“Development of Nanomaterial for Environmental Application”

A Major Project Report

Submitted in Partial Fulfillment of the Requirements
for the Degree of

MASTER OF TECHNOLOGY

IN

CHEMICAL ENGINEERING
(ENVIRONMENTAL PROCESS DESIGN)

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Dedicated
To
My Beloved Family

Certificate

This is to certify that the Major Project Report entitled "Development of Nanomaterial for Environmental Application" by Mr. Chauhan Ricky J. (06MCH 014), towards the partial fulfillment of the requirements for the award of Degree of Master of Technology in Chemical Engineering (EPD) of Nirma University of Science and Technology is the record of work carried out by him under our supervision and guidance. The work submitted has in our opinion reached a level required for being accepted for examination. The results embodied in this major project work to the best of our knowledge have not been submitted to any other University or Institution for award of any degree or diploma.

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ABSTRACT

Noble metal supported catalysts are work horses in the petroleum, petrochemical and environmental pollution abatement catalysts. Generally conventional methods are used for the preparation of such materials. To increase the efficacy of the above catalysts we have made an attempt to adopt preparation methods known in the nano science. Particularly, use of capping agents like PVP and also polyol methods in the preparation of Pt, Pt-Pd supported nano catalysts.

A great interest at this time in the field of nanoscience is the dependence of the different properties of nanoparticles on their shape, size and also distribution. The morphology and particle size distribution of nanoparticles was found to play a crucial role in determining their catalytic properties. Platinum in nano forms play important role in many applications because of its extraordinary physico- chemical properties. For instance, it serves as a major catalyst in the industrial processes like reforming, oxidation, reduction and also selective oxidation. A major application, where mixer of noble metals used in the reduction of pollutant gases emitted from automobiles. All theses applications require the use of Pt in the finely divided state. For this reason, various chemical protocols have been developed for preparing nanoparticles.

Variations used in our preparations are:

1) Methods of preparation (PVP as capping agent, Polyol method)
2) Noble metal carriers (Alumina , Silica and β-Zeolite)
3) Preparation parameters studied are reflux duration, temperature and pH)
4) Noble metals (Pt, Pt-Pd bimetallics), Concentration of active metals

Materials prepared are tested with ICP for bulk analysis, UV for noble metal oxidation state, TGA for possible compounds/ complexes and TEM for nano particle size and shape characterization.

To know the catalytic properties of the materials prepared, we have chosen a model reaction of complete oxidation of propane under fixed HC/O_2 ratio. Light of curve have been built based on experimental data. To make useful correlations, we have bench marked our samples with proven commercial catalyst, which is being used for the nitrogen purification by completely oxidizing the HC. Pt loading from 0.02 to 0.3% was investigated; out of these samples polyol 0.08 Pt-Alumina(E) was found to be most active

catalyst. It is concluding that polyol 0.08 Pt- Alumina (E) gives light off temperature T_{97} at 205^0 C and commercial catalyst at 400^0C for combustion of propane under optimized conditions. Based on the above studies, we have zeroed on the above samples and proposed to test for commercial utilization.

Index

Chapter 1 Introduction

Chapter 2 Literature Review

Chapter 3 Experimental Methodology

Chapter 4 Results and Discussion

Chapter 5

List of Figures

List of Tables

Nomenclatures

GC	Gas Chromatograph
FID	Flame Ionization Detector
VOC	Volatile Organic Compound
ppm	Parts Per Million
WPV	Water Pore Volume
E	Engelhard
S	Sinopec
UV	Ultraviolet Visible
TGA	Thermogravimatric Analyzer
WHO	World Health Organization
NMHC	Non Methane Hydrocarbon
nm	Nanometer
SWCNTs	Single-walled Carbon Nanotubes
AAGR	Average Annual Growth Rate
$	Doller, U.S.A., currency
PVP	Polyvinylprrolidone
EG	Ethylene Glycol

Chapter 1

Introduction

1.1 Introduction

Air pollution [1,2] is the presence of any substance in the atmosphere at a concentration high enough to produce an undesirable effect on humans, animals, vegetation or materials, or to significantly alter the natural balance of any ecosystem. Air pollutants can be solids, liquids or gases. Health effects associated with chronic exposure to air pollution are a worldwide problem.

The World Health Organization (WHO) has estimated that ≈ 2.7 million deaths are attributable to air pollution throughout the world each year. Among the air pollutants of greatest concern are ozone, suspended particulate matter, nitrogen dioxide, sulfur dioxide, carbon monoxide, lead and other toxins. Of these pollutants, ozone is one of the most prevalent air pollutants in large cities and has been associated with increased respiratory illness and decreased lung function, particularly in children. Photochemical smog is a complex mixture of constituents that are emitted directly to the atmosphere (primary pollutants) and constituents that are formed by chemical and physical transformations that occur in the atmosphere (secondary pollutants). Ozone (O_3) is generally the most abundant species formed in photochemical smog. Extensive studies have shown that O_3 is both a lung irritant and a phototoxic. It is responsible for crop damage and is suspected of being a contributor to forest decline in Europe and in parts of the United States. Ozone is a secondary pollutant formed by the reactions of hydrocarbons (including volatile organic compounds (VOCs)) and NO_x.

1.1.1 VOC Emissions

Volatile organic compounds (VOCs) [2] include any organic carbon compound that exists in the gaseous state in ambient air. In some of the older literature the term VOC is used interchangeably with non-methane hydrocarbons (NMHC). VOC sources may be any process or activity utilizing organic solvents, coatings or fuel. Emissions of VOCs are problematic: some are toxic and most are precursors of O_3 and other species associated with photochemical smog. As a result of control measures designed to reduce O_3, VOC emissions are declining in the United States. Figure 1.1 shows estimates of nationwide emissions of VOCs. Emissions peaked » 1970 and have declined by » 40%

from that peak. Major sources continue to be industrial processes, solvent use (including solvents used in architectural coatings such as paints and varnishes), non-road sources (such as marine and garden equipment engines) and vehicular sources.

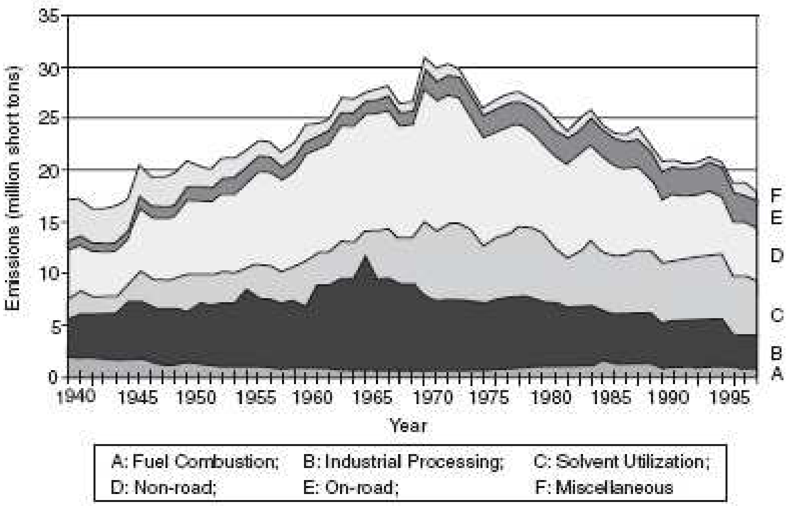


Figure 1.1: Trends in emissions of VOCs 1940-1998, in USA

Regulations on controlling VOCs have been issued world-wide .Germany having one of the strictest emission regulations: "TA-Luft", gives an emission limit of gaseous organic compounds of 50 mg/m^3 and 0.50kg/h. Indoor air quality has become a growing environmental issue over the past 20 years. An increasing number of health and comfort problems have been reported in once buildings, schools, residences and similar no industrial settings. In the 1980s and 1990s, it became clear that there are hundreds of measurable organic compounds in indoor air, presents either as gases or associated with particles. Field investigations of residences, once buildings and schools show that these contaminants come pre-dominantly from indoor sources such as new materials, cleaning materials, once machines and appliances and moist areas with favorable conditions for microbial growth. Furthermore, indoor concentrations are highly variable with time and place within a building. Any of hundreds of substances can be the most important with respect to concentration or potential health impact in a given space, at a given time. The health concerns them- selves are numerous. They range from vague dissatisfaction to frank irritation to chronic disease. Governmental regulatory bodies have set very few indoor air quality standards. The U.S. Food and Drug Administration (FDA) have set an indoor limit of 100 mg/m^3 of ozone for spaces where ozone is being generated.

1.2 VOC Removal Techniques

Many different techniques [3] for the removal of VOCs exist. An overview of various VOC control techniques is presented in Figure 1.2. They are classified into two different groups: Process and equipment modification: where control of VOC emissions are achieved by modification of the process equipment, raw materials (including solvents) or a change of process. Add-on control techniques: This can be added, typically as end-of-line equipment, to control the emissions

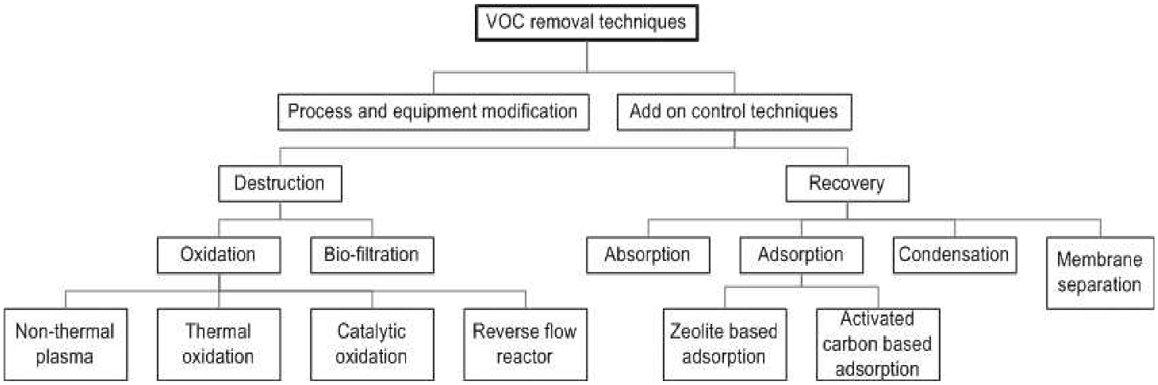


Figure 1.2: Classification of VOC control techniques.

Process and equipment modifications will usually be the most effective, but the applicability of this method is often limited, since the equipment and process have already been optimized. Therefore, add-on control techniques usually have to be used to meet the emission limits. The add-on control techniques are divided into two sub-groups, namely the destruction and the recovery of VOC. The choice of technique for VOC control depends on the type, value and concentration of VOC. The VOC control techniques shown in Figure 1.2.

Thermal oxidation for example, where the whole gas volume will have to be heated will require additional supply of heat. Furthermore, thermal oxidation happens at temperatures of 700-1000°C, which can produce elevated levels of nitrogen oxides, NO_x, (from nitrogen in air) that require further treatment of the off gas. Catalytic oxidizers decrease the operating temperatures to 300-500°C, leading to lower NO_x levels and lower energy requirements or auto thermal conditions. The major problems with catalytic oxidizers are the cost of the catalyst and the possible poisoning by non-VOC materials such as halogens, sulphur containing compounds, phosphorous and heavy metals. Furthermore, the VOC concentration must generally be above 1000 ppmv to function autothermally. Catalytic oxidation is the method of choice if the concentration of VOC allows performing the process adiabatically. For VOC concentrations lower than 1000 ppmv a two-step adsorber-incinerator process can be used. In this process the VOCs are first concentrated by adsorption at low temperature until the breakthrough occurs. The adsorbent is regenerated by desorption by heating and purging with inert gas. The desorbed, concentrated VOC is then passed through an incinerator and converted to harmless compounds by catalytic oxidation. The heat of combustion can be used for desorption. Adsorption of VOCs is normally carried out on activated carbon or zeolites. Activated carbon is cheaper, but zeolites have the advantages of being nonflammable, thermally stable and hydrophobic.

1.3 Catalysis in Pollution Control

A catalyst [4] is a material which influences a chemical process so that it will proceed towards chemical equilibrium faster, without consuming the catalyst. Often, several chemical reactions will take place at the same time, but if the catalyst is appropriately designed it will only lower the barrier for the desired reaction resulting in a much better selectivity and thereby a cleaner product.

Catalysts come in many forms. Most are complex solid materials, where the catalytic processes take place on the surface of the catalyst (heterogeneous catalysis). Heterogeneous catalysts are generally classified as bulk or supported catalysts. An example of a bulk catalyst is the Pt/Rh wire gauzes used for the oxidation of ammonia to NO for the production of nitric acid. However, most heterogeneous catalysts are supported catalysts, where an active catalytic phase (and sometimes promoters) is supported on a high surface area carrier, which serves to facilitate the dispersion and stability of the active catalytic phase. The surface areas of common supports (activated carbon, zeolites, silica gels, activated Al_2O_3) range from about 1.5 to 1500 m^2/g. The final catalyst may be formed into pellets or monoliths optimized for heat and mass transfer as shown in Figure 1.3. There are also catalysts which are dissolved in a fluid (homogeneous catalysis). The biological catalysts, the enzymes, belong to this class and are responsible for most chemical processes in living organisms.

Figure 1.3: Catalysts in the shape of pellets and a monolith.

Catalysts are widely used within chemical production, power production, refinery processes, and conversion of natural gases, chiral synthesis, agro chemistry, pharmaceutical processes, polymer and material production and bio-technology. The economic impact of catalysis is perhaps best illustrated by the fact that in the industrialized world heterogeneous catalysis is involved in 20-25% of the gross national products and 85-90% of the products of chemical industry are made by catalytic processes. *Many of the major problems society is encountering, such as the need for creating a production in balance with the environment, better use of fuels, more economical energy production and the reduction of* CO_2 *and other green house gases, will require solutions where catalysts play an important role.*

Important examples of *applications of catalysis in environmental protection are the reduction of toxic emissions from automobiles and energy production*. Catalysts are also applied extensively in refineries in order to produce cleaner transport fuels. This area receives currently great attention due to new and strict regulations being introduced world wide.

Furthermore, the development of new catalysts and catalytic processes can open for new selective chemical processes which may lead to a considerable reduction of undesired by-products or waste products.

1.3.1 Role of nanocatalysis in hydrocarbon combustion

The word nanocatalysis, [5] infact, does not apply to the catalytic phenomenon itself but to the intrinsic properties of the catalysts, which may change in the nanoscale. Properties of nanometer sized, supported metal particles directly affect their catalytic activities.

Nanocatalysis is one of the most exciting subfields of nanoscience. Unlike the common practice in catalysis where the catalytic performance scales with surface to volume ratio for the dispersed catalytic agent. Nanocatalysts are distinguished by their unique and non-scaleable properties that originate form the highly reduced dimensions of the active catalytic aggregates.

The aim of nanocatalysis is the promotion, enhancement, steering and control of chemical reaction by changing the size, dimensionality, chemical composition, morphology, or change state of the catalyst or the reaction center, and by changing the kinetics through nanopatterning of the catalytic reaction centers.

Many different technologies have been developed for VOC abatement, but one of the most versatile is catalytic oxidation to carbon dioxide. Volatile organic compounds (VOCs) are among the major contributors to environmental pollution, in a direct and indirect way [6].

Catalytic oxidation is one of the most important processes for VOC destruction because it takes place at much lower temperatures than those required for the thermal destruction [7]. Supported noble metals are very active for complete VOC oxidation [8].

Alkanes are amongst the most prevalent environmental VOC emissions due to their use as transportation fuels as well as being essential feedstocks for chemicals production.

Noble metal catalysts, such as Pd [9] and Pt [10] dispersed on a high area metal oxide, are the commercial catalysts of choice due to their high intrinsic oxidation activity. Palladium catalysts are the most active for the total oxidation of short-chain alkanes. Pt catalyst is most active for combustion of propane.

So, here we have developed efficient nanocatalyst with Pt, Pt-Pd noble metal for complete oxidation of propane.

Chapter 2

Literature review

2.1 Nanomaterials

A key driver in the development [11] of new and improved materials, from the steels of the 19th century to the advanced materials of today, has been the ability to control their structure at smaller and smaller scales. The overall properties of materials as diverse as paints and silicon chips are determined by their structure at the micro- and nanoscales. As our understanding of materials at the nanoscale and our ability to control their structure improves, there will be great potential to create a range of materials with novel characteristics, functions and applications. Although a broad definition, we categorise nanomaterials as those which have structured components with at least one dimension less than 100nm.

Materials that have one dimension in the nanoscale (and are extended in the other two dimensions) are layers, such as a thin films or surface coatings. Some of the features on computer chips come in this category. Materials that are nanoscale in two dimensions (and extended in one dimension) include nanowires and nanotubes. Materials that are nanoscale in three dimensions are particles, for example precipitates, colloids and quantum dots (tiny particles of semiconductor materials). Nanocrystalline materials, made up of nanometer-sized grains, also fall into this category. Some of these materials have been available for some time; others are genuinely new. The aim of this chapter is to give an overview of the applications of nanomaterials.

Two principal factors cause the properties of nanomaterials to differ significantly from other materials: increased relative surface area, and quantum effects. These factors can change or enhance properties such as reactivity, strength and electrical characteristics. As a particle decreases in size, a greater proportion of atoms are found at the surface compared to those inside. For example, a particle of size 30 nm has 5% of its atoms on its surface, at 10 nm 20% of its atoms, and at 3 nm 50% of its atoms. Thus nanoparticles have a much greater surface area per unit mass compared with larger particles. As growth and catalytic chemical reactions occur at surfaces, this means that a given mass of material in nanoparticulate form will be much more reactive than the same mass of material made up of larger particles [12].

In tandem with surface-area effects, quantum effects can begin to dominate the properties of matter as size is reduced to the nanoscale. These can affect the optical, electrical and magnetic behavior of materials, particularly as the structure or particle size approaches the smaller end of the nanoscale. Materials that exploit these effects include quantum dots, and quantum well lasers for optoelectronics. For other materials such as crystalline solids, as the size of their structural components decreases, there is much greater interface area within the material; this can greatly affect both mechanical and electrical properties. For example, most metals are made up of small crystalline grains; the boundaries between the grain slow down or arrest the propagation of defects when the material is stressed, thus giving it strength. If these grains can be made very small, or even nanoscale in size, the interface area within the material greatly increases, which enhances its strength. For example, nanocrystalline nickel is as strong as hardened steel. Understanding surfaces and interfaces is a key challenge for those working on nanomaterials, and one where new imaging and analysis instruments are vital. Nanomaterials are not simply another step in the miniaturization of materials.

2.1.1 Significance of Nanomaterials

A nanometer (nm) is one thousand millionth of a meter. For comparison, a single human hair is about 80,000 nm wide, a red blood cell is approximately 7,000 nm wide and a water molecule is almost 0.3nm across. People are interested in the nanoscale (which we define to be from 100nm down to the size of atoms (approximately 0.2nm)) because it is at this scale that the properties of materials can be very different from those at a larger scale.

Nanoscience define as the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales, where properties differ significantly from those at a larger scale; and nanotechnologies as the design, characterisation, production and application of structures, devices and systems by controlling shape and size at the nanometer scale. In some senses, nanoscience and nanotechnologies are not new. Chemists have been making polymers, which are large molecules made up of nanoscale subunits, for many decades and nanotechnologies have been used to create the tiny features on computer chips for the past 20 years. However, advances in the tools that now allow atoms and molecules to be examined and probed with great precision have enabled the expansion and development of nanoscience and nanotechnologies.

Properties of materials can be different [11] at the nanoscale for two main reasons. First, nanomaterials have a relatively larger surface area when compared to the same mass of material produced in a larger form. This can make materials more chemically reactive (in some cases materials that are inert in their larger form are reactive when produced in their nanoscale form), and affect their strength or electrical properties. Second, quantum effects can begin to dominate the behavior of matter at the nanoscale particularly at the lower end affecting the optical, electrical and magnetic behavior of materials. Materials can be produced that are nanoscale in one dimension (for example, very thin surface coatings), in two dimensions (for example, nanowires and nanotubes) or in all three dimensions (for example, nanoparticles**).**

2.2 Environmental Application of Nanomaterial

The applications of nanoparticles in environmental technologies [13] are collectively referred to as "environmental nanotechnology." Because nanoparticles have enhanced structural, magnetic, electrical, and optical properties, they have a significant potential to replace existing materials. Because of their superior properties, lower quantities will be used that will not only lower costs but also leave a reduced environmental footprint. Nanoparticles are finding applications in newer sensing technologies to detect pollutants at lower concentrations with greater selectivity and precision. Because of inherent size advantages they can be used to probe more difficult-to-reach regions, such as in the subsurface environment or complex engineered systems.

Nanomaterials also find great applicability in existing processes to reduce or prevent emissions or to convert effluents to useful by products. Nanoparticles can also be used to clean up contaminants that are present in the environment because of deleterious past practices.

2.2.1 Material Substitution

Hazardous materials [14] in manufacturing can be replaced by the more functional nanomaterials that are designed for specific, targeted functions resulting in reduced production of wastes. The more mature field of "green chemistry and green engineering” can guide the increased usage of nanomaterials. For example, nanomaterial-based catalysts can be used in place of more harsh catalysts for the synthesis of compounds. Film reactors with environmentally benign nanostructured photocatalyst films have been demonstrated to be effective in the synthesis of partial oxygenates from different precursors.

In contrast to conventional processes that use harsh operating conditions and toxic materials, these processes are environmentally benign. New classes of nonmaterial can also replace conventional materials with less toxicity and better performance. As an example, field emission displays constructed with carbon nanotubes can provide better functionality than the conventional cathode ray tubes that contain many toxic metals [13]. The field emission displays use only 0.5 g of carbon nanotubes per monitor compared with the large amount of lead in cathode ray tubes.

2.2.2 Nanoparticle Sensors and Detectors

The need of sensing [15] of pollutants and other compounds is of immense importance not only for public health protection but also in the design of safe and effective manufacturing processes. With the increase in potential terrorism acts, there is an increased need for effective sensors, and they are finding use in many homeland security applications. Developments in sensor technology have been under way for the last 2 decades, with an emphasis on miniaturization. Various nanostructured materials have been used in sensors. Upon exposure to gases such as NOx, the electrical resistance of single-walled carbon nanotubes (SWCNTs) has been found to change dramatically. A chemically functionalized SWCNT with covalently attached poly *m*-aminobenzene sulfonic acid has been demonstrated to have improved sensor performance for detection of ammonia, thus allowing higher sensitivity (as low as 5 ppm) than existing solid-state sensors. Boron-doped silicon nanowires have been developed that are highly sensitive sensors for chemical and biological species. These are developed a fully automated gas sensing and electronic parameter measurement system for testing miniaturized nanoparticle- based gas sensors. Such systems allow for the quick optimization of gas sensor configurations and for the understanding of their size-dependent properties. Gas sensing properties of zinc oxide (ZnO) nanostructures were found to have a sensitive response, good selectivity, and very short response time to very low concentrations of ethyl alcohol. Single crystal ZnO nanowires synthesized by gas-phase routes have been shown to be very sensitive to oxygen concentrations [16]. The detection sensitivity of these nanowires could be modulated by altering the gate voltage of the n-type semiconductor to extend the concentration range over which oxygen could be detected.

2.2.3 Nanostructured Sorbents for Process Emissions Control

Understanding particle formation and growth dynamics in combustion systems would allow developing strategies to minimize emissions. Several methods [13] have been proposed for the control of toxic metal emissions from combustors. The capture of heavy metal species in combustion systems by bulk sorbents has been demonstrated. However, once the outer surface has chemisorbed the metallic species, the inner volume is rendered ineffective, thus requiring a large volume of bulk sorbent to trace metal that is being captured. Furthermore, the bulk sorbents have been ineffective in certain environments; for example, when chlorine is present. They do not effectively suppress the nucleation of the heavy metal species that result in the formation of the sub micrometer sized aerosol that is difficult to capture in conventional particle control devices. An alternative is the use of a nanostructured sorbent [17] agglomerate process to capture the heavy metals in combustion environments. Several studies have been conducted to understand the effectiveness of this process for heavy metals, such as lead.

Capture efficiencies of lead exceeded 95% in a high-temperature environment on injection of a precursor that resulted in the formation of a nanostructured silica sorbent particle. The understanding of metallic species formation and growth pathways has resulted in the use of sorbent injection methods to control and prevent the release of toxic metal species, such as lead, cadmium, and arsenic, from a variety of combustion systems. The objective of the sorbent process is to suppress the homogenous nucleation pathway (to prevent eventual formation of the difficult-to-capture submicrometer-sized particles) and promote chemisorption of the metallic species vapors (to firmly bind the metal species to the sorbent to prevent leaching into the water body when disposed), as illustrated in figure 2.1. This is promoted by a large available specific surface area (increasing with decreasing particle size) of the sorbent material. It is essential that the sorbent particle is in a size range (preferably 500 nm) that would result in its effective capture in a particle control device.

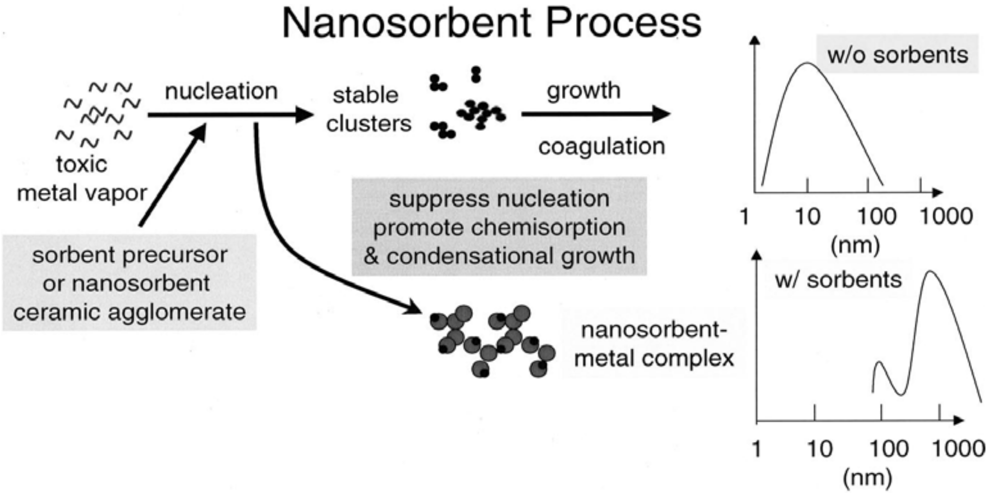


Figure 2.1 Mechanistic pathways of toxic metal species in combustion system resulting in particle formation

2.2.4 Remediation and Waste Treatment

Groundwater is often contaminated by [13] spills, agricultural practices, past waste disposal practices, and leaking underground storage tanks. Contaminated groundwater poses threats to human health by entering drinking water source streams, and it also damages ecosystems. Restoration of contaminated sites in the United States alone has been estimated to be a multibillion dollar industry. Remediation is often difficult because of inaccessibility and slow mass transfer rates from nonaqueous phases.

Size effects on reactivity at the solid-liquid interface are due to various reasons, such as the proportion of surface sites at edges or corners, the presence of distorted high-energy sites, contributions of interfacial free energies to chemical thermodynamics, the effects of altered surface regions, and quantum effects. Effective in situ remediation [18] is possible by transporting nanoparticles through porous media. Injection of iron nanoparticles into the subsurface has been demonstrated to be effective in the degradation of chlorinated organic compounds to benign forms.

Fundamental studies have also been conducted on the transport of nanoparticles in porous media and deposition onto surfaces. Nanoparticles can also be anchored onto substrates for the remediation of contaminated air and water streams. Various methods of anchoring onto substrates, such as carbon, zeolites, silica gel, and membranes, have been demonstrated for the treatment of contaminated streams. The use of nanostructured film reactors has also been demonstrated to be effective at remediation. Different deposition techniques have been studied to control film characteristics to obtain optimal reactor performance. Various configurations of nanoparticles in different geometries have been proposed to adsorb species, such as organics and heavy metals.

2.2.5 Paints

Incorporating nanoparticles in paints [11] could improve their performance, for example by making them lighter and giving them different properties. Thinner paint coatings (‘light weighting’), used for example on aircraft, would reduce their weight, which could be beneficial to the environment. However, the whole life cycle of the aircraft needs to be considered before overall benefits can be claimed. It may also be possible to substantially reduce solvent content of paints, with resulting environmental benefits. New types of fouling resistant marine paint could be developed and are urgently needed as alternatives to tributyl tin (TBT), now that the ecological impacts of TBT have been recognised. Anti-fouling surface treatment is also valuable in process applications such as heat exchange, where it could lead to energy savings. If they can be produced at sufficiently low cost, fouling-resistant coatings could be used in routine duties such as piping for domestic and industrial water systems. It remains speculation whether very effective anti-fouling coatings could reduce the use of biocides, including chlorine. Other novel, and more long-term, applications for nanoparticles might lie in paints that change color in response to change in temperature or chemical environment, or paints that have reduced infra-red absorptivity and so reduce heat loss.

2.3 Nanocatalysis

21st century is the time to evaluate the "total quality" in terms of the environment, energy and resources of the world. All the nations have to unite in resource protection, depollution, reuse and recycling concepts. In order to adopt sustainable development, scientist has to try the way to find out processes and products that maximize economic and environmental benefits and social responsibility. Catalysis is an economically and ecologically important field in the production integrated environmental protection. There are numerous examples of catalytic applications in various industries for a cleaner production and non-stop research is going on in the field of catalysis and green chemistry.

The field of nanocatalysis (the use of nanoparticles to catalyze reactions) has undergone an explosive growth during the past decade, both in homogeneous and heterogeneous catalysis. There have been more than 3000 papers [19,20] published in both types of nanocatalysis together.

Figure 2.2 [19] a shows the number of journal publications that have been published in the area of catalysis with nanoparticles for each year in the past decade. It can be seen that catalysis with nanoparticles is a growing field. Figure 2.2 b [20] shows the number of publications that have been published in the area of catalysis with nanoparticles in the top ten journals. The top five journals in this field in terms of the number of publications include Journal of Physical Chemistry B, Langmuir, Journal of the American Chemical Society, Journal of Catalysis, and Chemistry of Materials. The use of supported nanoparticles in heterogeneous catalysis accounts for majority of the publications, while colloidal nanoparticles in homogeneous catalysis accounts for only about 15-20% of the work.

The global market for nanocatalysts is projected to approach \$3.7 billion in 2004 and \$5.0 billion in 2009, at an average annual growth rate (AAGR) of 6.3% [19].

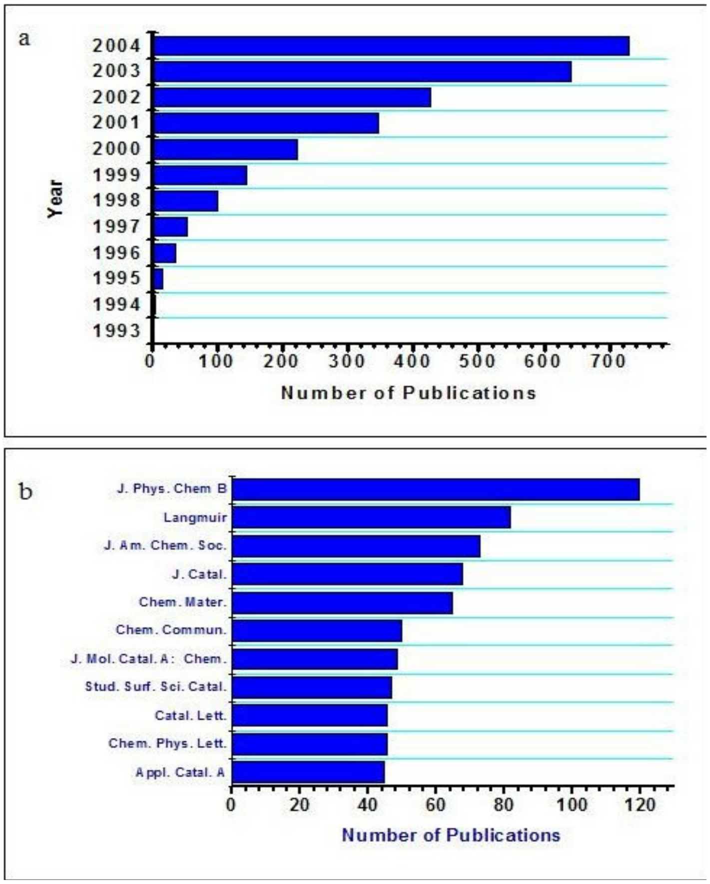


***Figure 2.2** —Statistics of the number of journal publications per year during the past decade in the area of catalysis with nanoparticles (a) and statistics on the 10 journals with the most publications in the area of catalysis with nanoparticles (b). The statistics are obtained using Scifinder Scholar.*

2.4 Synthetic Methods for the Preparation of Colloidal Noble Metals Nanoparticle

The synthetic methods which have been used include development of established methods of metal colloid preparation such as the mild chemical reduction of solutions of transition metal salts and complexes and newer methods such as radiolytic and photochemical reduction, metal atom extrusion from labile organometallic, and the use of metal vapor synthesis techniques.

2.4.1 Salt reduction

The reduction of transition metal salts [21] in solution is the most widely practiced method of generating colloidal suspensions of the metals. In aqueous systems, the reducing agent must be added or generated insitu, but in non-aqueous systems the solvent and the reducing agent can be one and the same. Easily oxidized solvents such as alcohols can thus function both as reducing agents and as the colloid diluents, and these have been widely used in colloid preparations, socalled “alcohol reduction process”, which is a very general process for the production of metal nanoparticles, often stabilized by organic polymers such as poly (vinylprrolidone), poly (vinyl alcohol), and poly (methyl vinyl ether).

The reduction of metal salts by added reducing agents [22] in non-reducing solvents is the oldest established procedure for the preparation of aqueous suspensions of colloidal metals. A wide range of reducing agents have been used in metal colloid syntheses, and they are frequently interchangeable from metal to metal. Thus, hydrazine hydrate has been used also for preparation of colloidal platinum, gold, copper, and bimetallic colloidal nanoparticle.

2.4.2 Thermolysis, Sonochemical Reduction Method

Oragnometallic compounds of tranisiton metals [25] decompose thermally to their repective metals under relatively mild conditions; these compounds provide a rich source of nanoparticle precursors. This method is widely applicable. The thermolysis of carbonyl-containing complexes of rhodium, iridium, ruthenium, osmium, palladium, and platinum in polymer solutions has been used to prepare polymer stabilized colloidal metals with particle sizes in the range 1- 10 nm. Sonochemical reduction is another method of synthesizing colloidal transition metal nanoparticles. Sonication is an acoustic cavitations phenomenon that involves the formation, growth, and explosion of bubbles in liquid media.

The sonochemical reduction method of precursor transition metal salts involves generation of the active species, reduction of the transition metal, and growth of the colloid in a sonicated liquid medium. These steps occur in different compartments: in gas phase into the cavitations bubbles where high temperature and pressure allow water pyrolysis to form H and OH radicals, at the interface between the cavitation bubbles and the solution, and finally in the solution. The sonochemical reduction method [25] has been applied for the generation of colloidal platinum, palladium, gold, and silver nanoparticles. In the case of transition metal salts, the reduction process mainly takes place at the bubble/solution interface and in solution and does not take place in the gas phase due to the low vapor pressure of the precursor transition metal salts.

2.4.3Photolysis and Radiolysis

Photochemical [23] colloid synthesis falls into two categories: reduction of metal salts by radiolytically produced reducing agents such as solvated electrons and free radicals, and the photolysis of photolabile metal complexes. Again, the essence of the preparative procedure is the generation of zero-valent metal under conditions which prevent at least retard the formation of bulk metal precipitates.

Pyrolysis [23] method has a long and important history in the formation of photographic images in silver halide emulsions. Research over the past decades by this method, encompassing both main group metals such as cadmium, thallium, lead, and other noble and non-noble transition metals. Radiolytic methods differ in the identity of the reducing species formed under irradiation, this being a function of solvent and any added solute. The radiolysis of aqueous solutions of metal ions produces solvated electrons, which may react either with the dissolved metal ions directly or with other solutes to produce secondary radicals, which then reduce the metal cation.

2.4.4 Ligand Displacement Method

The ligand displacement method [26] of forming colloidal transition metal nanocatalysts results from the reduction or ligand displacement of organometallic compounds. Platinum and palladium nanoparticles can be generated using this method. The reduction of zerovalent organometallic complexes can also be used to synthesize other transition metal nanoparticles such as ruthenium, nickel, cobalt, or copper nanoparticles

2.4.5 Condensation of Atomic Transition Metal Vapor

Transition metal vapors can be [24] co-condensed with organic vapors to form transition metal nanocatalysts. This method involves the evaporation of relatively volatile transition metals at reduced pressure and a subsequent co-condensation of these transition metals at low temperature with the vapors of organic salts. The colloidal transition metal nanoparticles are formed by nucleation and growth when the frozen metal/organic mixture is warmed to the point of melting.

The condensation process is carried out in acetone to form palladium and gold colloidal nanoparticles and has also in fluorinated solvents. This method of generating colloidal nanoparticles can lead to particles that are stable for several months, but a limitation of this method is that there is no precise control of the size of the nanoparticles. This is a major limitation in terms of applications in catalysis since control of size of the nanoparticles is necessary to conduct reproducible catalytic reactions.

2.4.6 Electrochemical Reduction Method

An electrochemical method [27] for preparing size-controlled transition metal nanoparticles in colloidal solution has been developed. This method involves the use of a sacrificial anode as the metal source, which is oxidized in the presence of a quaternary ammonium salt, which acts as both the electrolyte and the stabilizer. The precursor transition metal ions are reduced at the cathode to yield the colloidal transition metal nanoparticles. This method has been successfully used to synthesize palladium, nickel, copper, platinum, rhodium, and ruthenium nanoparticles. An advantage to this method of synthesizing transition metal nanoparticles is that the particle size can be controlled by the current intensity. When the current intensity is increased, smaller transition metal nanoparticles are produced. This involves the reduction of metal salts by reducing agents, such as hydrogen, alcohol, formaldehyde, hydrazine, alkali metals, anthracene activated magnesium, or boron hydrides. The synthesis often employs stabilizers which prevent undesired formation of metal powders. These include ligands (e.g. phenanthroline derivatives), polymers (e.g. polyvinylpyrrolidone), and surface-active agents. (e.g. tetra-alkylammonium salts**).**

2.5 Stabilizers in Colloidal Transition Metal Nanoparticles

Stabilization of the transition metal nanoparticles in colloidal solution is necessary in order to prevent agglomeration and aggregation. For catalytic applications, the choice of stabilizers for the transition metal nanoparticles is especially important. A good stabilizer is one that protects the nanoparticles during the catalytic process, but does not passivate the nanoparticle surface fully. If full passivation of the nanoparticles occurs, there will be a drastic loss of catalytic activity since there will be very few active sites available for catalysis.

On the other hand, a stabilizer that doesn't passivate the nanoparticle surface well and has many free sites available for catalysis will result in the nanoparticles falling apart during the course of the catalytic process. As a result, in the course of deciding a stabilizer to use for capping transition metal nanoparticles, one must find a balance between the passivation of the nanoparticle surface and the fraction of available sites for catalysis. In addition, the choice of stabilizer will also affect the size and shape of the colloidal transition metal nanoparticles formed. This is another important factor that should play a role in deciding the stabilizer to use to cap transition metal nanoparticles in colloidal solution. Some of the common types of stabilizers that have been used to cap colloidal transition metal nanoparticles such as polymers [28, 29, 30], block copolymers[31], dendrimers[32,33] surfactants[34], and other ligands[35] are discussed below **.**

2.5.1 Polymers

There have been numerous types of polymers [28] that have been used as stabilizers for colloidal transition metal nanoparticles. Some kinds of polymers that have been utilized include PVP, polyacrylate [29], polystyrene [30], etc. PVP has been used for cap spherical shaped palladium, platinum, and rhodium nanoparticles. It has also been used to prepare tetrahedral shaped platinum nanoparticles. Tetrahedral shaped nanoparticles are very attractive as catalysts due to a large fraction of their surface atoms being present on their edges and corners as opposed to their (111) facets.

2.5.2 Block Copolymer Micelles

The formation of colloidal metal nanoparticles in the micelles of block copolymers [31] has also been a common method of stabilizing the transition metal nanoparticles. Block copolymers used as stabilizers provide better protecting action compared to polymers by themselves. There have been many different block copolymer combinations that have been used as catalysts such as poly(ethylene oxide)-block-poly-2-vinylpyridine, polystyrene-*b*-poly-(sodium acrylate), *tert*-Bu acrylate-2-cinnamoyloxyethyl methacrylate, polystyrene-block-poly-4- vinyl pyridine, etc.

2.5.3 Dendrimers

The use of dendrimers [32] as stabilizers for transition metal nanocatalysts has been a fairly recent phenomenon. The encapsulating action of dendrimers is dependent on the generation of the dendrimers that is used. The higher generation dendrimers have closed, increasingly compact structures which can provide effective encapsulating action for the metal nanoparticles. The most common types of dendrimers [33] that are used in preparing colloidal metal nanoparticles are PAMAM based dendrimers and PPI based dendrimers. Higher generation dendrimers have a strong encapsulating action for the stabilization of the transition metal nanoparticles, but can lead to reduced catalytic activity if the dendrimer generation used is too high. This is an important factor to take into consideration when deciding which generation of dendrimers to use as stabilizers for transition metal nanocatalysts.

2.5.4 Surfactants

Surfactants combine both electrostatic and steric stabilization in order to stabilize transition metal nanoparticles in solution. Surfactants have a polar head group that is able to generate an electric double layer that is able to provide steric repulsion. Some kinds of surfactants[34] that have been use as stabilizers include N,N-dimethyl-N-cetyl-N-(2-ydroxyethyl)ammonium chloride salt, monoalkyl-monocationic surfactant, N-alkyl-N-(2-hydroxyethyl)ammoniumsalts, ammonium Bu_4N^+)/polyoxoanion etc.

2.5.5 Other Stabilizing Ligands

There are also many other kinds of ligands [35] that have been used to stabilize colloidal metal nanoparticles. Some of these ligands include phosphines, thiols, and amines. Platinum, palladium, nickel, and gold nanoparticles in colloidal solution have been stabilized using phosphine ligands.

Chapter 3

Experimental methodology

3.1 Design of Catalyst s

The design and development [36, 14] of catalysts with optimum performance which entirely depends on following five aspects:

a) Nature of active species.
b) Selection of suitable prometers
c) Nature of support.
d) Deposition of the active components
e) Pretreatments

The progress in understanding the phenomenon of catalysis on a molecular level [37] and the development of theories that describe the interrelationships between preparation- structure-properties- activity of catalysts, have, over a period of time, provided scientific bases for the development of catalysts.

3.1.1 Active species

The choice of active phase [38] to be used for catalyzing a particular reaction can be performed only by considering the reaction in detail. The major desired reaction alongwith all possible side reactions have to be considered first, without any reference to the surface. Next stage is to recongnise the types of reactions and general classes of catalysts, which have been used for each. Then a literature survey covering previous studies on the same reaction, studies on analogous catalyst reaction systems and activity patterns of relevance can provide the general guideline to the required type of system. This gives information about what is required from the catalyst. Another important factor is the active phase loading which has to be decided after considering the cost of the metal, solubility of the metal salts and specifity [39].

3.1.1.1 Noble Metals

Noble or precious metals like Pt, Pd, Ag, and Au frequently alloyed with closely related metals. Ru, Rh, Os, and Ir. Theses are usually supported on a metal oxide such as α-alumina, silica. The most frequently used precious metal components are platinum (Pt), Palladium (Pd) and Rhodium (Rh). The precious metals are most commonly used because of their ability to operate at lower temperatures.

As a general rule, platinum is more active for oxidation of paraffinic hydrocarbons, and palladium is more active for the oxidation of unsaturated hydrocarbons and CO. It is proven in the open literature that palladium is more active than platinum for methane oxidation while platinum is most active for propane oxidation than palladium. Platinum is better than palladium to active the mobility of oxygen on its surface.

Each precious metal or base metal oxide has unique characteristics, and the correct metal or combination of metals must be selected for each exhaust control application. The metal loading of the supported metal oxide catalysts is typically much greater than for noble metals, because of the low inherent activity per exposed atom of catalyst. This higher overall metal loading, however, can make the system more tolerant of catalyst poisons.

Historically, oxidation reactions have been carried out over either noble metal (e.g. Pt, Pd, Au and Ag) or transition metal oxides. Noble metals are more active. The main advantage of metal oxide catalysts is the lower cost of raw materials.

Most often supported rather than unsupported catalysts are applied, because they combine a high dispersion with a high degree of thermostability of the catalytic components.

The first factor to be considered in designing a combustion catalyst is the nature of the materials that are to be used. Typically, Pt and Pd are the active components for the vast majority of combustion applications. The high activity of the precious metals is related to their ability to activate H_2, O_2, C-H, O-H bonds. They far outperform other materials as catalysts for combustion reactions. In addition these metals are generally more resistant to deactivation and can be regenerated when necessary using relatively simple methods.

3.1.2 Choice of Promoter

Promoters are generally [14] used along with the catalytically active species with an intention to modify the properties of the catalyst in order to achieve better activity, selectivity and stability. This may be effected either by modifying the properties of the support or that of the active species.

3.1.3 Nature of Support

The metal catalyst [36, 40] is generally dispersed to a high surface area carrier, i.e., the carrier is given a washcoat of catalyst, such that small (2-3 nm diameter) precious metal crystallites are widely dispersed over the surface area, serving two basic functions. It maximizes the use of the costly precious metal, and provides a large surface area thereby increasing gas contact and associated catalytic reactions.

Proper selection of the carrier is critical. For example, in most cases, the carrier of a precious metal catalyst is a high surface area alumina having an effective surface area in the order of 120 m^2/g of material. Alumina used because of its unique phase transformation properties.

Efforts to redesign catalyst formulations involve both catalyst and washcoat. Altering the compositions of alumina washcoat by including various nonprecious metal oxides, such as oxides of barium, cerium and lanthanum as stabilizers, is being looked at promote catalyst activity before sintering and stabilize precious metal dispersion.

A particular advantage of using precious metal catalysts in supported form is that the support disperses the metal over a greater surface area and reduces thermal degradation. After the catalytic element is placed on the high surface area carrier, it is deposited on a mechanical support structure which determines the form of the catalyst. The support structure may have many forms, such as spheres, pellets, woven mesh, screen, honeycomb or other ceramic matrix structures designed to maximize catalytic surface area. The catalytic property of precious metals is also well known to be remarkably modified by using proper support materials in many catalytic materials. However, the effect of support materials on low-temperature catalytic combustions has not been examined, except that the activity of supported platinum catalyst in the combustion of methane was reported.

The choice of support has to be made on the basis of the properties of the active species, the nature of reaction, transport properties of reactants and products and conditions of reaction. The options for the selection of a support are really wide ranging from naturally occurring materials such as diatomaceous earth, kieselguhr, activated carbon, pumice, kaolin, bentonite, etc to inorganic supports such as alumina, silica, magnesia, zirconia, alumino silicates, etc. high surface area is an important prerequisite. But high surface area leads to increased dispersion and hence high activity. Loss of selectivity is generally a consequence of high activity and hence one should choose an optimum surface area rather than high surface area so as to maintain optimum activity. the support may have some interaction with the active species which may modify the catalytic action. This factor known as strong metal support interaction (SMSI) helps in many system to stabilize the active species and improve the activity.

3.1.4 Deposition of the active components

Dispersion [36] of oxides on high-area supports is carried out by one of four methods:

(1) impregnation
(2) ion exchange
(3) precipitation
(4) adsorption

3.1.4.1 Impregnation

Impregnation method is also known as ‘incipient wetness’. It is the simplest and most direct method of deposition. [41] The object is to fill the pores with a solution of metal salt of sufficient concentration to give the correct loading. In this method, support particle is heated to remove moisture. The amount of Solution is taken sufficient to fill the pores and wet the outside of particles. Amount of solution is calculated by the water pore volume method.

3.1.4.2 Ion exchange

A porous carrier is usually contacted with a solution containing one or more of the suitable metal ions for a period of time, then dried and calcined, to form the final catalyst [14]. The variables in this method are nature of metal salt solution and its concentration, equilibration time, the presence of competitive adsorbate ions alongwith metal salt, pH of the solution etc.

3.1.4.3 Precipitation

Precipitation [14] method involve the precipitation of support and active precursor together from basic solutions as hydroxides, hydroxyl carbonate etc. experimental parameters such as the nature of the precipitant (ammonia, ammonium carbonate, sodium hydroxide, sodium carbonate etc), final pH of the solution, hydrothermal treatments, aging etc determine the structure of the material formed which is generally a complex one.

3.1.4.4 Adsorption

Adsorption is [36] an excellent method for depositing small amounts. Powders or particles are dehydrated and “soaked” in the appropriate solution for suitable periods. Deposition is uniform, providing all pores are penetrated during the soaking time.

Adsorption from solutions may be either cationic or anionic depending on the properties of the surface. In general, zeolites are strong cation exchangers, silica is a weak cationic adsorber, alumina adsorbs both cations and anions weakly, magnesia is a strong anion adsorber and carbon prefers to form charge-transfer complexes with electron donation but also weakly adsorbs cations.

3.1.5 Pretreatments

Once the active species [14] is incorporated on the support, the excess solvent has to be removed by drying, without adversely affecting the deposited form of the active species. This step is very important in the pore filling impregnation method. A slow uniform heating rate and a minimal required temperature develops a gradientless distribution across the pellet. The dried catalysts have to again undergo a high temperature treatment known as calcinations in order to fire the active species on to the support surface firmly.

3.2 Complete Oxidation of Propane

In the current study the VOC model molecule was propane. The propane will be destroyed by total (complete) oxidation according to the following reaction scheme [42]:

$$C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O$$

3.3 Catalytic combustion [43] is an alternative to conventional thermal combustion. The two main advantages offered by catalytic combustors over flame combustors are:

1. Catalytic combustion can be carried out over a wide range of fuel concentration in air and at lower temperatures.
2. The lower temperatures result in attaining NO*x* emission levels substantially lower than possible with conventional combustors.

The support, which is itself usually not catalytically active, is a thermostable, highly porous material onto which active component is applied. Frequently used supports are: γ-Al_2O_3 (E), γ-Al_2O_3 (S), silica, and β-zeolite.

3.3 Validation for the Reaction System

A number of trail runs were taken before really arriving on the final design of the experimental setup and to ensure that the results obtained are reliable.

3.3.1 Thermal Homogeneity of Reactor Furnace

By measuring the temperature profile of the furnace under process condition, it has been ensured that, the catalyst bed is in isothermal region, which extends well below and above it.

3.3.2 Reaction with commercial catalyst

Numbers of trails runs were taken by charging the reactor with commercial catalyst (reference catalyst) to bench mark the reaction, where conversion has been established.

3.3.3 Feed and Product Analysis

On-line monitoring schemes such as Gas Chromatographs are very effective in order to continuously monitor reactor outlet composition and detect transient phenomena, or instant concentration to calculate the pollutant destruction efficiency.

3.3.4 Gas Chromatography

Gas chromatography [44] is a method of separation which employs a gas mobile phase and either a solid (GSC) or a liquid (GLC) adsorbed on a solid as a stationary phase. Gas chromatography is capable of separating very complex mixtures and the selectivity can be adjusted to separate almost any given pair of solutes by judicious choice of the stationary phase. The major limitation of gas chromatography is the requirement that the solute have a reasonable vapor pressure at a temperature.

SHIMADZU Gas Chromatograph GC 17-A is an analysis system designed to perform qualitative and quantitative analysis. The GC-17 A is a high grade gas chromatograph which has been developed for capillary analysis. The underlying is “easier and more precise capillary gas chromatography” [44].

The reaction was analyzed through SHIMADZU GC-17 a Gas Chromatograph with FID as a detector. The conditions of operation of GC were indicated in the Table 3.1.

Table 3.1 Conditions of GC Operation [45]

Detector	**Detector-1 : FID** **Range : 0** **Flame : ON**
Temp (°C)	**Column Oven Temp : 100/100** **Inj. : 125/470** **FID 1 : 125/470**
Flow	**Make-up (ml/min.) (AX2A) : 35, Pr. = 45 Kpa** **H2 (ml/min.) (AX3A) : 50, Pr. = 63 Kpa** **Air (N2/Air) (ml/min.) (AX3B) : 50, Pr. = 5 Kpa**
Flow Car-1 (He)	**Control Mode : Flow** **Toatl Flow (ml/min.) : 10** **Column Dia. (mm) : 2** **Column Length (m) : 2**

3.4 Preparation of Catalyst

We have prepared Supported Pt, Pd and Pt-Pd bimetallic catalyst using incipient technique adopting PVP capping agent as well as Polyol Process. Prepared catalysts were tested for complete oxidation of propane to carbon dioxide.

3.4.1 Preparation of supported Pt nanocatalyst by PVP process

Step 1: Preparation of Pt colloidal nanoparticle

The nanoparticle synthesis[46] was performed in a 150 ml two-neck round bottom flask equipped with a condenser, an oil bath and a magnetic stirrer, suitable quantity of PVP and $H_2PtCl_6.6H_2O$ dissolved in a mixed solvent of methanol and distilled water, then alkali (KOH, NH_3 etc) was added to adjust pH at 10 with vigorous stirring. The mixture was refluxed for 3 hr. to give a homogenous black colloidal solution – PVP-Pt.

Step 2 Impregnation / transfer of Pt nanoparticle on Support

PVP-Pt solution obtained from above mentioned process taken as WPV (calculation for WPV is in **APPENDIX 1**) and impregnated on to support. The final catalyst has dried at 120°C for at 12 hr and substantively calcined at 450°C for 3hr.

Samples prepared for our experimental study are described in Table 3.2.

Table 3.2 Composition for Preparation of Pt colloidal Solution by PVP Process

Catalyst Name	Pt(21.14 mg/ml) solution(ml)	methanol (ml)	D.W. (ml)	PVP (gm)	Alkali	Calcination (°C)	Relfux (hr)
Effect of Reflux time							
PVP 0.3Pt- Al_2O_3(E)-3h	4	10	10	1	~ 10-pH(KOH)	450	3
PVP 0.3Pt- Al_2O_3(E)-7h	4	10	10	1	~ 10-pH(KOH)	450	7
PVP 0.3Pt- Al_2O_3(S)-12h	4	10	10	1	~ 10-pH(KOH)	450	12
Effect of calcinations temperature							
PVP 0.3Pt- Al_2O_3(E)-450°C	4	10	10	1	~ 10-pH(KOH)	450	12
PVP 0.3Pt- Al_2O_3(E)- 650°C	4	10	10	1	~ 10-pH(KOH)	650	12

Reflux temperature: 80°C

3.4.2 Preparation of Supported Pt nanocatalyst by Polyol Process.

(a) Preparation of Pt Colloidal Nanoparticle

Step 1: Preparation of Pt Colloidal Nanoparticle

The nanoparticle synthesis[47] was performed in a 150 ml two-neck round bottom flask equipped with a condenser, an oil bath, PVP dissolve in EG solution in a beaker and $H_2PtCl_6.6H_2O$ take in a beaker, then both of this added to round bottom flask. The mixture was refluxed for 1 hr. to give a homogenous black colloidal solution-PVP-Pt.

Step 2: Impregnation of Pt nanoparticle on Support

PVP-Pt solution obtained from above mentioned process taken as WPV and impregnated on to support. The final catalyst has dried at 120°C for at 12 hr and substavely calcinationed at 650°C for 3hr.

Now here we have prepared different composition of the solution and different supports used for the preparation of 10 g of the catalysts as shown in Table 3.3

Table 3.3 Composition for Preparation of Pt colloidal Solution by Polyol Process

Catalyst Name	(21.14mg/ml)Pt solution(ml)	PVP (gm)	EG (ml)
Polyol 0.08Pt-alumina (s)	0.5	0.00705	17.5
Polyol 0.15Pt- alumina(s)	1.05	0.01	12.11
Polyol 0.30Pt -alumina(s)	1.89	0.02667	12.11
Polyol 0.02Pt-alumina(E)	0.18	0.00254	25
Polyol 0.035Pt-alumina(E)	3	0.0042	25
Polyol 0.08Pt-alumina(E)	0.5	0.00705	17.5
Polyol 0.15Pt-alumina(E)	1.05	0.01	12.11
Polyol 0.30Pt-alumina(E)	1.89	0.02667	12.11
Polyol 0.08Pt -Silica	0.85	0.01199	15.15
Polyol 0.15Pt -Silica	1.6	0.0225	14.4
Polyol 0.30Pt -Silica	5.8	0.08	36.33
Polyol 0.08Pt –β-Zeolite	0.85	0.01199	15.15
Polyol 0.15Pt - β-Zeolite	1.6	0.0225	14.4
Polyol 0.30Pt - β-Zeolite	5.8	0.08	36.33

Reflux temperature 160°C and duration is 1 h

(b) Preparation of supported Pt/Pd nanocatalyst

Step 1 Preparation of Pt/Pd colloidal nanoparticle

The nanoparticle synthesis[48] was performed in a 150 ml two-neck round bottom flask equipped with a condenser, an oil bath, $PdCl_2$ powder dissolve in ethanol and HCl in a beaker. PVP dissolve in EG solution in a beaker and $H_2PtCl_6.6H_2O$ take in a beaker, then Pd and Pt solution added to round bottom flask. The mixture was refluxed for 1 hr to give homogenous black colloidal solution Polyol-Pt/Pd.

Step 2 Impregnation of Pt/Pd nanoparticle on Support

PVP-Pt solution obtained from above mentioned process taken as WPV and impregnated on to support. The final catalyst has dried at 120°C for at 12 hr and substavely calcinationed at 650°C for 3hr.

We have prepared different composition of the solution used for the preparation of 10 g catalysts as shown in Table 3.4

Table 3.4 Composition for Preparation of Pt-Pd (bimetallic) Colloidal Solution by Polyol Process

Sample Name	**PVP (gm)**	**Pt(21.14mg/ml) Pt Soln. (ml)**	**$PdCl_2$ (gm)**	**EG (ml)**
Polyol 0.076 Pt-0.0394Pd/ alumina(E)	**0.017**	**0.66**	**0.00012**	**13.5**
Polyol 0.072 Pt-0.008Pd/ alumina (E)	**0.017**	**0.63**	**0.00014**	**13.5**
Polyol 0.07Pt-0.013Pd/ alumina (E)	**0.017**	**0.601**	**0.00022**	**13.5**
Polyol 0.1Pt-0.2Pd/ alumina (E)	**0.02**	**0.4**	**0.034**	**13.6**
Polyol 0.15Pt-0.2Pd/ alumina (E)	**0.02**	**0.56**	**0.034**	**12.4**

Reflux temperature 160°C and duration is 1 h

3.5 Characterization of Polyol0.08Pt/ γ-alumina

3.5.1.1Texture properties [26]

(A) Surface Area

Principle: - Measurement of surface area involves the principles of physical adsorption, which differ from chemical adsorption.

Physical adsorption is equilibrium coverage similar to surface liquefaction. Produced by van der Waals forces originating in surface atoms, interactions with the surface are similar to those between molecules and are approximately the same for all materials. First adsorption on surface atoms then followed by the generation of additional layers before complete monolayer forms. Process is exothermic at a equilibrium, amount decreases as temperature increases. Theoretical model for measurement of surface area was first derived by Brunauer, Emmett, and Telller, which known as BET equation. The surface area as in table 3.5

Table 3.5 Characterization of Polyol 0.08Pt/ γ-alumina: Surface Area

Parameter	Unit	Observed Surface Area
Surface area	m^2/gm	169

(B) Pore Size [26]

Pore size distribution is important feature of particle characterization. Macropores have been measured with mercury porosimeters and mesopores with nitrogen adsorption-desorption isotherm.

Table 3.6 Pore Size Distribution: Characterization of Polyol0.08Pt/ γ-alumina

Parameter	Unit	Observation
Micro pore (< 20A Radii)	%	0
Meso pore(20A To 500A Radii)	%	88.8
Macro pore (> 500A Radii)	%	11.2
Avg.Pore Radius	A^o	94

3.5.1.2 Inductively coupled plasma spectroscopy

The primary goal of ICP [49] is to get elements to emit characteristic wavelength specific light which can then be measured. The technology for the ICP method was first employed in the early 1960's with the intention of improving upon crystal growing techniques.An inductively coupled plasma (ICP) is a type of plasma source in which the energy is supplied by electrical currents which are produced by electromagnetic induction, that is, by time-varying magnetic fields. It is an analytical technique used for the detection of trace metals in environmental samples.

Table 3.7: Pt Loading: Characterization of Polyol 0.08 Pt/ γ-alumina

Parameter	Unit	Observation
Pt loading	%	0.077

3.5.1.3 TGA [50]

The thermogravimetric analysis is used to characterize any material that exhibits weight loss or phase changes as a result of decomposition, dehydration, and oxidation. Two modes are commonly used for investigating thermal stability behavior in controlled atmospheres:

(1) dynamic, in which the temperature is increased at a linear rate, and

(2) Isothermal, in which the temperature is kept constant.

The TGA is use for measuring the amount and rate of change in sample mass as a function of temperature and time.

Principle: The TGA-functioning portion of the instrument operates on a null balance. Physically attached to taut-band meter movement, the balance arm is maintained in a horizontal reference position by an optically actuated servo loop. When the balance is in a null position, a position sensor flag blocks an equal amount of light to each of the photodiodes(the light is supplied by a constant current infrared LED). As sample weight is lost or gained, the beam becomes unbalanced, causing an unequal amount of light to strike the photodiodes. The unbalanced signal, called the error signal, is acted upon by the control circuitry and reduced to zero, or nulled. This is accomplished by an increase or decrease in the current to the meter movement, causing it to rotate back to its original position (null position). The change in current necessary to accomplish this task is directly proportional to the change in mass of the sample. This current is converted to the weight signal.

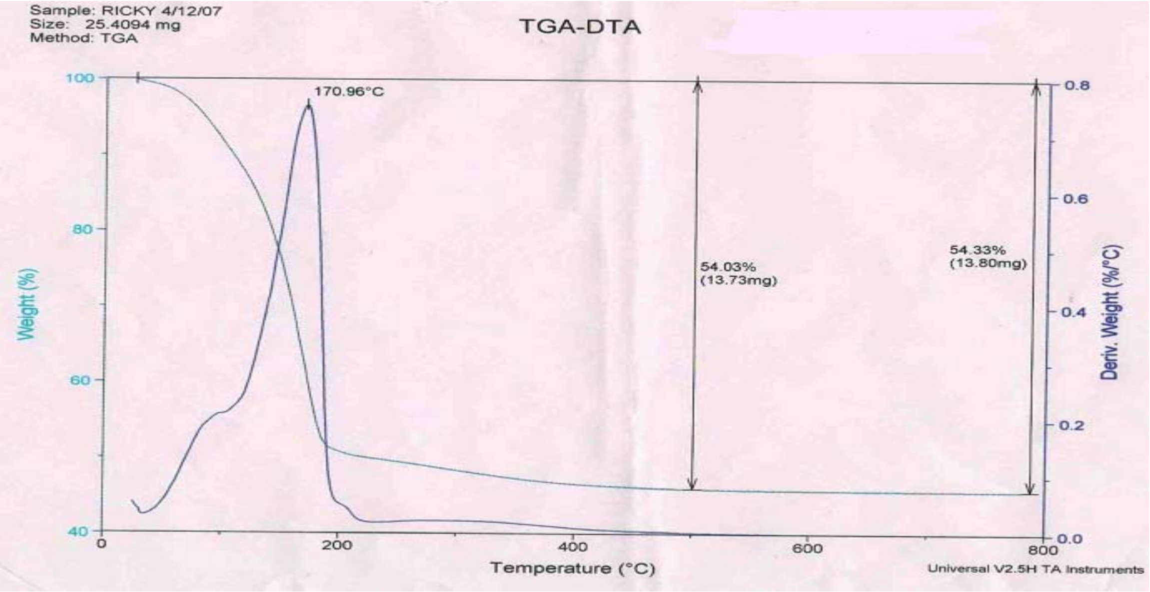


Fig. 3.1 TGA analysis : Polyol0.08Pt/ γ-alumina (E)

Thermal degradation behavior of the 0.08 wt. % Platinum catalyst synthesized by polylol process was examined by TGA as shown in Figure 3.1. It is observed that PVP and EG present in catalyst were exhibits a weight loss stage around 190°C – 200°C followed by a final decomposition of the EG that begins around 200 °C. Weight loss in the final stage can be attributed to decomposition of the EG present.

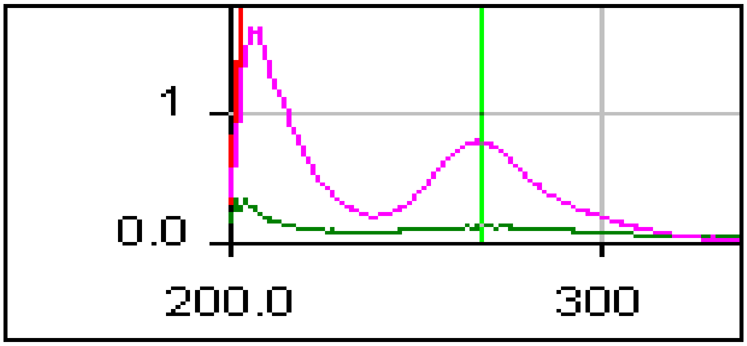
3.5.1.4 UV Analysis [51]

Ultraviolet-visible spectroscopy or ultraviolet-visible spectrophotometer (UV/ VIS) involves the spectroscopy of photons in the UV-visible region. It uses light in the visible and adjacent near ultraviolet (UV) and near infrared (NIR) ranges. In this region of the electromagnetic spectrum, molecules undergo electronic transitions. This technique is complementary. It measures the intensity of light passing through a sample

(I), and compares it to the intensity of light before it passes through the sample (I_o). The ratio I / I_o is called the transmittance, and is usually expressed as a percentage (%T). The absorbance, A**,** is based on the transmittance:

$A = -\log(\%T)$

The Pt colloidal solution prepared by PVP process [42]. From fig. 3.2 we observed peak in pink line is for the concentrated $PtCl_6^{2-}$ and after reflux Pt sol for 160°C for 1 hr. finally disappeared, corresponding change in the solution color from pale yellow to black dark color. The chemical transformation of Pt (IV) to Pt (O) appeared [52].



Absorbance v/s Wavelength (nm)

Fig. 3.2 UV-visible spectra: 0.08Pt Colloidal Solution.

3.5.1.5 Transmission electron microscopy: Microscopy technique [52] whereby a beam of electrons is transmitted through an ultra thin specimen, interacting with the specimen as it passes through it. An image is formed from the electrons transmitted through the specimen, magnified and focused by an objective lens and appears on an imaging screen, a fluorescent screen in most TEMs, plus a monitor, or on a layer of photographic film, or to be detected by a sensor such as a CCD camera. The first practical transmission electron microscope was built by Albert Prebus and James Hillier at the University of Toronto in 1938 using concepts developed earlier by Max Knoll and Ernst Ruska. Schematic diagram [53] of TEM as shown in fig. 3.3

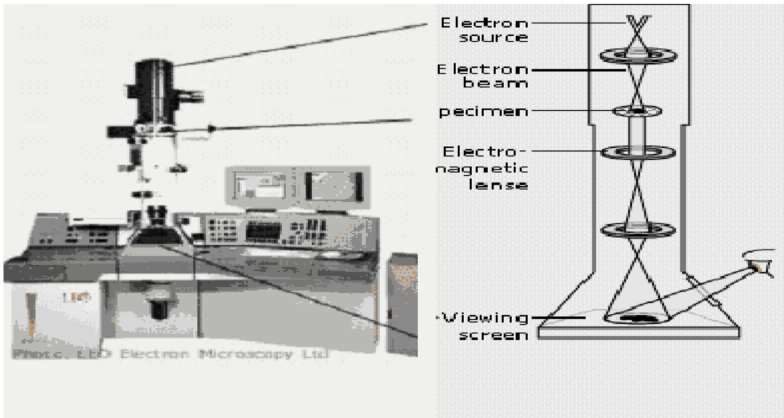
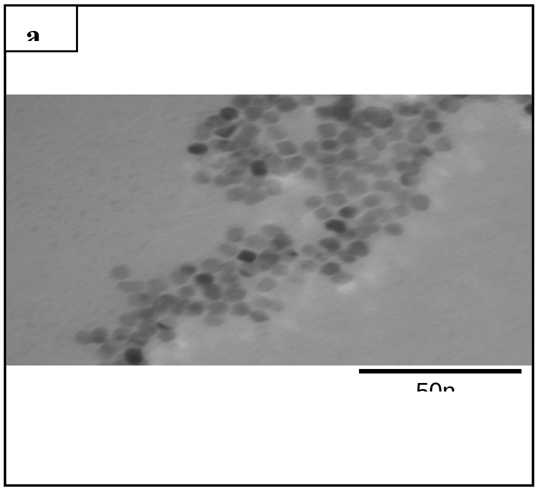
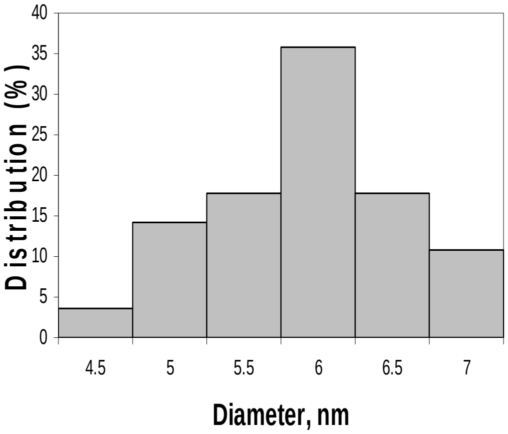


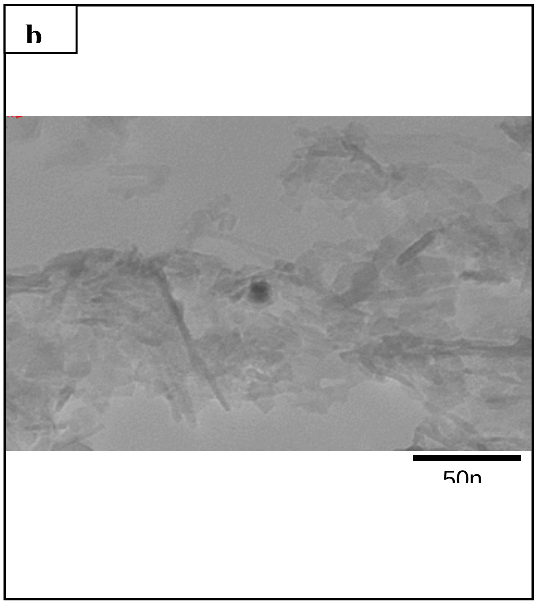
Fig. 3.3 Schematic diagram of TEM

The nanoparticle size were determined at 200KV using a Philips Technai 20 TEM equipped with a field emission source. The metal nanoparticle sample PVP-Pt colloid solution [54] as well as PVP-Pt supported [55] dispersed in ethanol was spotted by placing drop of on carbon coated copper grid and allowing it to evaporate in the air. TEM images of different samples like Pt colloid solution, after drying, calcination and after reaction has been studied.

Fig. 3.4 Photograh of TEM (Philips Technai 20)







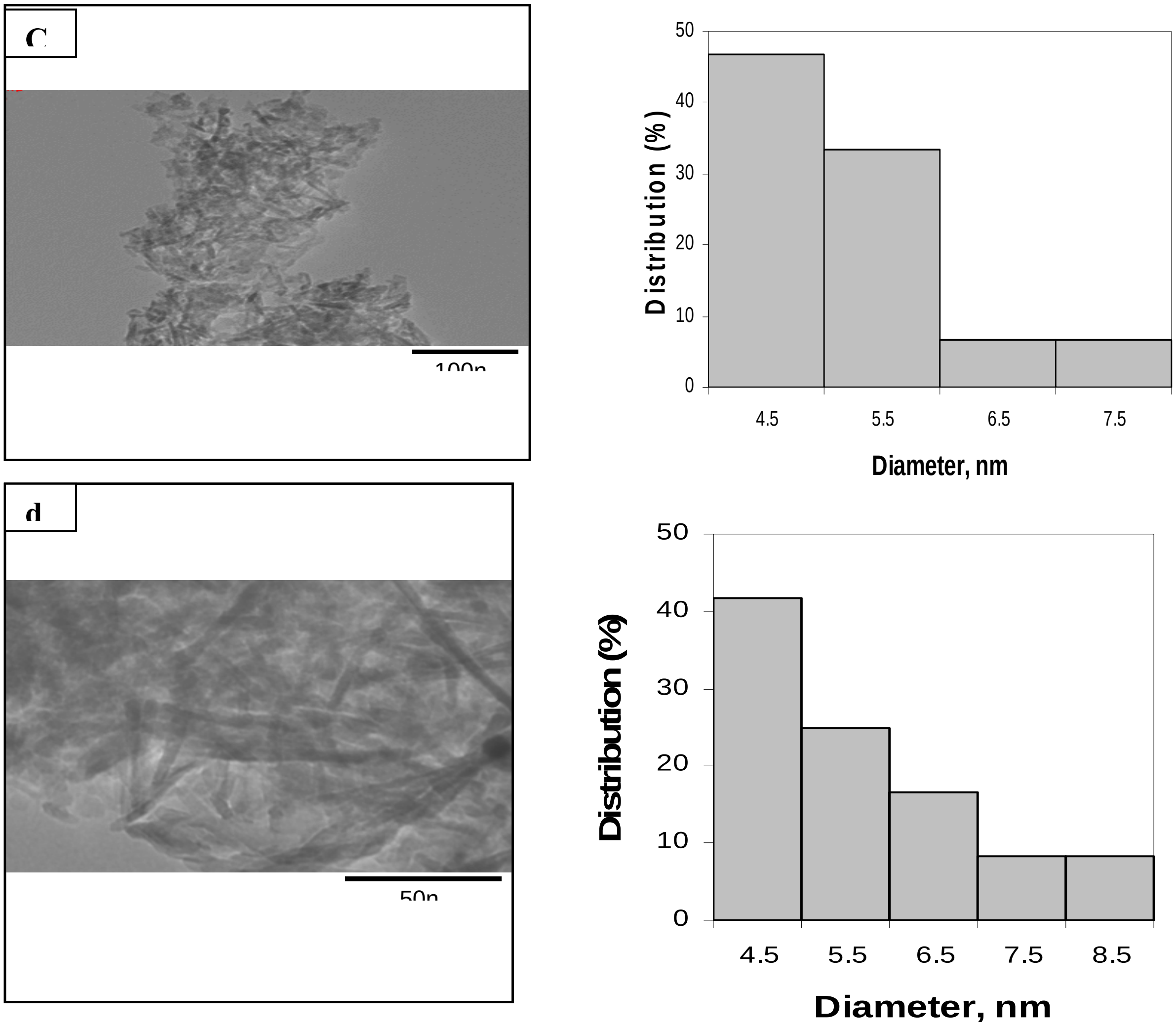


Fig.3.5 (a) TEM image(left) Polyol 0.08Pt colloid solution and the particle size distribution histogram(right) (b) TEM image of Polyol 0.08Pt-alumina after drying, (c) TEM photograph(left) and the particle size distribution histogram(right) Polyol 0.08Pt-alumina(E) after calcination (d) TEM photograph(left) and the particle size distribution histogram(right) Polyol0.08Pt-alumina after reaction.

From fig.3.5, (a) TEM photograph showed that the average diameter of Pt in colloidal solution [53] was 5.7 nm and the size distribution was narrow within a range of

4.5-8 nm. (b) From TEM image it is observed that the average particle size of Pt on alumina after drying, has observed 7.6 nm. (c) Showed TEM photograph of Pt on alumina after calcination, the average particle size was 4.8 nm. In case of Fig 3.5 (d) average particle size Pt on alumina after reaction was found 5.6 nm.

Chapter 4

Results and Discussion

4.1 Experimental Setup for Evaluation of Catalyst

Detail catalyst preparation was discussed in chapter 2. We have prepared supported Pt, Pt-Pd (bimetallic) catalyst by PVP as well as Polyol Process. The catalytic activity and evaluation of prepared catalyst was carried out in a fixed-bed down-flow quartz reactor (fig. 4.1) using the 3 ml of catalyst. The total gas flow rate was calibrated keeping in mind the H/C concentration, stoichiometric oxygen demand, GHSV and other reaction condition for the particular reaction. Propane gas was selected as the model reactant. A quantity of 3 ml of catalyst is charged in the quartz reactor as per the GHSV value 9000/hr and reactant gas flows are adjusted accordingly.GHSV calculation are indicated in the **APPENDIX-2**. For propane oxidation curves, the reaction was carried out from 120^0C to 350^0C.

Fig. 4.1 Experimental setup for catalyst evaluation

4.2 Laboratory Evaluation Conditions

The optimized laboratory evaluation conditions for total oxidation of propane are as follows.

Table 4.1 Laboratory Evaluation Conditions

Catalyst Volume	**3 ml**
GHSV hr-1	**9000**
Hydrocarbon	**Propane -6000 ppmv**
Oxygen	**As per stoichiometry for total oxidation**
Evaluation	**Propane conversion (97%)**

4.3 Process Parameter for 0.3% Pt Supported on Alumina by PVP

4.3.1 Effect of Alkali Reagents

We have studied the effect of alkali agents (NH_3 & KOH) as a chemical reducing agent for preparation 0.3% Pt supported on alumina. It is observed that, in case of ammonia there is no color change from yellow to dark black color, so it means that it is not efficient reducing agent while using KOH black dark color has observed using three hour reflux.

4.3.2 Effect of Reflux Time

0.3% Pt supported on alumina has been prepared by varying the reflux time from 3 to 12 hours. The corresponding colloidal solution is transferred on support as discussed in chapter 2. We observed that the catalytic propane conversion is increases with reflux time from upto 7 hours and no further change in conversion at 12 hours as shown in Table 4.2

Table 4.2 Effect of reflux time on conversion, Propane=6000 ppm, Oxygen=Stoichiometric, GHSV=9000 hr $^{-1}$

Catalyst	**Reflux Temp (°C)**	**Conversion (%)**
PVP 0.3Pt- Al_2O_3(E)-3h	**160**	**17**
PVP 0.3Pt- Al_2O_3(E)-7h	**160**	**97.37**
PVP 0.3Pt- Al_2O_3(E)-12h	**160**	**97.37**

4.3.3 Effect of support

Here we have prepared supported 0.3% Pt catalyst using two types alumina support provided by Engelhard and Sinopec. The effect of support on propane conversion as shown in figure 4.2 We observed using alumina (Engelhard) support the propane conversion has achieved 97% at 350°C and in the case of alumina Sinopec is about 20% at 350°C.

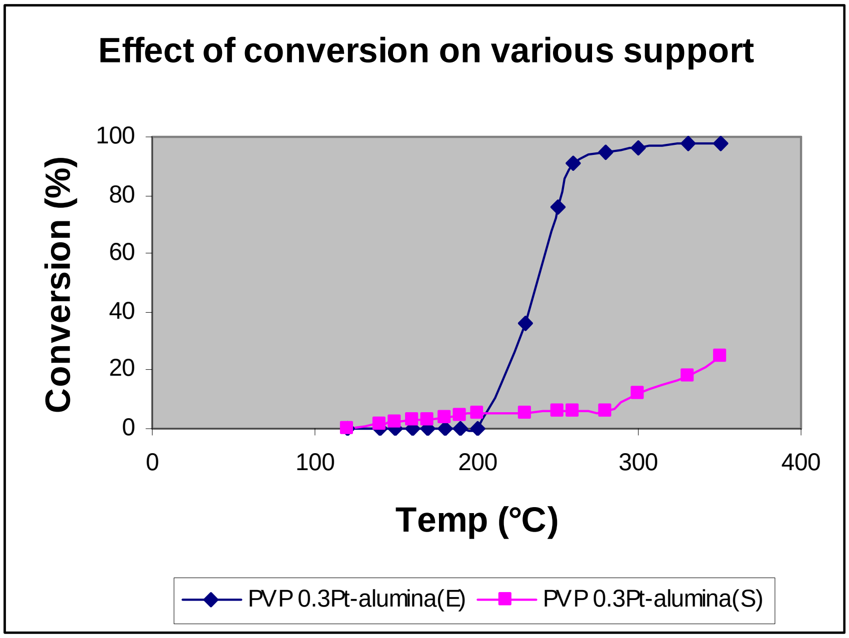


Fig 4.2 Effect of supports, 0.3% Pt, alumina (E), alumina(S)
(Propane=6000 ppm, Oxygen=Stoichiometric, GHSV=9000 hr $^{-1}$)

4.3.4 Effect of Calcination Temperature

We studied the catalyst calcinations temperature from 450°C to 650°C. At 450°C From fig 4.3 we observed that conversion of propane is 26% at 260°C. The reason for low conversion is that here we used PVP as a capping agent, so it may be blocking the some part of the active site of the catalyst and also is not completely removing the PVP at same temperature. At 650°C we are able to achieve conversion of 90%.

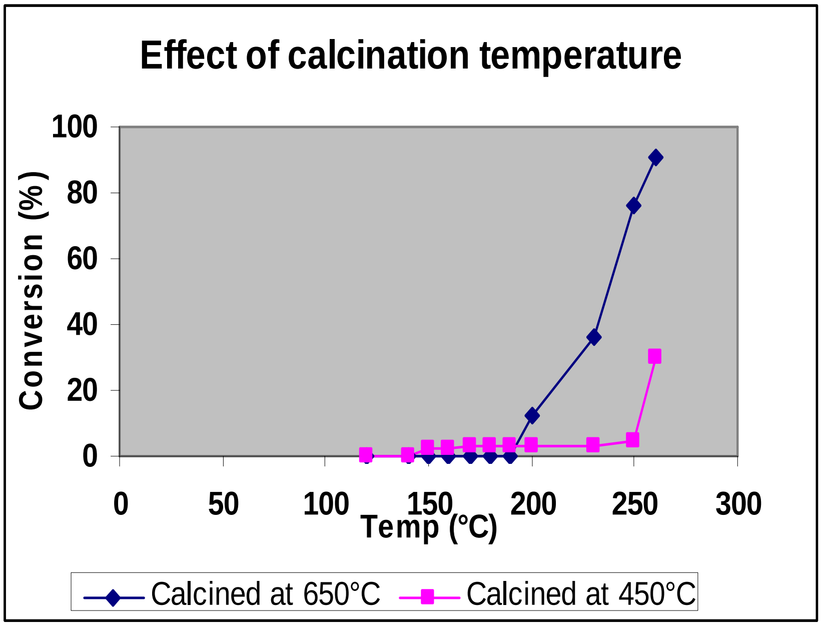


Fig. 4.3 Effect of Calcination Temperature: PVP 0.3Pt-alumina (E)
(Propane=6000 ppm, Oxygen=Stoichiometric, GHSV=9000 hr $^{-1}$)

4.4 Process Parameter for Pt Supported on Alumina by Polyol Process

On the basis of above results we have also prepared Pt supported catalyst using polyol process and studied for propane combustion.

4.4.1 Effect of Pt Concentration Variation on Different Supports

Here we studied effect of 0.08% to 0.3 % of Platinum concentration on different support such as alumina (E), alumina(S), silica, and β-zeolite under same reaction conditions as shown in fig.

From the fig 4.4 it seem that 0.08% to 0.3 % Pt supported on alumina (E) is giving excellent conversion compared to other supports so we are keeping Polyol 0.08Pt-alumina(E) for further process optimization study.

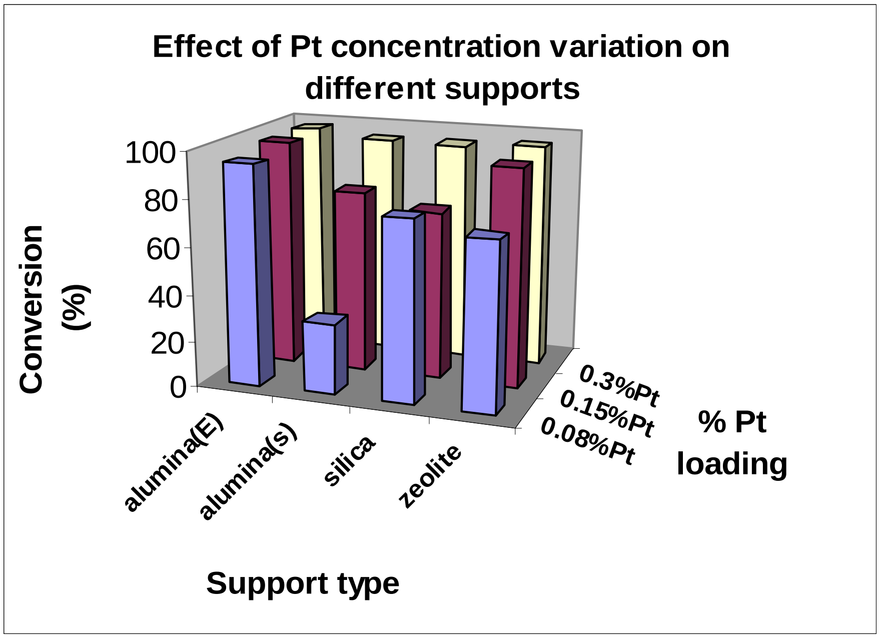


Fig. 4.4 Effect of Pt Concentration Variation on Different Supports
(Propane=6000 ppm, Oxygen=Stoichiometric, GHSV=9000 hr $^{-1}$)

4.5 Performance of Polyol-Pt/Pd (bimetallic) on Alumina (E)

Palladium is one of active metal for oxidation. So we have evaluated Pt/Pd bimetallic system for Propane Conversion. Here we have prepared different samples of low Pd loading in Pt/Pd bimetallic system and studied the effect on propane conversion. The observed results are shown in fig 4.5

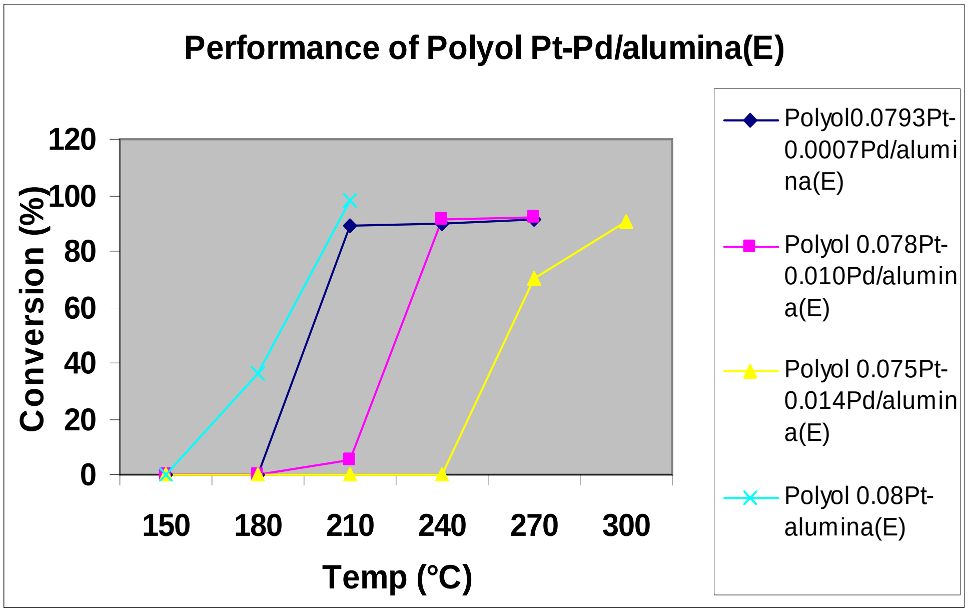


Fig. 4.5 Performance of Bimetallic Catalyst
(Propane=6000 ppm, Oxygen=Stoichiometric, GHSV=9000 hr $^{-1}$)

We were also carried out study of Pt/Pd bimetallic system by increasing the Pd concentration as shown in fig 4.6. After increasing loading also we are not able to achieve the higher conversion. Catalyst behavior is generally explained by the competitive adsorption of hydrocarbon and oxygen on same metal site and by difference the reactivity of adsorbed oxygen on metal surface. We conclude that reactivity of adsorbed oxygen molecules on Pd surface is less.

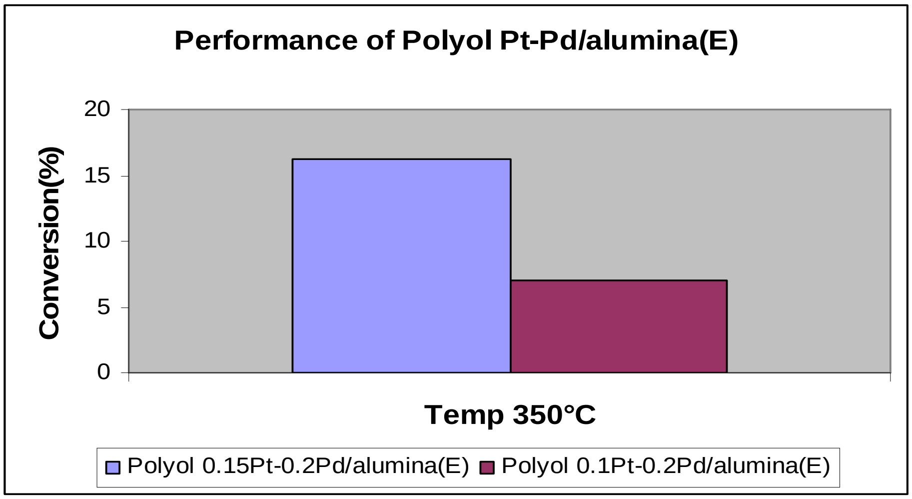


Fig. 4.6 Performance of Bimetallic Catalyst
(Propane=6000 ppm, Oxygen=Stoichiometric, GHSV=9000 hr $^{-1}$)

4.6 Effect of Pt Concentration on alumina (E)

We have performed Pt concentration from 0.02% to 0.3% Pt on alumina (E) as shown in fig. 4.7. We found that all the metal loading is giving encouraging results. So we are able to continue our all study by Polyol0.08Pt-alumina (E) i.e.98% conversion at 205°C.

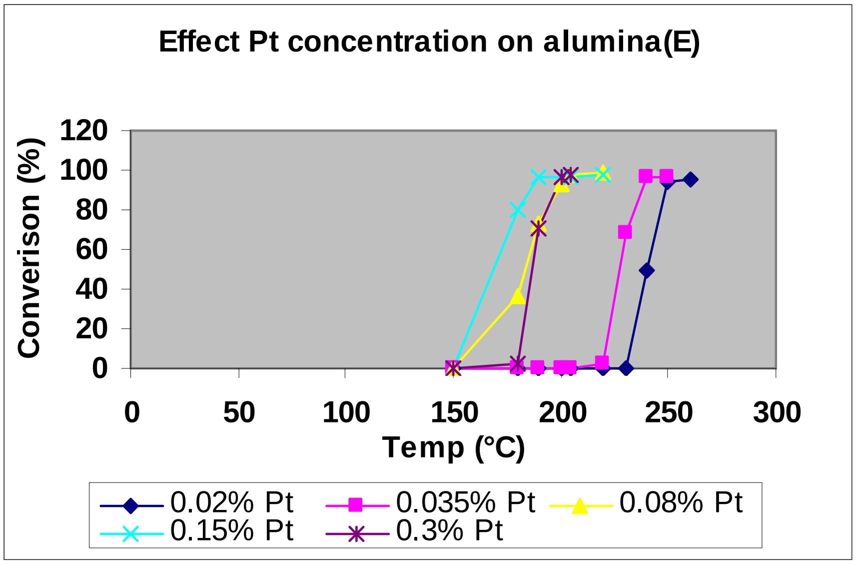


Fig. 4.7 Effect of Pt Concentration Variation for Propane Conversion (Propane=6000 ppm, Oxygen=Stoichiometric, GHSV=9000 hr $^{-1}$)

4.7 Effect of GHSV

In gas phase reactions Gas Hourly Space Velocity (GHSV) is most important parameter. GHSV is defined as the volume flow rate per catalyst volume. Here for Polyol 0.08Pt-alumina (E), we have varied the GHSV from 9000 to 27000/hr. It is observed that as GHSV increase beyond 9000/hr the propane conversion decrease substainly as shown in fig 4.8.

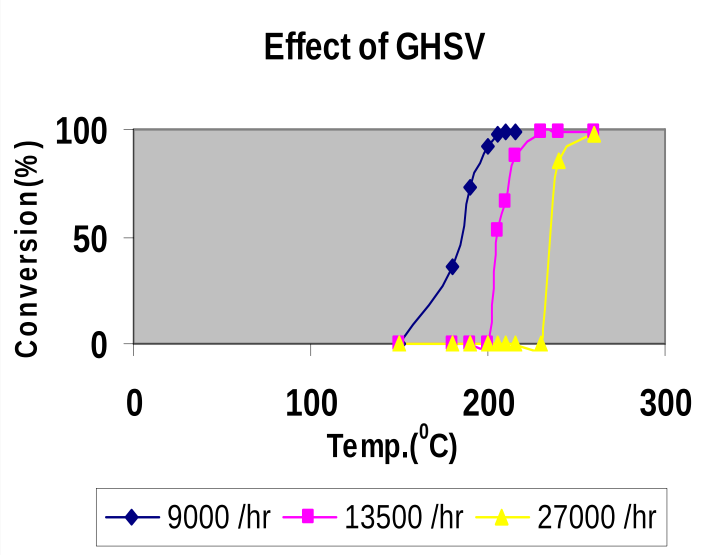


Fig. 4.8 Effect of GHSV Variation: Polyol 0.08Pt-alumina(E)
(Propane=6000 ppm, Oxygen=Stoichiometric, GHSV=9000 hr $^{-1}$)

4.8 Effect of Calcination Time on Conversion

We have studied the effect of catalyst calcination time from 1 to 5 hr at 650°C. In case of Polyol 0.08Pt-alumina (E). we observed that as calcination time increase conversion increase upto 3 h and start decrease at 5 h. as shown in fig. 4.9. If calcination time increases after 3 h it may be some adverse effect on catalyst surface.

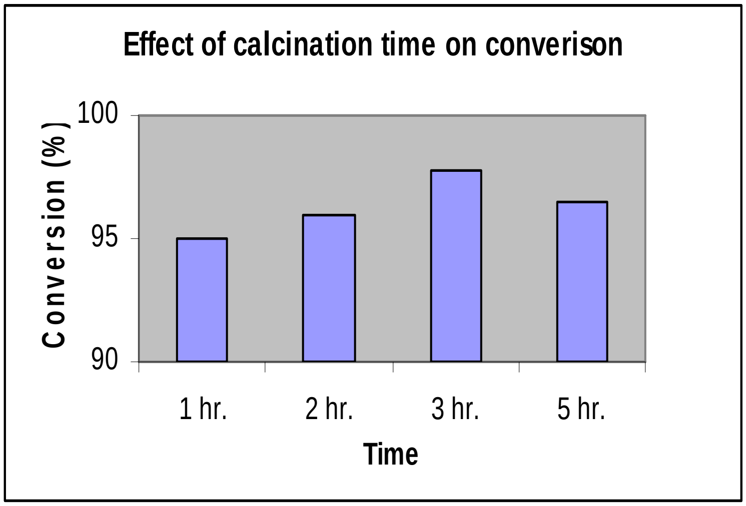


Fig. 4.9 Effect of Calcination time: Polyol 0.08Pt-alumina (E)
(Propane=6000 ppm, Oxygen=Stoichiometric, GHSV=9000 hr $^{-1}$)

4.9 Light-off curve study

Light –off curves are widely used to compare the intrinsic reactivity. We studied light-off curves at T 50 and T 97. T 50 & T 97 corresponds to the temperature required to reach 50% 97% respectively. Here we have compared the various Pt loading from 0.02 to 0.3% Pt on alumina with commercial catalyst under same reaction conditions as shown in from fig 4.10 to 4.14

Fig.4.10 Light-off Curve Study & Performance Comparison with Commercial Catalyst (Propane=6000 ppm, Oxygen=Stoichiometric, GHSV=9000 hr $^{-1}$)

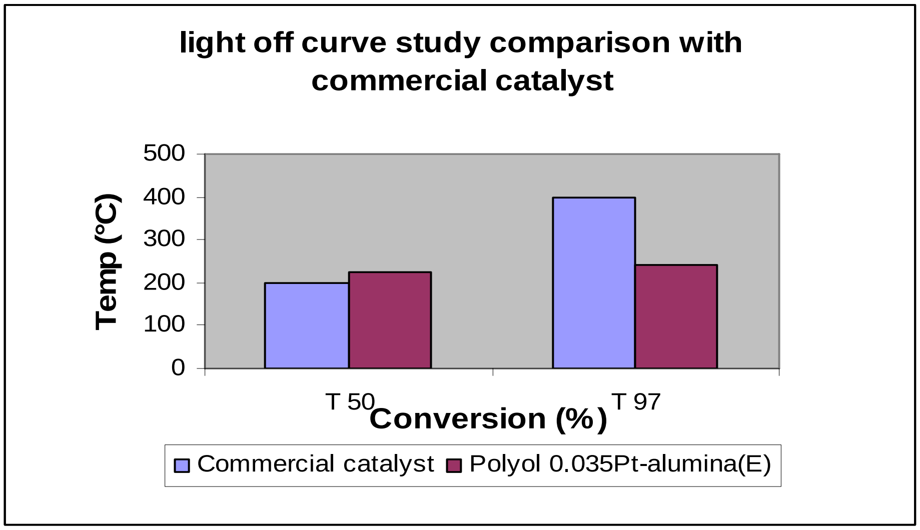


Fig. 4.11 Light-off Curve Study & Performance Comparison with Commercial Catalyst (Propane=6000 ppm, Oxygen=Stoichiometric, GHSV=9000 hr $^{-1}$)

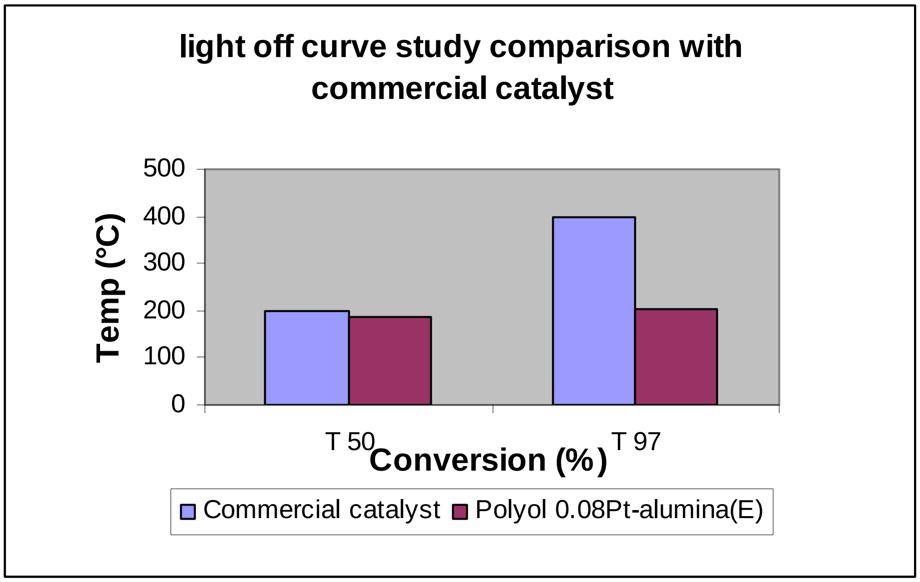


Fig. 4.12 Light-off Curve Study & Performance Comparison with Commercial Catalyst (Propane=6000 ppm, Oxygen=Stoichiometric, GHSV=9000 hr $^{-1}$)

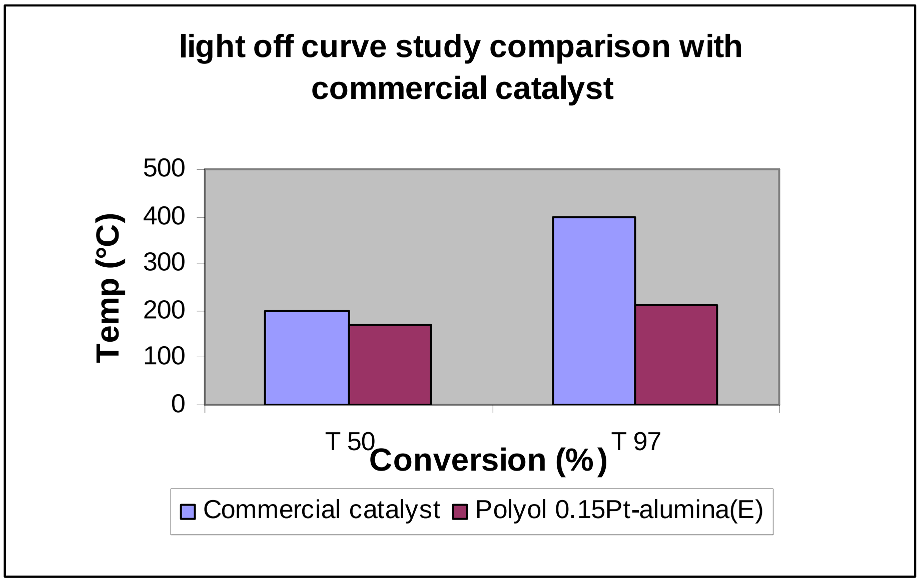


Fig. 4.13 Light-off Curve Study & Performance Comparison with Commercial Catalyst (Propane=6000 ppm, Oxygen=Stoichiometric, GHSV=9000 hr $^{-1}$)

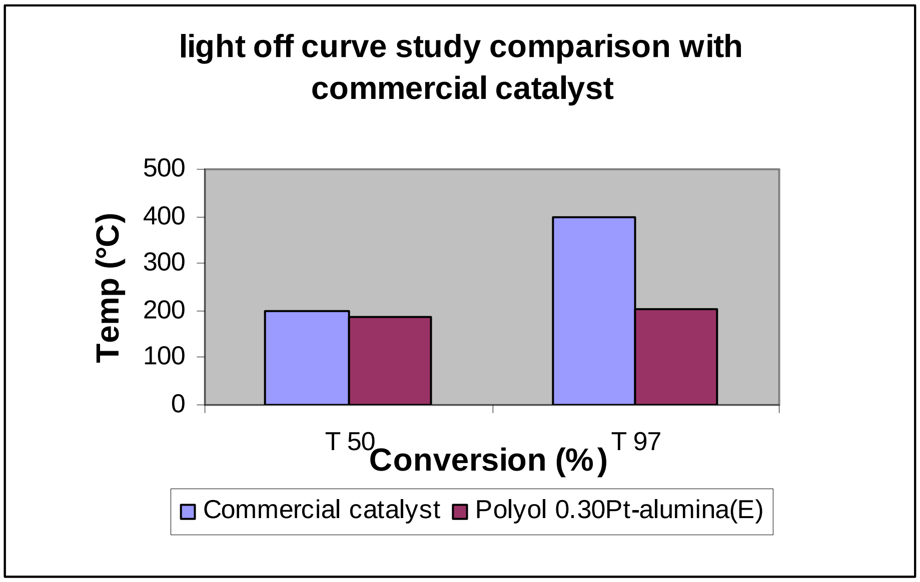


Fig. 4.14 Light-off Curve Study & Performance Comparison with Commercial Catalyst (Propane=6000 ppm, Oxygen=Stoichiometric, GHSV=9000 hr $^{-1}$)

4.10 Comparison of Polyol 0.08 Pt-alumina (E) with Commercial Catalyst

We have compared the catalytic activity of optimized Polyol 0.08Pt-alumina (E) catalyst with commercial catalyst. It is observed that this novel Pt based nanocatalyst is highly active at lower temp and also have low metal loading compared to commercial catalyst as shown fig. 4.15

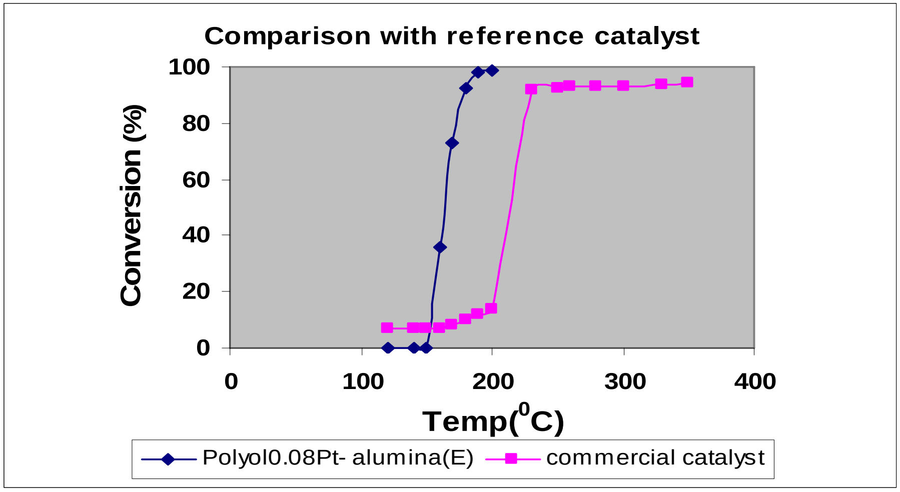


Fig. 4.15 Performance Comparison: Polyol 0.08Pt-alumina(E) with Commercial Catalyst (Propane=6000 ppm, Oxygen=Stoichiometric, GHSV=9000 hr $^{-1}$)

4.11 Time on stream activity study

The result of the conversion of Propane is presented here as a function of time on stream in fig. 4.16 for severe reaction condition to ascertain the activity and stability of the Polyol 0.08Pt-alumina (E) for several hours on stream.

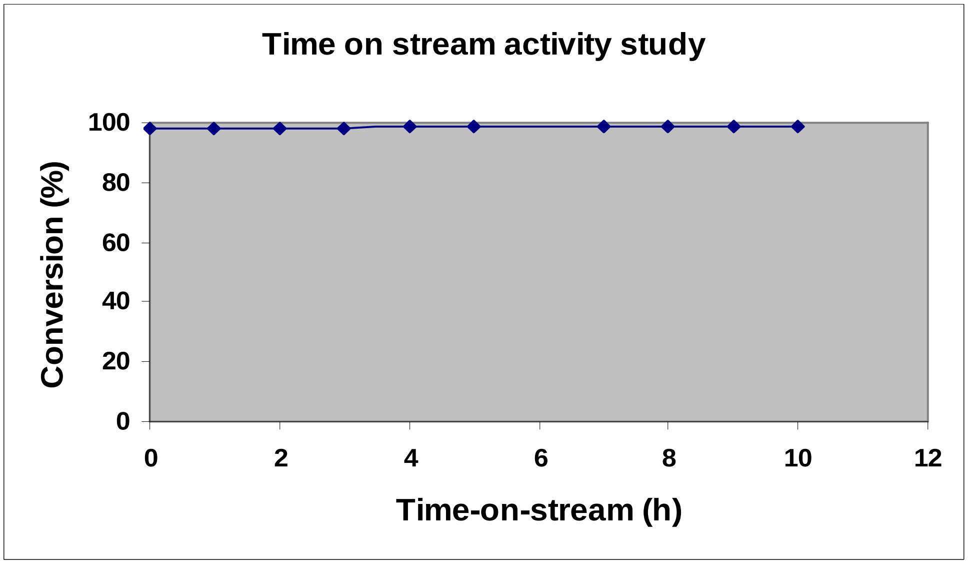


Fig. 4.16 Time on Stream Activity Study of Polyol 0.08Pt-alumina (E) for Propane Conversion at 215°C.

Reaction condition: Propane=6000 ppm, Oxygen=Stoichiometric, GHSV=9000 hr $^{-1}$

We investigated Polyol 0.08Pt-alumina (E) for 10 hours on stream under similar reaction conditions. We observed that the catalyst is highly stable and after 10 hr also the catalyst has not deactivated and giving 98% conversion of the hydrocarbon as shown in fig 4.16. The detailed result sheet of the study is outlined in the APPENDIX-3

4.12 Kinetic Study:

Experimental kinetic data were generated for the different flow rates (i.e. W/F) at constant catalyst loading at the three different temperatures of 182°C,186°C, 190°C, and 194°C.

Effect of W/F

Figure 4.17 describes the effect of W/F on conversion of Propane at different temperatures. Detailed Calculation given in **APPENDIX-4**

$$\text{Conversion of Propane} = \frac{\text{(Propane in feed)}-\text{(Propane in Product)}}{\text{(Propane in feed)}} \times 100$$

Effect of W/F on Conversion of Propane

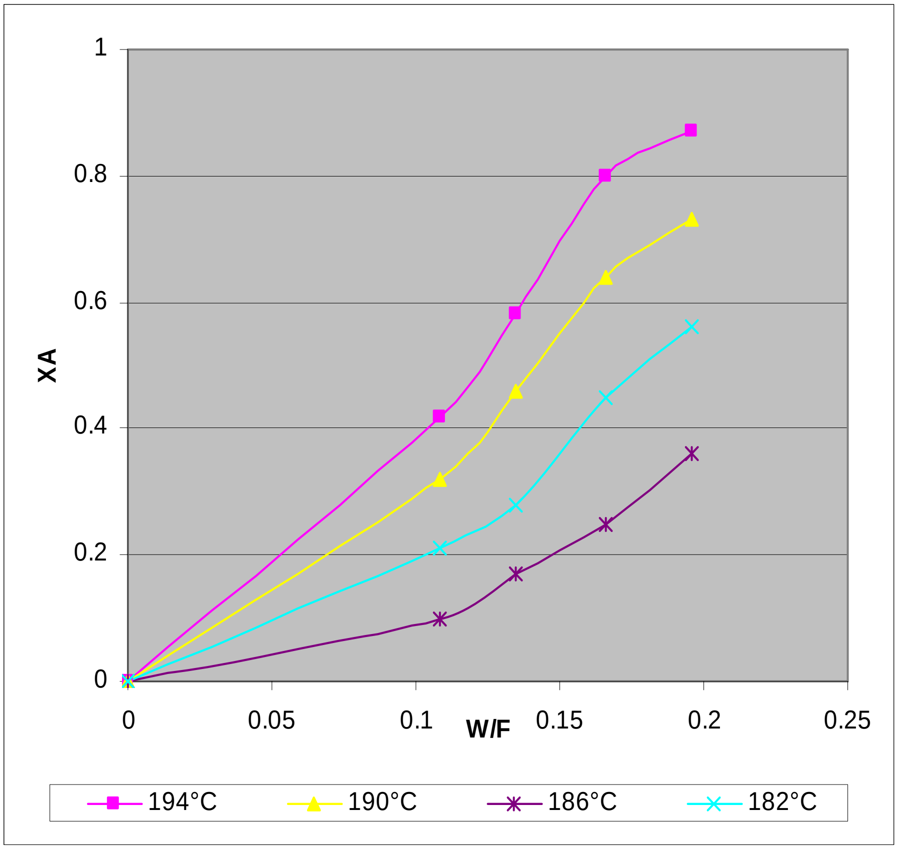


Fig. 4.17Effect of W/F on Conversion over Polyol 0.08 Pt on alumina (E)

The conversion of Propane as a function of W/F at different temperature are presented in Table 4.3

Table 4.3: Conversion of Propane at different W/F over polyol 0.08 Pt on alumina (E)

T=194°C	
W/FAO, (kg.cat.hr/mol)	**XA, Conversion**
0.196	0.86
0.166	0.72
0.135	0.38

T=190°C	
W/FAO, (kg.cat.hr/mol)	**XA,Conversion**
0.196	0.73
0.166	0.53
0.135	0.15

T=186°C	
W/FAO, (kg.cat.hr/mol)	**XA, Conversion**
0.196	0.56
0.166	0.38
0.135	0.01

T=182°C	
W/FAO, (kg.cat.hr/mol)	**XA, Conversion**
0.196	0.36
0.166	0.10
0.135	0

The intrinsic rate of reaction was calculated from the W/F v/s Conversion data. The conversion of each reaction was calculated which was explained earlier. The W/F v/s conversion data are shown in Table. The intrinsic rate of each reaction was then calculated from W/F v/s Conversion data. The data were fitted in to 1st order polynomial curve of the type

$$X = a\,(W/F) + b.$$

Then the equation is differentiated with respect to W/F to obtain the rate of the reaction r =dX/d(W/F) as a function of W/F. So from these equation became

$$\frac{dX}{d(W/F)} = a$$

From the equation rate and concentration presented in Table 4.4

Table 4.4: Reaction rates and concentration of reactant

T=194°C		
W/FAO, S^{-1}	**XA, Conversion**	**Rate, (mol/kg.cat.hr)**
0.196	0.86	**4.66**
0.166	0.72	
0.135	0.38	

T=190°C		
W/FAO, S^{-1}	**XA, Conversion**	**Rate, (mol/kg.cat.hr)**
0.196	0.73	**6.66**
0.166	0.53	
0.135	0.15	

T=186°C		
W/FAO, S^{-1}	**XA, Conversion**	**Rate,(mol/kg.cat.hr)**
0.196	0.56	**6**
0.166	0.38	
0.135	0.01	

T=182°C		
W/FAO, S^{-1}	**XA, Conversion**	**Rate,(mol/kg.cat.hr)**
0.196	0.36	**8.622**
0.166	0.10	
0.135	0	

Rate equation for first order reaction is $-r_A = k\, C_A$ (Power law equation), so from the rate equation we find out the rate constant. After find out the rate constant with the help of Arrhenius plot we can find out the activation energy.

Table 4.5: Rate constants using power law equation for four different temperatures

Rate	**T,°K**	**C_A**	**K**
4.66	467	$1.8*10^{-3}$	2513.6
6.66	463	$3.1*10^{-3}$	2140.1
6	459	$4.1*10^{-3}$	1461.6
8.622	455	$5.9*10^{-3}$	1446.57

The rate constants follow the Arrhenius law & rate constants are expressed as

$k = A_o \exp(-E/RT)$

Where the A_o is pre exponential factor and E is the activation energy. Fig 4.18 shows the plot of logarithmic of rate constant k (ln k) and 1/T which is a straight line following the Arrhenius law.

ln K	**1/T (°K)**
7.82	0.00214
7.66	0.00215
7.28	0.00217
7.27	0.00219

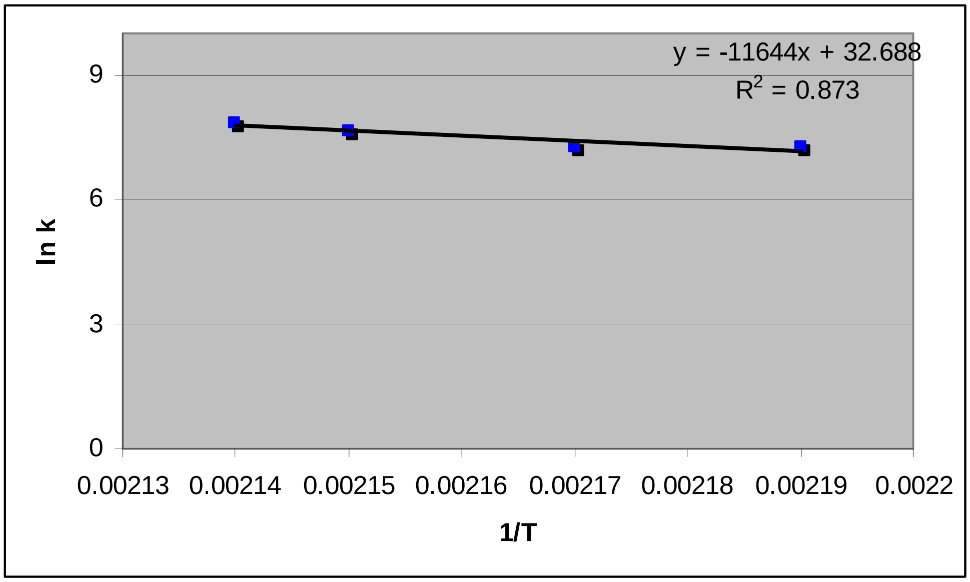


Fig 4.18 Arrhenius plots: Power law rate constant v/s 1/T

Slop= -E/R
= -11644*1.98
= 23055cal/mol
Activation Energy: 23.05 Kcal/mol

Table 4.6 Kinetic parameter for the reaction scheme

Reaction	**Pre-exponential Factor (Ao)**	**Activation Energy(E) Kcal/mol**
Oxidation of Propane	**0.16**	**23.05**

Chapter 5

Future scope

5 Future Scopes

Based on present studies, we can recommend the suitable catalyst for complete oxidation of industrial gaseous effluents. In addition to the above, the catalyst could be used for nitrogen purification in polymer plants, particularly PET. New materials synthesis with the above perfected method may serve to develop new catalysts, which could found usage in auto exhaust, petroleum and petrochemical catalysts.

The forward path will be the preparation, full characterization of supported Pt nanoparticle by other processes like microwave, sonication, etc.,and application of this catalyst for combustion of hydrocarbon likely methane, ethane and also may be useful for other industrially important processes.

Chapter 6

Conclusions

6 Conclusions

The present dissertation deals with development of nanomaterial for environmental application. In our work we had prepared different formulations of supported Pt, Pt-Pd (bimetallic) nanocatalyst by PVP as well as polyol process. We have evaluated and compared the prepared nanocatalyst with commercial catalyst for complete oxidation propane.

To derive the proof for the nano materials synthesis, following techniques are adopted. UV is used for nano particle formation in solution, ICP for bulk chemical analysis, TGA for compounds formation and TEM for particle size measurements at various stages of preparation. Important methods / techniques used in nano materials synthesis have been introduced during the project.

We have studied various Pt concentrations on different supports. A systematic study was conducted to cover the effects of various parameters on the rate of reaction under otherwise similar conditions. It is concluding that polyol 0.08 Pt-Alumina (E) gives light off temperature T_{97} at 205^0 C and commercial catalyst at 400^0C for combustion of propane under optimized conditions. The catalyst developed during the study would result in complete combustion at low temperature, and low metal loading thus substantial savings in energy consumption can be achieved and also the process becomes safer and economically viable in consonance with basic principles of green chemistry.

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Appendices

APPENDIX-1

- **Water pore volume measurement (WPV)**

a) Pore size distribution method
b) Equilibrium adsorption method

a) Pore size distribution method

In the pore size distribution method following steps are followed to measure the WPV of the support that is in this case for alumina(E)

1. First take 10 gms. of alumina(E) support in the conical flask
2. Take 5 gms. of water and shake the conical flask well.
3. Keep repeating the same procedure until whole water volume is soaked by the support. No water should remain there as it is.
4. It gives the value of the water pore volume of the particular support.

b) Equilibrium adsorption method

It is a more accurate method of WPV measurement. In this method care must be taken regarding the time for which the support is kept in the distilled water for water pore volume measurement.

In the equilibrium adsorption method following steps is followed to measure the WPV of the support.

1. Take 100 ml of distilled water in the flask.
2. Add 10 gms. of support
3. Keep it as it is for 24 hours.
4. Now decent the support material.
5. Measure the remaining water.
6. Subtract the amount of water remained from the actual 100 ml water taken.
7. It will give the value of WPV of the support.

Result:

Support	Pore size distribution method
Alumina (E)	1.4 ml/gm

APPENDIX-2

- **GHSV Calculation**

Calculating GHSV for Gas Volumetric Flow rate = 450 ml/min

Catalyst volume = 3 ml

$$\textbf{GHSV} = \frac{\text{Gas volumetric flow rate}}{\text{Catalyst volume}}$$

$$= \frac{450(\text{ml/min.}) \text{ X } 60 \text{ (min./hr)}}{3 \text{ (ml)}}$$

$$= 9000/\text{hr}$$

- **Calculating GHSV for Gas Volumetric Flow rate = 675 ml/min**

Catalyst volume = 3 ml

$$\textbf{GHSV} = \frac{\text{Gas volumetric flow rate}}{\text{Catalyst volume}}$$

$$= \frac{675(\text{ml/min.}) \text{ X } 60 \text{ (min./hr)}}{3 \text{ (ml)}}$$

$$= 13{,}500/\text{hr}$$

APPENDIX-3

- **Time on stream activity study**

Reaction condition

Propane=6000 ppm,

Oxygen=Stoichiometric,

GHSV=9000 hr $^{-1}$

Catalyst volume = 3 ml

Temp (°C) = 210

Catalyst type = 0.08% Pt on alumina(E)

Time (hr)	**Conversion (%)**
0	98.1
1	97.98
2	98.1
3	98.2
4	98.5
5	98.45
7	98.46
8	98.45
9	98.43
10	98.43

APPENDIX-4

- **Conversion of pollutant calculation**

With the application of GC calculating the on line and off line area and based onthat calculating conversion efficiency for pollutant

$$\textbf{Conversion efficiency} = \frac{\text{Area count with reaction Off-line} - \text{Area count with reaction On-line}}{\text{Area count with reaction Off-line}} \times 100$$