal-oxygen (M-O) bond, the strength of the M-O bond, the crystal structure, and the surface acidity and basicity. Successful correlations, with limited groups of reactions have been reported from previous research studies.

To date, there is no distinct correlation between the catalytic activity and selectivity with the properties of metal oxide in the entire class of selective oxidation reactions. The potential economic relevance of selective oxidation is the key driving factor to solve this problem.

1.4.3 Catalytic Oxidation

Development of new catalysts and catalytic oxidation processes are the most important elements in the modern chemical industries. In the future, however, the petrochemical industry will probably gear towards the direct use of alkanes, which is even more economical due to the readily available raw materials, and low toxicity as compared to aromatics (Albonetti S, Cavani F et al. 1996).

Selective oxidation catalysis contributes significantly to the wellbeing of mankind, producing about 25 % of the most important industrial chemicals and intermediates used in manufacture of products and consumer goods. One of the most important applications of selective oxidation catalysts is the functionalisation of alkenes and aromatics because of the easy processing in which they can be obtained from petroleum (Pasquon 1987). The selective oxidation of lower alkanes to other chemicals is a new, promising and important target in the field of vapor -phase heterogeneous catalysis. However, such oxidations are usually accompanied by many difficulties due to low reactivities of alkanes as compared to alkenes and dienes. There are three categories to make an effective catalyst for oxidation reactions (Satterfield 1980):

- 1) Transition metal oxide in which oxygen is readily transferred to and from the structure. Most, but not all of the industrial catalysts of this type are mixed oxides, containing two or more cations; and the compounds are non-stoichiometric. Examples are iron molybdate catalyst for oxidizing methanol to formaldehyde, and bismuth molybdate for oxidizing propene to acrolein or ammoxidation of propylene to acrylonitrile.
- 2) Metals onto which oxygen is chemisorbed. Examples are ethylene to ethylene oxide on a supported silver catalyst, ammonia oxidation to nitric oxide on platinum gauze, and methanol to formaldehyde on bulk silver.
- 3) Metal oxides in which the active species is chemisorbed oxygen, as a molecule or in atomic form. These may also provide a significant additional mechanism under some conditions with metal oxide catalysts that also contain interstitial oxygen as an active species.

The achievement of high selectivity in oxidation of hydrocarbons is particularly challenging for both physical chemists and chemical engineers because the final result depends on many factors. Among the factors, the following lists are the most important:

- 1) In hydrocarbon oxidation processes, thermodynamic conditions favour the formation of carbon dioxide and water. Therefore, all products of partial oxidation are derived by kinetic control of the reaction;
- 2) The hydrocarbon-oxygen mixture can usually react along many different pathways in network of competing parallel and consecutive reactions and therefore, the catalyst must strictly control the relative rate of reactions, the acceleration of the series of consecutive elementary steps leading to the desired product, and the reactions which form unwanted by products.
- 3) The C-H bonds in the initial reactant are usually stronger than the intermediate products, which makes this intermediates prone to rapid further oxidation;
- 4) All oxidation processes are highly exothermic and thus, efficient heat removal must be ensured to control the reaction temperature and to prevent over-oxidation leading to catalyst damage with the appearance of localized hot spots in the reactor (Haber 2002).

Partial oxidation processes use air or oxygen to manufacture a variety of chemicals whereas complete catalytic oxidation is a practical process for elimination of organic pollutants in gaseous streams (Haber 2002).

1.5 Aim of the Study

The principal aim of the study is to develop and to evaluate in details the catalytic performance of complex system $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.125}$ oxide. Many catalytic systems that are employing molybdenum oxides as catalyst resulting in the vast investigations on the properties of this particular catalyst as well as its catalytic performance in the reaction.

The general focus area of this work is to develop novel and well-defined model catalytic system for selective oxidation of propane. Therefore, the approach to control the real and nano structure is much more important than the influence of additives. This research work concentrated on the following major objectives:

- a) To develop synthesis methods for mixed Mo-V-Te-Nb-O model systems with well-defined structures, morphologies and compositions.
- b) To determine the bulk and surface characteristics of mixed Mo-V-Te-Nb-O systems as well as the effect of surface modification by leaching technique.
- c) To screen the performance of each catalyst prepared using high throughput system for selective oxidation propane to acrylic acid
- d) To establish and optimize the structure-reactivity/selectivity relationships for propane oxidation over mixed Mo-V-Te-Nb-O catalytic systems.
- e) To modify the surface structure by leaching process.

In order to gain a better understanding, the work is planned based on flow-chart as depicted in Figure 1.6. The following subsections describe an overview on the scope of work. In this work, the as-prepared MoVTeNb oxide catalyst is extracted with three different solvents at different extraction time. Finally, all the catalysts are screened for its catalytic performance before further investigated by characterization techniques. The related flow-chart will be explained in details in Chapter 3.

The ultimate goal of this work is to contribute the fundamental understanding of partial oxidation catalysis i.e. to understand the function of a catalytically active material. A model catalyst system should be well-studied in order to aid the development of a more complex catalyst system in the industries (Knobl 2004).

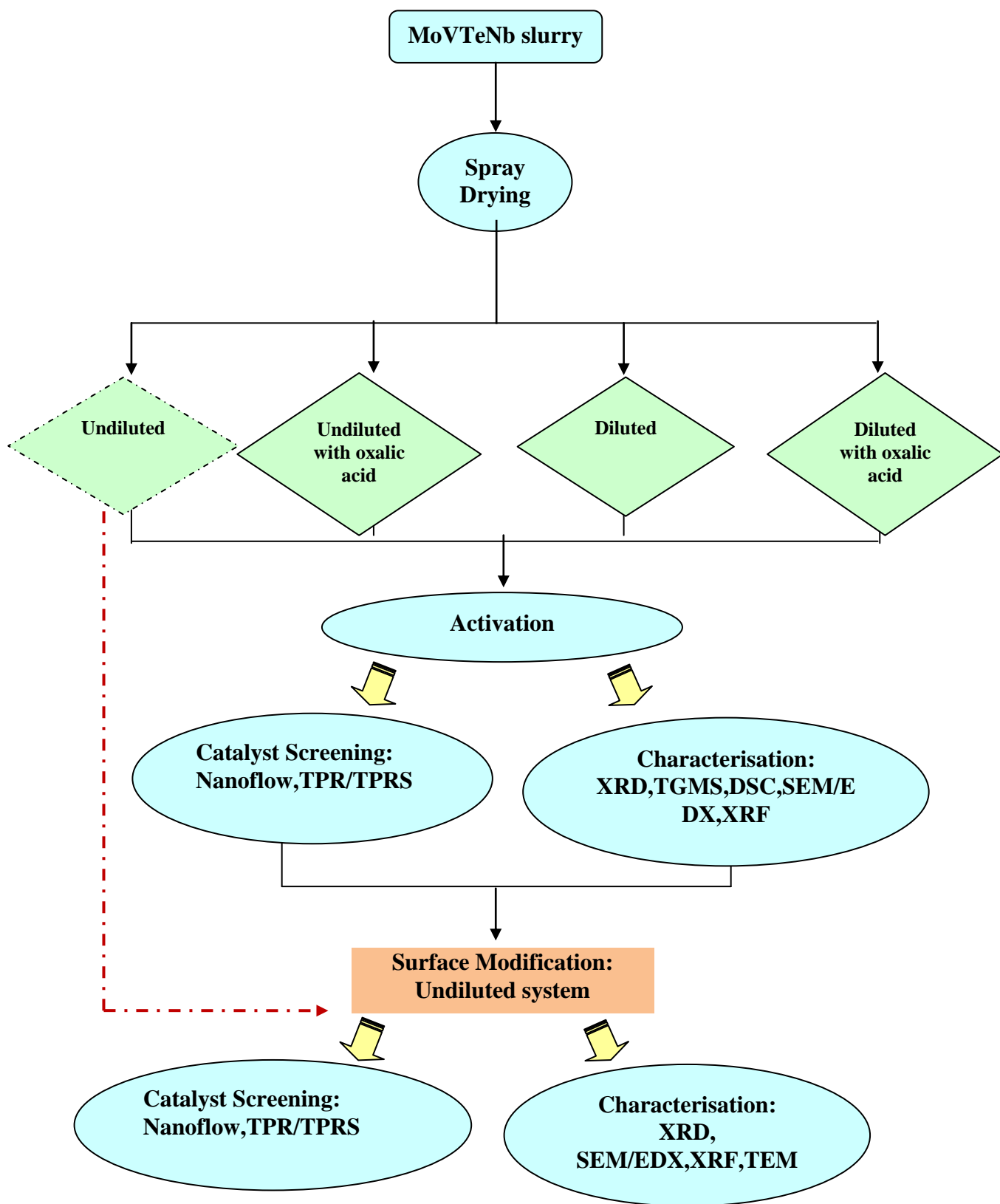


Figure 1.6: Flow-chart on work program