

**TITANIA DERIVED NANOTUBES AND
NANOPARTICLES: CATALYST SUPPORTS IN
HYDROGENATION, OXIDATION AND
ESTERIFICATION REACTIONS**

Lucky Mashudu Sikhwivhilu

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CATALYST SUPPORTS IN HYDROGENATION, OXIDATION
AND ESTERIFICATION REACTIONS**

Lucky Mashudu Sikhwivhilu

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Declaration

I declare that this thesis is my own, unaided work. It is being submitted for the degree of Doctor of Philosophy in the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University, nor has it been prepared under aegis or with the assistance of any other body or organisation or person outside the University of the Witwatersrand, Johannesburg.

Lucky Mashudu Sikhwivhilu

23RD Day of May 2007

Abstract

Nanotubular titanates were synthesized by a simple methodology using a commercial TiO_2 (Degussa P25 containing anatase and rutile phases) and a base (KOH) solution. Prior to the removal of KOH, the samples of TiO_2 were aged for three different time intervals (0, 2 days, 61 days). The freshly prepared synthetic samples were characterized for their structural and morphological properties by BET, XRD, Raman, TEM, HRTEM, EDX and SEM. Both TEM and SEM analysis revealed that ageing time influenced the tubular structure and morphology of the new materials. Raman and surface analysis data also showed that ageing time affected both the structural and surface properties of TiO_2 . The XRD results showed that the crystallinity of the TiO_2 decreased with increasing ageing time. Energy dispersive X-ray spectroscopy (EDX) showed that the tubes derived from TiO_2 are comprised of potassium, titanium and oxygen. Catalysts **A**, **B** and **C** were prepared by the addition of 1 wt% Pd (wet impregnation) to the titanate formed after ageing of the TiO_2 in KOH for 0, 2 and 61 days, respectively. The catalysts were tested for the vapour phase hydrogenation of phenol in a fixed-bed micro reactor within the temperature range of 165 to 300°C under atmospheric pressure. Of the three catalysts, catalyst **B** showed the best activity (conversion 97%) and total selectivity to cyclohexanone (99%). In contrast, catalyst **C**, which showed a moderate activity favoured selectivity to cyclohexanol. These results are attributed to differences in surface morphologies between the two catalysts **B** and **C**, associated with the surface area and a change in the surface acid-base properties. Catalyst **B** also showed a higher resistance towards deactivation and maintained a higher total selectivity to cyclohexanone than did catalyst **C**.

A hydrothermal treatment of NaOH and TiO_2 was employed to prepare two materials, TiO_2 -B and TiO_2 -C with relatively small crystallite size and large specific surface area. The hydrogenation of phenol was used to evaluate the activity of the

catalysts Pd/TiO₂-B and Pd/TiO₂-C. The reaction proceeds in a single step and involves the formation of a partially hydrogenated product, namely cyclohexanone. The larger surface area catalyst (Pd/TiO₂-C, 89 m²/g) showed better activity and selectivity to cyclohexanone than its counterpart (Pd/TiO₂-B, 45 m²/g). The catalyst activity showed significant dependency on the surface area whereas the selectivity was greatly influenced by surface basicity.

Titania derived nanotubes synthesized by treating P25 Degussa TiO₂ with a concentrated KOH solution and aged for 2 days was used as a catalyst support for the hydrogenation of o-chloronitrobenzene (O-CNB) with Pd as the active phase. The vapour-phase hydrogenation of O-CNB was carried out in ethanol at 250 °C and atmospheric pressure over a Pd/TiO₂ derived nanotube catalyst (Pd/TiO₂-M). Pd/TiO₂-M gave complete conversion (100%) of O-CNB with a selectivity to ortho-chloroaniline (O-CAN) of 86 %. The stability of the Pd/TiO₂ catalyst was tested over 5 hours during which time the conversion slowly dropped to 80 % (selectivity 93 %) due to poisoning. TPR analysis revealed the existence of a strong palladium-support interaction and this was found to be crucial to the overall activity of the catalyst.

It has been found that gold supported on potassium titanate, KTiO₂(OH) can, under some circumstances, exhibit a superior performance for the oxidation of carbon monoxide, relative to that obtained with titania as a support. It appears that the dispersions of gold on the two types of support are sufficiently similar that other factors are responsible for the improved activity noted. It may be that the higher basic character and detailed structural features of the titanate surface play a role.

The effect of the addition of alkali metal ions on the anatase to rutile transformation of titanium dioxide (P25 Degussa) was investigated using X-ray diffraction, Raman spectroscopy, and surface area measurements. Both Li and Cs ions accelerated the anatase to rutile transformation whereas Na and K ions did not show any effect. Furthermore, the effect was more pronounced after addition of the Li ions so that the

transformation temperature dramatically decreased from ~ 800 °C for commercial TiO_2 to ~ 600 °C. The surface area of the TiO_2 material decreased with sintering due to the increase in crystalline size. Moreover, the acceleration of the transformation occurred at lower temperatures and at higher Li content.

Mesoporous nanocrystalline TiO_2 (HSA TiO_2) was prepared by hydrothermal treatment of TiO_2 with NaOH. The material was very amorphous and underwent the phase transformation from amorphous to anatase phase and subsequently from anatase to rutile phase with sintering. The anatase to rutile transformation was delayed after doping and grain growth was inhibited. After sintering at 800 °C the material (HSA TiO_2) still contained a significant amount of the anatase phase. The complete transformation only occurred at ~ 1000 °C.

The esterification of benzoic acid and butyric acid with propanol over alkali metal ions supported on TiO_2 was investigated. K/ TiO_2 -D showed the highest conversion for both benzoic acid and butyric acid. The selectivity to propylbenzoate and propylbutyrate was influenced by the basic nature of the catalysts. Butyric acid was found to be more reactive than benzoic acid. The difference in reactivity was explained in terms of steric and inductive effects. The differences in boiling points and pH values were also considered.

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1. November 2002, CATSA conference 2002, Cape Town, Esterification of benzoic acid.
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Abbreviations and acronyms

Abbreviation or Acronym	Description
AN	Aniline
BET	Brunauer-Emmett-Teller
CAN	Chloroaniline
Cat.	Catalyst
CNB	Chloronitrobenzene
Conv.	Conversion
DMC	Dimethyl Carbonate
DP	Deposition Precipitation
DSC	Differential Scanning Calorimetry
Ed.	Edition
EDX	Energy-Dispersive X-ray
FID	Flame Ionisation Detector
Fig.	Figure
FTIR	Fourier Transform Infrared
GC	Gas Chromatography
GC-MS	Gas Chromatography – Mass Spectroscopy
h	hour
HNO ₃	Nitric Acid
HRTEM	High Resolution Transmission Electron Microscopy
IR	Infrared
n	Number of moles
NB	Nitrobenzene
O-CNSB	Ortho-chloronitrosobenzene

Abbreviation or Acronym	Description
Ref.	Reference
RT	Room Temperature
Select.	Selectivity
SEM	Scanning Electron Microscopy
t	Time
T	Temperature
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
TCD	Thermal Conductivity Detector
TNT	Titania derived Nanotubes
TOS	Time-on-stream
TPD	Temperature Programmed Desorption
TPR	Temperature Programmed Reduction
W/W	Weight by Weight
Wt.	Weight
XRD	X-Ray Diffraction

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1

General Introduction

Catalysis is key to efficient chemical processing. Most industrial reactions and almost all biological reactions are catalytic. Products made with catalysts include food, clothing, pharmaceuticals, plastics, detergents, and fuels. Catalysis is central to environmental protection technologies by conversion of noxious emissions into non-toxic products [1].

Catalytic processes can be classified roughly according to the nature of the product and the industry of application. In chemical manufacturing, catalysis is used to make bulk chemicals e.g. ammonia and sulphuric acid; commodity chemicals e.g. acetic acid and n-butyraldehyde; and fine chemicals e.g. fragrances and flavourings. Catalysis is used extensively in the manufacture of pharmaceuticals. In fuel processing, catalysis is used in almost all the processes of petroleum refining, in coal conversion and related synthesis gas (CO and H₂) conversion. Most of the recent large-scale developments in industrial catalysis have been motivated by the need for environmental protection. Many processes involved in the abatement of emissions are catalytic. Automobile exhaust conversion catalysts are now the most important of all catalysts in terms of sales volume. Catalysts for the conversion of nitrogen oxides in stationary power plant effluents are used on a massive scale in Japan and parts of

the USA. Most of the applications of catalysis in biotechnology are in fermentations which are often carried out in stirred reactors with gases, liquids, and solids present. The catalysts are enzymes, present in living organisms such as yeasts [2].

The recognition of carbon nanotubes in 1991 and other nanostructures has also impacted on research in catalysis. In the last decade a vast knowledge about the synthesis and properties of various nanomaterials has been collected with new discoveries emerging almost on a daily basis. Expectations regarding the application of nanomaterials as the upcoming functional materials for the 21st century are rising. As such the technological frontiers of micro-devices are almost certainly apparent. Thus, downscaling conventional technologies by an order of magnitude seems a feasible route as nanoparticles are a perfect building block for this purpose. With this development a whole new dimension can be imagined in terms of the production of nano-devices and nanomaterials. A reduction of the unnecessary amount of functional materials for production processes, thereby mimicking nature's most efficient ways of managing with less when it comes to chemical process, is viable [3]. Catalysts fit the above category of nanomaterials provided they can be retained in nanoform. This can be achieved by placing catalysts on supports.

The activity of a supported catalyst is largely determined by the interaction of the active component and the support. The formation of small metal particles in a catalyst system is expedited by the use of a support to which the particles are relatively well anchored and on which they are efficiently dispersed [4]. Studies have shown that the performance of the catalyst may be influenced by several factors such as method of synthesis, nature of the support, metal loading, pre-treatment conditions and reduction conditions [5-14].

Background

1.1. Historical aspects of catalysis

The science of catalysis is driven by technology, as it has been from the beginning of studies on catalysts. Some of the earliest known examples of controlled chemical transformations are catalytic. Fermentation was used in ancient times to make alcoholic beverages, and a number of the earliest examples of chemical technology were also exploitations of catalysis. For example, before the sixteenth century ether was made by distilling spirits in the presence of sulphuric acid. In 1746 nitric oxide was used as a catalyst in the lead chamber processes for the oxidation of sulphur dioxide to produce sulphur trioxide in the manufacture of sulphuric acid. In 1781, acids were used to catalyse the conversion of starch into sugar. In 1817 H. Davy discovered that in the presence of platinum, mine gases were oxidised at low temperatures; he designed a safety lamp for miners in which the platinum glowed if the flame was extinguished. Many more practical discoveries were made in the 1900s.

Haber and his contemporaries devised methods for catalyst testing and process development that are still very much in use today. These pioneers understood the interplay between chemical equilibrium and reaction kinetics. For example, the ammonia synthesis reaction is strongly equilibrium limited. The equilibrium conversion to ammonia is favoured by high pressure and low temperature. Haber therefore recognised that the key to a successful process for making ammonia from hydrogen and nitrogen was a catalyst with a high activity to allow operation at low temperatures where the equilibrium is relatively favourable [15].

1.2. Nanotechnology and nanomaterials

Nanotechnology encompasses technological developments on a nano scale (10^{-9} m) with a typical dimension ranging from 1 to 100 nm. This is about ten thousand times

smaller than the width of human hair and is in the range of the size of a large protein structure. However, in recent years the nano scale was redefined to range from subnanometer to several hundred nanometers. The prospects of research in nanotechnology also known as the science of the ultra small, was first made known by Nobel Prize winning physicist Richard Feynman in 1959. Since then the concept of nanotechnology surfaced with the idea that atoms could be used to build structures, with absolute control over properties and functions. While materials in the micrometer scale often exhibit physical properties the same as that of the bulk form, it is interesting to note that materials in the nanometer scale may exhibit physical properties uniquely different from that of bulk. A typical example is that of bulk semiconductors becoming insulators when the characteristic dimension is sufficiently small (within the nanometer region). The underlying difference is size-dependency with the effect becoming more prominent when the particles are 100 nm or less in diameter [16].

It was only in 1960 that Feynman described the idea of synthesizing and using nanoparticles for the first time in a groundbreaking talk entitled “There’s plenty of room at the bottom”. He suggested the idea of doing something really big and important with objects that are really small and distinct in their properties and behaviour from familiar large objects. Although much attention was subsequently devoted to nanotechnology, the development of technology to expand knowledge around nanotechnology is still in its early stages. It was only in 1981 when Binnig and Rohrer ‘saw’ atoms for the first time that techniques to evaluate technological progress became possible. The concept of nanotechnology is now showing the way to a world of materials that had not previously existed.

Nanotechnology, with all of its promises, has attracted enormous attention because it is an expected manufacturing technology that brings about inexpensive control of structure of matter by working with atoms. Nanotechnology is anticipated to revolutionise the world of production by promoting low cost production with no

pollution. It holds promise in areas such as the production of advanced nanomachines (nanodevices) like computers in its broadest sense [16].

Although the advanced concept of nanotechnology is still novel, research on the nanometer scale is not new at all. For example biological systems and the engineering of many materials such as colloidal dispersions and metallic quantum dots have been extensively studied at a nanometer level. Catalysis is also known to be the milestone field when it comes to the use of nanoparticles. This occurred long before the inception of the field of nanotechnology. The high surface area of catalyst particles means that the surface effects are far more important than in the bulk substance. Nanotechnology comprises of molecules, atoms and quantum dots and is dominated by surface effects such as Van der Waals forces of attraction, hydrogen bonding, electronic charge, ionic bonding, covalent bonding, etc. The vastly increased ratio of surface area to volume gives new possibilities to surface-based sciences such as catalysis.

Nanotechnology offers a broad range of potential applications in various industries. It is interesting to note that the applications of nanotechnology in different fields have distinctly different demands and hence face different challenges which require different approaches. For example, optical telecommunications and information technology is focussed on faster computers and advanced data storage, health care is focussed in terms of improved skin care and protection, while the pharmaceutical industry is focussed in terms of drug delivery systems and cancer treatment [17].

1.3. Catalysis

Many of the products that support our everyday lives - fuels, fertilizers, construction materials, medicines and artificial fibres, to name but a few – involve heterogeneous catalytic processes at one or several stages in their manufacture. By heterogeneous catalysis we mean that the catalyst has a distinct and separate phase from that of the

reactants so that the catalytic reaction takes place at a boundary, or interface, between phases. In most cases of practical interest the catalyst is a solid while the reactants are in the fluid phase (gas, liquid or solution), so that under these conditions the catalytic reaction takes place at the surface of the solid. The subject of heterogeneous catalysis is very broad and embraces a wide field of physical, chemical and engineering sciences [2].

Heterogeneous catalytic reaction systems, in which fluid reactants are passed over solid catalysts, are at present the most widely used catalytic processes in the man-made transformation of matter [18]. The ever-increasing demand for better quality products at affordable prices and the strong competition in open markets makes research in science, engineering, agriculture, etc. imperative. More than 90 % of the chemical manufacturing processes in use throughout the world utilize catalysts in one form or another. Much of the food we eat and the medicine we use, many of the fabrics and building materials that keep us warm and almost all the fuel that transports us by road, sea or air are produced by heterogeneously catalysed reactions. The science and technology of catalysis is therefore of central practical importance. Until recently, the majority of commercially significant catalysts were discovered and developed principally by empirical methods [19].

In recent years the development of industrial solid acid catalysts that might efficiently replace strong liquid acids (such as H_2SO_4 and HF) has been the object of active research. In fact solid catalysts, being less corrosive and easier to separate from the reaction products, may become more advantageous and are intrinsically more compatible with increasingly demanding environmental requirements [20].

Most of the largest-scale catalytic processes take place with gaseous reactants in the presence of solid catalysts. From an engineering point of view, these processes offer the following advantages, in contrast to those involving liquid catalysts:

- 1) Wide ranges of temperature and pressure are economically applied. The most direct way to increase the activity of a catalyst is to increase the reaction temperature, and high temperatures can be used economically with solid catalysts as the reactants are gases and there is no liquid phase to require a high pressure.
- 2) Solid catalysts are only rarely corrosive
- 3) The separation of gaseous or liquid products from solid catalysts is simple and costs little.
- 4) The mixing and mass transport in a fixed- or fluidised-bed reactor are facilitated by the solid catalyst particles through which the reactants and products flow.
- 5) Strongly exothermic and strongly endothermic reactions are routinely carried out with solid catalysts [2,21,22].

Nanotechnology provides a means to design, synthesize and control reaction at the nanometer scale. While workers in the area of catalysis have many techniques at their disposal to synthesize catalytic materials, at such a scale, the ability to fully design and control is still a concept to be improved upon. Nano-size noble metal particles have occupied a central place in heterogeneous catalysis for many years, long before the inception of nanotechnology [23,24]. It is interesting to note how nanotechnology has helped researchers advance towards a goal of evaluating what nanotechnology can do for heterogeneous catalysis. However, recently the focus has shifted towards catalysis aiding in the development of nanotechnology and this remains a much less explored aspect which deserves attention.

1.4. Scope and aims of thesis

Nanotechnology has made the synthesis of nanotubular materials possible, with carbon nanotubes at the forefront. Nanotubes of many semi-conducting metal oxides such as TiO_2 have also attracted much attention. Due to the outstanding physical and

chemical properties of the novel TiO₂ nanotubes many applications have been anticipated. The morphological feature and high surface area of the tubes have offered TiO₂ materials a variety of application in catalysis. Nanotubular TiO₂ materials are currently used as a support in areas such as catalysis. They have also been used as a photocatalyst in the treatment of water and due to the optical properties of the material, nanotubes of TiO₂ have been incorporated into flat panels for improved display.

To this effect the synthesis of titania nanotubes that can be functionalised in different ways has been widely studied. In this thesis a study on the use of various forms of TiO₂ (i.e. commercial P25 Degussa, modified titania and/or TiO₂ derived nanotubes) as a catalyst support for various processes is reviewed (Chapters 4-7).

1.4.1. Synthesis of TiO₂ nanotubes

Conventionally, the sol-gel method has been widely used to synthesize TiO₂ derived nanotubes in the presence of a template such as an organogel or with a porous anodic alumina [25-28]. This method is relatively inexpensive and it offers numerous advantages because it generates homogeneous and very pure products. However the removal of a homogeneously mixed template is invariably a challenge [29]. Most studies on the synthesis of titania nanotubes suggest that tube formation is underpinned by an acid-treatment step [30]. In this study a simple and relatively cheaper methodology to synthesize titania derived nanotubes which does not require the use of template and acid treatment step was employed. The effects of systematically varying synthesis variables such as ageing time, on the structure, morphology, crystallinity and the surface properties of the material were investigated (Chapters 4, 6 and 7).

1.4.2. Catalyst preparation

For the preparation of most catalysts, the impregnation method was used to add the active component to the support. An appropriate amount of metal oxide (preferably alkali or alkali earth metals) was dissolved in solvent (e.g. H_2O , acetonitrile or toluene) and then added to a support such as TiO_2 ; related gold based catalysts were prepared by a deposition-precipitation method (Chapters 4-10).

1.4.3. The study of anatase-rutile phase transitions

Titanium dioxide has two predominant phases, namely, anatase and rutile. The two are polymorphs. The ratio of the two polymorphs changes upon heating. In this thesis the effect of lithium insertion on TiO_2 was investigated in order to determine how lithium affects the anatase to rutile phase transition temperature (Chapter 8).

1.4.4. Esterification of acids over TiO_2 supported catalysts

Titania presents increasing interest as a catalyst or support. However, its low surface area is an important disadvantage for catalytic applications. This has been partially overcome by the application of new synthesis procedures in order to obtain titania with a high specific surface area [34-37]. So, the effect of titania with different surface areas in the esterification of acids was investigated. The esterification of acids such as benzoic acids, phthalic acid, propionic acid and butyric acid to give their respective products, namely ethylbenzoate, ethylphthalate, ethylpropionate and ethylbutyrate, was used to test different catalysts and their catalytic performance in the light of their bulk and surface properties [38]. For the process of esterification of acids the following parameters were varied in order to establish the optimum conditions for the conversion of reactant into product: temperature, reactant flow rate, reactant composition ratio, solvent and catalysts (Chapters 9 and 10).

1.4.5. Hydrogenation of phenol over Pd supported catalyst

Various methods are employed for the production of cyclohexanone on an industrial scale. This is achieved by either the oxidation of cyclohexane or the hydrogenation of phenol [31]. However, high temperature and pressure are essential for the reaction and the generation of by-products is inevitable. This industrial process is a homogeneous process and hence difficulties associated with the separation of products and reactants are needed. In the hydrogenation of phenol a one- or two-step process is employed to produce cyclohexanone. The two-step process involves the hydrogenation of phenol to cyclohexanol and subsequently the dehydrogenation of cyclohexanol to cyclohexanone. The one-step process is a direct method for the synthesis of cyclohexanone from phenol and it provides economic advantages in terms of capital costs and energy savings [32,33].

The development of an effective catalyst for such a process is required. To date there has not been any known report on the use of Pd on titania derived nanotubes as a catalyst for the hydrogenation of phenol. In this thesis both the synthesis and the use of titania derived nanotubes as catalyst support for the vapour-phase hydrogenation of phenol are reported. The effect of the morphological features, structural composition of the catalyst and the surface area of the nanotubular support on the activity and selectivity were investigated. Attempts to describe the interaction of the active component and the support in a catalytic system and to find a link between catalyst performance and the nature of support were made. The effect of TiO_2 surface area enlargement resulting from treatment with either KOH or NaOH base on the selective hydrogenation of phenol to give cyclohexanone was also investigated. A mechanism for the reaction was also proposed (Chapters 4 and 5).

1.4.6. Hydrogenation of ortho-chloronitrobenzene (O-CNB)

Selective hydrogenation of ortho-chloronitrobenzene to ortho-chloroaniline was carried out over Pd supported on a nanotubular TiO₂ derived catalyst to elucidate the influence of surface area and the effect of the nature of the support on the activity and selectivity of the reaction. Experimental parameters such as temperature and H₂/CNB mole ratio were systematically varied to test catalyst performance. The effects of the metal precursor and time on stream (TOS) were also investigated. The sites (e.g. weak or strong basic sites) primarily involved in the selectivity of products and conversion of the reactants were determined (Chapter 6).

1.4.7. CO oxidation reaction over Au/TNT

A supported gold catalyst was prepared by a deposition-precipitation procedure to investigate the influence of the morphology and surface area of the support on the catalytic activity for CO oxidation. To achieve this task gold was supported on a nanotubular TiO₂ derived support and the catalyst performance was compared with that of a commercial support (Au/P25 TiO₂ Degussa). Conversion and selectivity were evaluated and the catalysts were both tested for stability with prolonged catalyst use (time on stream). The influence of experimental variables such as temperature was also studied while the interrelations between catalyst activity and gold particle size were also studied. To the best of our knowledge, there has not been a report of CO oxidation reaction carried out over gold supported on TiO₂ derived nanotubes (Chapter 7).

1.4.8. Characterisation of catalysts

The development of sophisticated characterisation methods that provide fundamental information about the catalyst bulk structures, surfaces, and their properties are important in heterogeneous catalysis. These characterisation methods allow

researchers to “see” the surfaces of catalytic materials, their bulk structures (crystalline phases as well as amorphous phases), the influence of the process conditions on the catalytic material, as well as the effect of different synthesis methods on the catalyst structure. It is, therefore, hard to conceive of a modern heterogeneous catalyst, be it in research or manufacturing, without the aid of these new characterisation techniques [35,39].

Characterisation techniques that were used in this study include: powder XRD, Raman, TPD, TPR, BET analysis, TEM, SEM, EDX, TGA, IR, DSC and Malvern Analysis (Chapters 4-10).

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2

Literature Review

“Imagination is more important than knowledge”

Albert Einstein (1879-1955)

2.1. Introduction

Catalysis is, undoubtedly, a next generation approach for the systematic business-driven development of component-based systems. In development and application, since 1992, it has been used by companies in fields including finance, telecommunication, insurance, manufacturing, embedded systems, process control, flight simulation, travel and transportation, and systems management [1]. Catalysis is a proposed method, in use in many projects, and supported by tools and related products and services from several companies.

Catalysis is defined as an acceleration of the rate of a process or reaction, brought about by a catalyst, usually present in small managed quantities and unaffected at the end of the reaction. A catalyst permits reactions or processes to take place more effectively or under milder conditions than would otherwise be possible. The purpose of a catalyst is to reduce the height of the energy barrier which the reactants must surmount before they can interact [2].

This chapter is divided into five sections, and the information in the sections gives a background to topics covered in this thesis.

1) Solid base catalysis

In recent years the development of solid base catalysts which might efficiently replace strong liquid bases and acids in several industrial processes has attracted much attention in research [3]. The reactions in this thesis have been carried out in the presence of various solid base catalysts. The current work deals with the effectiveness of various solid base catalysts in the hydrogenation, CO oxidation and esterification processes.

2) Nanostructured TiO₂ materials

The modification of the surface chemistry of semiconducting nanoparticles is often required for optimising their catalytic performance. However, surface chemical modification should not deteriorate either the bulk characteristics or electrical properties of the material. This becomes fundamentally important for nanoparticles due to their high surface-to-bulk ratio. In this thesis, surface modifications of titanium dioxide nanoparticles by hydrothermal treatment with very concentrated aqueous base solutions such as NaOH or KOH are reviewed and employed. The modified materials are then used as either the catalyst or support.

3) Hydrogenation reactions

The fundamental application of hydrogen gas on a large scale is in hydrogenation and hydorgenolysis reactions which are associated with the heavy and fine chemical industries. Hydrogenation is defined to be the addition of H₂ to unsaturated organic compounds such as alkenes to produce alkanes, and aldehydes to give alcohols.

Hydrogenation reactions almost only take place in the presence of metal catalysts. Very few or none of the reactions between H_2 and organic compounds can occur at temperatures below 480 °C in the absence of metal catalysts. Precious metals such as platinum, palladium, rhodium and ruthenium have, to date, been used as effective catalysts. To a lesser extent, non-precious metals such as nickel have also been developed for use as an economical alternative [4]. The modification of the support in order to minimize the quantity of the precious metals while enhancing both the activity and selectivity of the catalyst is reviewed.

4) CO oxidation reaction over gold catalyst

Gold catalysis has attracted research interest since it was discovered that nanosized Au particles have exceptionally high activity for CO oxidation at low temperatures. TiO_2 has been widely used as a support for Au catalysts. However, TiO_2 supported Au catalysts are prone to deactivation during the reaction. The use of TiO_2 derived nanotubular supports to generate small particles of gold and to improve metal support interaction is known. The effect of metal size effect and the support dependency on the activity of TiO_2 supported Au catalysts is reviewed.

5) Anatase to rutile phase transformation

Titania has three naturally occurring polymorphs, namely: anatase, brookite and rutile. Rutile is considered the most stable polymorph in ambient conditions whereas both anatase and brookite are considered as kinetic products [5]. These polymorphs can be isolated successfully by physical or chemical means. This interconversion is discussed.

6) Esterification reactions

Esters are the products of a condensation reaction between an acid and an alcohol through a process called esterification. Esterification is one of the most important reactions in organic synthesis. This section outlines different methods used in the preparation of esters. The attention will be directed towards the esterification of aliphatic and aromatic compounds.

2.2. Introduction to solid base catalysis

A catalyst is defined to be a substance that increases the rate at which a chemical system approaches equilibrium, without being consumed in the process. In acid catalysis the catalyst acts as an acid and the reagent as a base whereas in base catalysis the catalyst is the base and the reagent acts as the acid [6].

At the moment there are two acid-base theories in use that have been developed in order to give an exact meaning to the acid and base concepts. They are the Brønsted-Lowry theory and the Lewis theory. Both Brønsted and Lowry proposed that an acid is a species having a tendency to donate a proton whereas “a base is a species having the ability to add on a proton” [7]. In contrast, in the Lewis definition an acid is a species that can accept electrons whereas a base is a species that can donate electrons [7].

2.2.1 Background on base catalysts

The volume of publications on zeolites as solid base catalysts suggests that zeolites are the most studied solid base catalysts. In comparison to the broad application of acidic zeolites as solid catalysts in chemical technology, much less attention has been paid to basic microporous and mesoporous materials, even though these solids do have considerable potential for a number of industrially important reactions.

Analysis of industrial application of solid acid and base catalysts showed that in only 8% of the processes were solid bases being used, and none of these reactions is performed over basic zeolite catalysts [8]. It is only with growing effort in the preparation, characterization and catalytic investigation of new microporous and mesoporous materials with basic properties that a break-through in their application may be achieved [9]. The use of basic catalysts up to the mid of the 1900s has been presented in the excellent reviews by Hattori [10] and Barthomeuf [11] which also contributed to a much better understanding of the “basicity” of the materials.

2.3. Nanostructured TiO₂ materials

Titania, also known as titanium dioxide, was discovered in 1821. It was mined as rutile and ilmenite (which is a mixture of iron, titanium and oxygen) [12]. Its primary use as a pigment for providing whiteness, brightness and opacity was discovered in 1913. The ever-increasing demand for this white pigment led to the start of the Titanium Pigment Corporation of Niagara Falls and the Titan Co. in New York and Norway respectively. The two companies concurrently began the production of the newly discovered white pigment of titania on a commercial scale in 1916. Since 1921 titanium dioxide was incorporated into paints for whiteness and durability. Other applications include use in coatings, plastic, paper, inks, fibres, food, sunscreens and cosmetics. However, in its sintered form titania has limited use because of its comparatively poor mechanical properties [12,13].

Because of its availability and relatively low costs titania has been widely used in catalysis as a catalyst or support. Moreover, its low surface area is an important limitation for catalytic applications [14-16]. In order to alleviate this problem scientists have developed a variety of new synthesis procedure so as to prepare titania with a higher specific surface area [17]. Nevertheless, for many other applications, titanium dioxide can also be modified by insertion of metal ions to enhance both performance and activity [18].

High surface area TiO_2 has been reported to provide a highly active photo-catalyst material [19] and it is being investigated for utility as a material for high efficient solar cells [20-22]. Titanium dioxide is a versatile material with a number of applications associated with its optical, semi-conductor and chemical properties. Although titania is a dielectric material it behaves like a semiconductor due to structural defects. Since titania has three naturally occurring polymorphs, viz. anatase, rutile and brookite its applications and functional properties may be largely influenced by the material phase. Rutile crystallises in the tetragonal system, in which six oxygen atoms form a distorted octahedron around the titanium atom with four shorter and two longer Ti-O bonds. Anatase has a similar tetragonal structure with slightly different octahedral.

TiO_2 behaves in areas of ceramics, as a powder and film of the required material as well as a catalyst support depending on the morphology and material properties. The presence of defects in the material may be significant for electro-optical properties while the material particle size may be crucial for alteration of parameters such surface area. These factors are all fundamentally important in catalysis. Clearly it is important to control the phase, particle size, the presence of defects and the morphology of TiO_2 during synthesis and/or prior to its use. The use of nanosized TiO_2 which is accompanied by the surface area enlargement and enhanced optical properties of the material holds promise in catalysis [23].

Although the idea of synthesizing nanosized TiO_2 was envisaged in the early 20th century the technology to analyse the material had not been developed. Today various forms of nanosized TiO_2 have attracted immense attention in catalysis. The interest in the development of titania materials with specialised properties was by and large driven by the desire to produce well-structured, porous, high surface area and complex forms of titania based materials which led to the development of titania nanotubes [23].

The discovery of carbon nanotubes in 1991 by Iijima promises to be a milestone in nanomaterial science research [24]. Because of its high specific surface area of the new material, which may influence photocatalytic activity, leading to a greater possibility of applications in areas such as the generation of hydrogen gas and environmental purification, titania nanotubes have also received much attention in research laboratories. Other applications of titania nanotubes include their use in gas sensors, flat panels and hydrogen solar cells [25-28].

2.3.1. Synthesis methods for TiO₂ derived nanotubes

Titania nanotubes have been successfully synthesized by various methods such as templating, electrode reactions, heating in a controlled atmosphere, a replica process, etc. [29-34]. Even today, researchers are still developing new methods of synthesizing titania nanotubes.

Early synthesis procedures involved the use of a polymer mold for the synthesis of titania nanotubes. Firstly a poly (methyl methacrylate) mold with polymer rods temporarily attached is prepared from Al₂O₃. Amorphous TiO₂ is then deposited on the mold via an electrochemical deposition method [35]. The dissolution of the mold resulted in the desired structure of amorphous TiO₂ in the form of nanotubes. The amorphous nanotubes produced via this method undergo a phase transition to anatase at 450 ° C [34]. The tubes have an internal diameter ranging from 70 to 100 nm with the wall thickness of 30-50 nm. The tubes grow to a length of 8 μm [34].

In 1998 Kasuga and co-workers developed a new method to synthesize TiO₂ nanotubes [36]. They used a hydrothermal treatment of a sol-gel derived TiO₂ (anatase) with NaOH followed by neutralisation with acid (HCl). The resultant product is finally washed with distilled water. Although sol-gel derived TiO₂ has relatively high surface area (150 m²/g) nanotubes have a much higher surface area,

400 m²/g. The needle-shaped nanotubes have a diameter of 8 nm and length of 100 nm. These nanotubes are made up of titanium and oxygen and suggested that the tubes had a titanium dioxide structure [36]. Due to their large surface area titania nanotubes produced by this procedure have shown high photocatalytic activities [37-40].

The use of commercial TiO₂ with both pure anatase as a starting materials yields similar results to that obtained with TiO₂ containing only the anatase phase [36]. Using pure rutile as starting materials also generated similar results [41] indicating that the tube formation is independent of the structure and particle size of the starting material.

Nowadays simpler and relatively cheaper methods are employed for the synthesis of TiO₂ nanotubes. Kasuga and his co workers have reported on the synthesis of titania nanotubes using a sol-gel procedure with TiCl₄ as the starting material [42]. They synthesized tubes with the internal diameters of 8-10 nm. The analysis of the tubes shows that the chemical formula for the tubes is TiO₂ with an anatase structure. The mechanism of formation of these tubes involves the formation of two-dimensional lamellar TiO₂ which is essentially rolled up to form one-dimensional tubes. Wang and his co-workers also made the same observation [43].

TiO₂ nanorods with either anatase or rutile structure can be synthesized via a sol-gel process using titanium tetraisopropoxide as a precursor [44]. The product material is subjected to heat-treatment to form the single-phase crystalline material. Anatase nanorod formation is favoured at low temperature whilst rutile nanorods are formed at high temperature indicating that rutile rods have a higher degree of crystallinity with larger crystallites than those of anatase. The anatase nanocrystalline produced by this method has a polygonal shape whilst the crystals of rutile have irregular octagonal and hexagonal shapes [44].

The sol-gel polymerisation of titanium tetraisopropoxide in the presence of an organogel as a template leads to the formation of a helical ribbon and subsequently a double-layered nanotube with TiO_2 structure. Tubes generated by this method are open-ended and have uniform shape and internal diameter [45]. The tubes are comprised of a hollow inner core and wall [46,47]. They are also made up of two layers with 8-9 nm lattice spacing implying that TiO_2 molecules adsorbed on both sides of the organogel template. However, the tubes have an internal diameter of about 500 nm which is generated by the helical ribbon growth. Clearly the tubes generated, although they are within the nano range, are relatively big cylinders [45,48-50]. This method can be successfully used to generate the helical nanotubes of other transition metal (Ta, V, etc.) oxides with unique nanostructures and properties making them potential candidates for applications in electronics, photocatalysis, and as optically functional materials [51,52].

The synthesis of nanotubular TiO_2 can also be achieved by an anodisation method. The procedure is carried out in an electrolyte medium with a platinum foil cathode and an anodising potential. Varghese and co-workers demonstrated that the length and the diameter of the tubes depend on the anodisation potential and time respectively. It is noteworthy that tubes synthesized by anodisation and annealed at 500 °C are highly sensitive to hydrogen gas [53].

2.3.2. High surface area mesoporous TiO_2 materials

Generally, mesoporous materials play a fundamentally important role in various fields of chemical technology such as electrochemistry, magnetochemistry, and catalysis. The high surface area, large pore volume, and regular pore structure make them very attractive for the design of new effective catalysts with increased or enhanced activity, selectivity and stability [54-57]. The ordered mesopores, together with functionalised groups, are of great use as supports for the active catalytic phases of metal oxides or organometallic compounds [58-61].

The conventional method of preparation of mesoporous nanostructures is based on a liquid crystal templating mechanism. However, this method is fairly long and is a multiple-step process [62]. Ultrasound irradiation has also been widely employed for the synthesis of various materials [62].

Yoshitake and co-workers synthesized mesoporous titania with BET surface area over $1200 \text{ m}^2\text{g}^{-1}$ by primary amine templating [63]. These surfactant templating syntheses provide, more or less, periodic structures of the mesoporous connections with a uniform pore size in addition to large surface area and high surface reactivity [63,64].

2.4. Hydrogenation reactions

The first documented hydrogenation reaction carried out in the presence of a catalyst was the reduction of acetylene and of ethylene to ethane using platinum black [65]. In 1874 Sabatier and co-workers developed a reduction method between hydrogen and organic compounds which became a universal reduction method and later won Sabatier a Nobel prize in 1912. The reaction was carried out in the vapour phase in the presence of either copper or nickel based catalysts [66].

Today almost all organic compounds that contain multiple bonds connecting two atoms can react with hydrogen in the presence of a catalyst. The hydrogenation of organic compounds is industrially important for the production of edible fats from liquid oils. It is also used in the manufacture of gasoline and petrochemical products through the destructive hydrogenation of hydrocarbons [66,67].

2.4.1. Catalyst

Various metal catalysts are commercially available for the hydrogenation reactions. These include platinum, palladium, rhodium, ruthenium, Raney nickel and catalysts

used for hydrogenation in the heterogeneous phase. Each catalyst exists in a different form depending on the preparation method [4].

Palladium can be used either as an unsupported or supported catalyst for hydrogenation reactions. The elemental Pd catalyst is prepared by the treatment of metal salts, such as palladium chloride, palladium nitrate, palladium acetate, etc., with sodium borohydride [68,69] while palladium oxide (PdO) is prepared by a fusion reaction using an appropriate palladium salt such as PdCl₂ and Pd(NO₃)₃ [70]. Supported palladium based catalysts are usually prepared in Pd contents of 5 or 10 % on supports such as charcoal, calcium carbonate and barium sulphate [71]. Pd catalysts are often modified, sometimes by using a special support, to enhance their selectivity. The advantage of using Pd catalysts is that they can be used both in strongly acidic and in basic media and they are particularly suitable for hydrogenolyses [69]. Early studies show that Busch and Stove were the first to give an insight into the preparation of Pd on a support, calcium carbonate [66]. Since then other inert materials such as barium sulphate and charcoal have been employed as supports for Pd based catalysts [72]. Today, numerous modern supports are used to prepare Pd based catalysts and they are commercially available worldwide. Some of the modern supports include activated carbon [73], titanium dioxide derived nanotubes [74], zeolites and silica [75], etc.

2.4.1.1. Metal particle size, dispersion, and activity

The use of nanosized metal particles in heterogeneous catalysis is well known. The small metal particles can become very reactive catalysts as the proportion of surface atoms increases as a result of decreasing particle size when compared with the bulk metals. This is because the surface atoms are active centers for a catalytic process. The surface atoms lying on the edges and corners are more active than those in planes [76]. The quantity of both the edge and corner atoms increase with a decrease in particle size and hence very small metal particles are required for active catalysts. The activity of the catalyst is also related to the particle size of the support. This is

because small support particles facilitate better transport of reactants to the catalysts resulting in an improved activity [76,77].

Previous studies have shown that the activity for hydrogenation is, as expected, dependent on the size of the metal (Pd) and the dispersion on the support [78]. Tessonnier and co-workers reported on the deposition of Pd nanoparticles on the multi-walled carbon nanotubes [79-81]. The low surface tension of the solvent resulted in a total filling of the tubes with Pd nanoparticles by capillary action. This subsequently resulted in formation of small metal particle size with the average diameter of 5 nm and a strong metal-support interaction (SMSI) necessary for the enhancement of catalytic activity. The deposition of the active phase into the nanotubular structures is an effective way to avoid aggregation which may reduce the activity [82,83]. The introduction of the metal nanoparticles into the nanotubular structures modifies the physical and chemical properties of both the encapsulated nanoparticles and the support via electron transfer between the graphite structure and the metal nanoparticles [84,85].

Wang and co-workers have reported on the preparation of Pd supported on TiO₂ nanotubes [86]. The tubular form of TiO₂ is particularly important because it has larger specific surface area and higher photocatalytic activity [87]. The Pd metal particles are better dispersed on the nanotubular form of TiO₂ than on the conventional form (i.e. P25 Degussa) and hence better catalytic activity and selectivity was observed. The morphology of the tubular support also enhances the catalytic activity [86]. However, limited information is available on the use and preparation of Pd supported on TiO₂ nanotubes.

It must be realised that when an impregnation method is used to add the active phase to a support it is difficult to obtain a homogeneous distribution over all support particles. This gives rise to the formation of particles with a range of sizes. The use of supports with large specific surface area like activated carbon ($> 100 \text{ m}^2/\text{g}$) and

use of a low metal content is a requirement to generate high metal dispersion and catalyst activity [88].

2.4.1.2. Activation and deactivation

The presence of foreign materials on the surface of the catalyst can either increase or decrease the rate of a hydrogenation reaction. In certain cases the presence of foreign materials can lead to a total inhibition of the hydrogenation process whereas on the contrary certain materials can enhance the selectivity of a catalyst [89].

The presence of sulphur, sulphur compounds and chloride ions, even in small amounts, are known to be detrimental and poisonous to the activity of many catalysts. Several nucleophiles such as sulphides, cyanide, iodide, ammonia, acetates, etc. are also known to be inhibitors particularly for Pd, Pt and Rh catalysts [90]. The extent of deactivation (partial or total deactivation) depends on the quantity of the inhibitor. The deactivation may occur in various ways such as blocking of the active sites by overly strong adsorption or by the interaction of the inhibitor and support which result in the alteration of the nature of the material undergoing hydrogenation [90].

Furthermore, the presence of certain alkali metal ions such as Li^+ , Na^+ and K^+ in contact with Pd catalysts has a promotional effect [91,92]. The development of bimetallic catalyst systems proves to be the solution for issues relating to sulphur formation and lower selectivity. The function of the second metal (e.g. as in Pt-Pd catalysts) is to enhance the sulphur tolerance due to changes in electronic properties and the selectivity of the active metal centers [93].

2.4.2. Hydrogenation of phenol

The hydrogenation of phenol to give cyclohexanone both in gas [94,95] and liquid [96,97] phases have been widely reported for various Pd [96-98] based catalysts. The hydrogenation of phenol in the presence of a Pd catalyst yields cyclohexanone as the

main product and cyclohexanol as a by-product. Although a high selectivity of ~ 95 % can be obtained it is difficult to maintain this high selectivity at high conversion (> 80 %). Both conversion and selectivity are significantly influenced by the changes in catalyst structural properties. Factors such as metal content, surface acidity/basicity, and the addition of promoters such as alkali metal ions have shown a dramatic influence on the performance of Pd catalysts [94,98,99].

Scire` and co-workers have reported on the use of a promoter such as Ca for the modification of electronic surroundings of Pd atoms which effectively enhances the electronic enrichment of the metallic phase [100]. They demonstrated that the effect of the promoters is related to a variation of H adsorption on Pd and that a change in the acid/base properties of the promoted catalyst could also be crucial [100]. It was found that the addition of Ca to Pd catalyst supported on Al₂O₃ leads to a decrease in acidic sites while the number of corresponding basic sites increased. The promoter was found to significantly enhance the catalytic performance of the catalyst system. This resulted in an improved catalytic activity. The activity and selectivity to cyclohexanone increased with an increase in the number of basic sites [101]. Mahata and Vishwanathan also made similar observations [102].

Although Pd promises to be a superior catalyst for hydrogenation reactions an acceptable explanation about its catalytic properties is still to be achieved [103]. The catalytic behaviour is believed to emanate from variables involved in the preparation and pre-treatment of the catalyst. Such variables include the metal precursor. In a supported catalyst, dispersion of the metal is dependent on the precursor-support interaction and on the size of the precursor. A residual component of the precursor (e.g. Cl⁻) attached to the active component after the pre-treatment can influence the properties of the catalyst support and/or of the active component. It is noteworthy that the precursor determines the properties of the final catalyst [104-106]. Inevitably these factors significantly influence the hydrogenation of phenol to give cyclohexanone. Scirè and co-workers have demonstrated that a Pd catalyst prepared

from an acetate precursor, $\text{Pd}(\text{CH}_3\text{COO})_2$, showed better conversion of phenol and selectivity to cyclohexanol than did the related chloride precursor, PdCl_2 [107]. This is also consistent with the results reported by many other researchers [108-111].

2.4.3. Hydrogenation of aromatic nitro compounds

The hydrogenation of aromatic nitro compounds was a milestone in the reduction of organic compounds [112]. The nitro group is often reduced to amines depending on the extent of the reaction. The reduction of nitro aromatic compounds can occur via multiple reduction intermediates and all the intermediate stages of the process can be catalytically regulated [4]. In the presence of a catalyst the reduction of the nitro group (partial reduction) can be easily controlled so as to avoid the reduction of the aromatic ring (complete reduction). Catalysts that have been widely used for the hydrogenation of aromatic nitro compounds include platinum, rhodium-platinum oxide, palladium, Rainey nickel, copper chromite, rhenium sulphide, etc. [113-116]. Among these catalysts Pt shows the better selectivity to amines than the rest and permits a fast rate of reduction of the nitro group.

Halogenated aromatic nitro compounds are susceptible to hydrogenolyses of the C-X bond (X = halogens) during a reduction reaction. The hydrogenation of the nitro groups occurs prior to halide hydrogenolysis in the absence of any added base or basic support material [112]. However, with the use of catalysts such as Pt the hydrogenolysis can be minimized [117,118]. In order to obtain high activity and selectivity researchers have developed new catalytic systems by devoting attention to the preparation of the catalyst which includes alloying [119], metal dispersion control [118], and metal-support interactions [120]. Another alternative route is the use of specific additives (promoter, inhibitors) such as bases or other electron rich compounds [121,122]. The interaction with the metal particles modifies the electronic properties of the catalyst [123].

2.5. CO oxidation reaction over gold catalyst

The carbon monoxide (CO) oxidation reaction involves the reaction of CO and O₂ in the presence of a catalyst to produce CO₂. The CO oxidation at low temperature is an important reaction type in many industrial and stationary processes. It is widely used for environmental protection and detection in closed spaceships and submarines that are used for long-term missions [124,125]. The process is also useful in air purification and detection that often involves situation in which the CO in low concentrations in air containing considerable amounts of water and /or other pollutants needs to be oxidised. It is therefore important for the catalyst to retain its activity for long periods of time at low temperature and in the presence of water in the reactant stream.

Hopcalite catalysts which mainly consist of MnO_x and CuO are the most commonly used commercial catalysts for the oxidation of carbon monoxide. However, the major setback with these catalysts is that they are not stable in a water environment and do not show any activity at low temperature (around room temperature) [126]. Interesting to note is that when tested for CO oxidation, Pt, Pd, Rh, and Ru, catalysts all showed substantial activity only at temperatures higher than 150 °C [127]. As the search for a suitable catalyst that could exhibit catalytic activity at lower temperature continued it was found that when Au was supported on metal oxides such as TiO₂, Fe₂O₃, and etc. the catalyst showed high oxidation conversions of CO at temperatures as low as -70 °C [126]. These findings geared the research interest towards gold catalysis which has since received much attention due to their potential in terms of improving catalytic activity for CO oxidation carried out at low temperatures. The reactions also give an insight on the reaction mechanism over gold based catalyst [128-130].

Like many other catalysts, gold-based catalysts also have some disadvantages. For example, Au/MnO_x [131], Au/TiO₂ [129], and Au/ZrO₂ [132] catalysts show

substantial activity for CO oxidation but prove to be very sensitive to water with a rapid deactivation of the Au in the presence of water. It is noteworthy that Au supported on TiO₂ is the most studied catalyst for CO oxidation due to its remarkable catalytic activity. It is therefore clear that there is a need to develop a catalyst with a hydrophobic surface and that is highly active for the CO oxidation.

2.5.1. Catalyst preparation

Prior to 1980 catalysis studies using gold metal received very little attention due to the assumption that the electronic configuration of the noble metal was associated with very low activities. It is now known that bulk gold itself is an inert material [133]. However, small gold particles have shown a remarkable catalytic activity, although the reason is still not known [134]. The catalytic activity of gold is largely dependent on numerous factors such as support material, preparation method, and the activation procedure [135]. Attempts to explain the activity of gold catalysts have been mainly related to the size of gold particles and the nature of the metal oxide support [134].

Au supported on TiO₂ is the most studied and used catalyst for CO oxidation at low temperature. This catalyst gives the optimum gold particles of 2-3 nm [136]. The trick to obtain such particle sizes is underpinned by a suitable preparation method as well as the conditions of preparation. Deposition precipitation in the presence of NaOH is a widely used method for the preparation of Au/TiO₂ catalysts. In this procedure the gold particle size is regulated by controlling both the pH and the calcination temperature [137]. Haruta and co-workers have demonstrated that the calcination of the catalyst at 300 °C is required to form metallic gold particles which strongly interact with the metal oxide support [138].

2.6. Anatase to rutile phase transformation

The isolation of individual polymorphs of titania (anatase, rutile or brookite) has led to enhanced photocatalytic effects which show potential in many applications involving water sterilization and antibiotic facilities [139,140]. Attempts to understand and to control the anatase to rutile transformations have been made. Although much data has been made available several issues such as the effect of particle size and preparation conditions remain unresolved. Earlier (and recent) studies on the anatase to rutile phase transformation have been concerned with the effect of TiO_2 preparation [139,140].

The preparation of TiO_2 via the sol-gel route produces nanoparticle materials by means of a chemical reaction. The sol-gel procedure is advantageous in terms of the control of the pore structure, dopant concentration, and chemical purity [141]. The presence of certain additives such as alumina, silica, zirconia, etc. in the TiO_2 material can be stabilised by the anatase phase (inhibition of phase transformation). Furthermore, the sulphate ions are also known to stabilise the anatase phase. On the contrary, the presence of chloride ions has an accelerating effect on the anatase to rutile phase transformation under hydrothermal conditions [142,143].

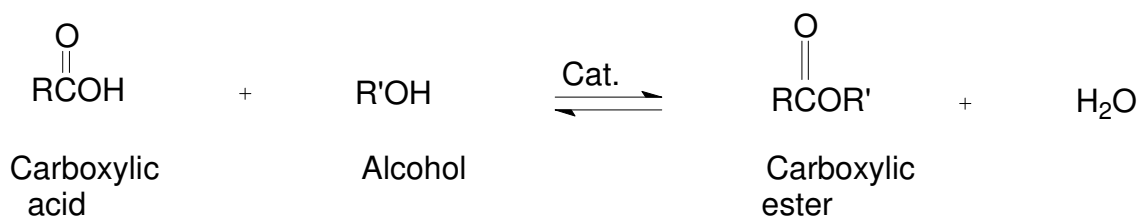
The thermodynamic stability of individual polymorphs can be dependent on the particle size. Both the anatase and brookite phases have lower surface enthalpies than the rutile phase, and are stable at small particle size [144]. A large surface area of the TiO_2 material is believed to influence the anatase to rutile transformation. Rutile is often obtained at higher temperature than anatase. Sintering of nanoparticles of TiO_2 increases their size at the expense of the total active surface area. The transformation mechanism for nanocrystalline TiO_2 material is underpinned by nucleation and growth. The kind of nucleation sites available in TiO_2 nanocrystalline material differs with the synthesis conditions [145,146].

The TiO₂ lattice adopts two sites, viz. interstitial and substitutional. The dopant can occupy these sites during thermal treatment of the material [147]. The dopants that can generate a high concentration of oxygen vacancies will tend to catalyse the anatase to rutile transformation. However, the dopants that reduce the concentration of vacancies will stabilise the anatase phase [148].

2.7. Esterification reactions

2.7.1. Various synthesis methods

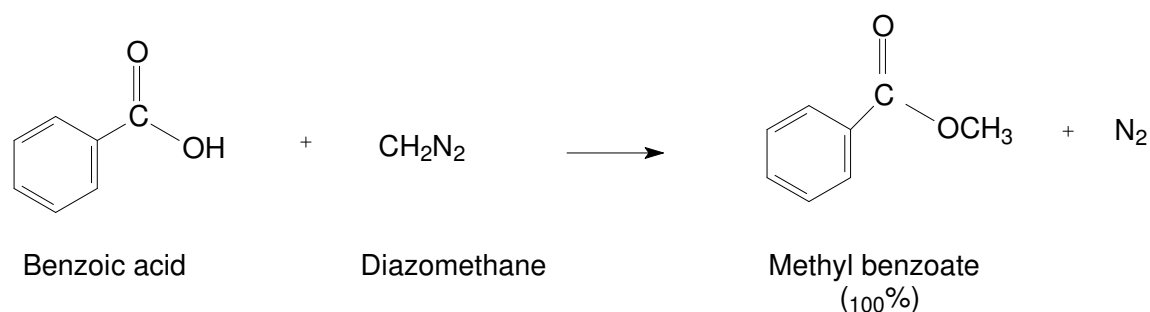
In 1895 Fischer and Speier made a startling discovery that esters could be produced homogeneously by heating a carboxylic acid with methanol or ethanol solution containing a small amount of mineral acid as a catalyst. Hence this type of reaction is called a Fischer esterification reaction [105]. In order to obtain high yields an excess amount of alcohol is necessary. The general reaction is illustrated in **Scheme 2.1**.



Scheme 2.1: General equation representing the esterification of carboxylic acid with an alcohol to produce an ester.

Another breakthrough came about in 1894 when von Pechmann discovered a synthesis method which is not equilibrium limited. The method involves the reaction of a carboxylic acid with a diazomethane, CH₂N₂. This is a simple reaction that gives a high yield (100 %) of an ester under ambient conditions and it takes place instantly.

In this reaction, unlike the reaction of a carboxylic acid with an alcohol, the bond that is cleaved during the reaction is the COO-H bond of the carboxylic acid rather than the CO-OH bond and hence this process is not a nucleophilic acyl substitution reaction. Nevertheless, the mechanism of the reaction is relatively cheaper and simpler since it occurs under mild, neutral conditions and releases nitrogen gas as the only by-product. However, the disadvantage is that diazomethane is toxic and explosive and must only be handled in small amounts by skilled persons [105]. The reaction is shown in **Scheme 2.2**.



Scheme 2.2: A diazomethane method for the synthesis of esters.

Esters can be produced from many different starting materials and one such example is the Tishchenko reaction. This is concerned with the reaction of an aldehyde with an alcohol to produce an ester product. For example, benzaldehyde is reacted with benzyl alcohol in the presence of a catalyst to produce benzyl benzoate. The process takes place in a homogeneous phase [113].

Galema and co-workers applied microwave heating to the esterification of stearic acid with butanol in the presence of toluene-p-sulfonic acid (TPSA) as a catalyst to produce butyl esters of stearic acid [106]. Butyl esters are imperative since they find widespread applications as solvent, spreading or softening agent in polymers (plastic). They are also used in the textile, cosmetic and rubber industries. Microwave heating showed better conversion than conventional heating [107].

Most esterification procedures require either the presence of strong acids [149] such as HCl, H₂SO₄, etc. [150] or unsafe reagents such as alkyl halides [151], diazomethane [152], chloroformates [153], etc. Thus, there is still a need for alternative methods which are simpler and cheaper for the esterification of various acids.

2.7.2. Solid catalysts

Although many different methods have been used for the production of various esters the drawback is that many of the reactions are still catalysed by acids. The use of acid catalyst in homogeneous process causes environmental complications. However, attempts to replace homogeneous catalysts with solid catalysts have been successfully made. Most of the attempts were devoted to the use of solid acid catalysts. Some of these catalysts include Amberlyst 15 resin, zirconium oxide, zeolites, heteropolyacids, etc. as solid acid catalysts. [154-157].

Vapour-phase esterification of alcohols with the acids in the presence of a solid catalyst has also received great interest over the last few years because the conversions obtained are higher than that achieved with the corresponding liquid-phase reactions [114]. An example is the production of ethyl acetate which is carried out in the vapour phase using catalysts such as silica gel, zirconium dioxide, activated charcoal and potassium hydrogen sulphate. Recently phosphoric-acid treated coal and calcium phosphate catalysts have also been used for the same reaction and other similar reactions [116].

The presence of Lewis and Brønsted acid centers promotes solid acid catalysts and allows them to efficiently function in organic transformations with excellent selectivity [155]. The Lewis acidity is often associated with the metal atoms lying on

the edge sites while the Brønsted acidity is associated with the metal ions lying on the planes [158].

The use of solid base catalysts for the esterification reactions was established a few decades ago, but they have been rarely used compared to the solid acid catalysts. Tanabe and co-workers reported on the heterogeneous solid base catalysed reaction of benzaldehyde with benzyl alcohol to form benzyl benzoate. Alkali earth metal oxides have been used as catalysts for this reaction due to their basic properties. The activity of the catalysts increases with an increase in basicity [114].

2.8. References

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3

Experimental Methods and Apparatus

3.1. Background on catalyst synthesis

Over the years a number of reviews have shown, and it remains a subject of continuous scientific and technological research, that in heterogeneous catalytic processes activity and selectivity are underpinned by the nature of the support and the preparation of the catalyst [1].

3.1.1. Catalyst support

The preparation of catalysts is often achieved by adding small amounts of a catalytically active component to a relatively large amount of a more inert solid which is called a support. Chakrabarty demonstrated that the role of the support includes the facilitation of the dispersion of the active component on a large surface thereby effectively exposing the active component to reactant molecules. It is believed that the support is not an inert carrier and that it generally interacts with the active components to form surface compounds that may or may not be catalytically more active [2]. The advantages of using a support in a catalytic system include the following:

1. The porous nature of the support allows the active component to be dispersed and this will result in the use of a small amount of the active component.
2. The intimate contact of the support with micro-crystalline particles of the active component inhibits catalyst sintering.
3. The interaction between the active component and support may lead to the formation of surface complexes which may be more active and selective than either the support or the active component.
4. The transport of the reactants and product molecules is underpinned by the porosity of the support and consequently this will affect the overall conversion and selectivity of the catalyst [2].

3.1.2. Support preparation

The preparation of many metal oxide supports is achieved by treatment of a metal halide, alkoxide, etc. with water. This material is then subsequently calcined to form the metal oxide. The sol-gel route involves the formation of a sol and subsequently the formation of a gel. In the substitution route a colloidal product is formed when a base and a metal oxide (i.e. titanium dioxide) are blended in a liquid medium. However, the formation of tubular supports is achieved by various methods such as the sol-gel method and substitution reactions but requires specified reaction conditions.

Kasuga and co-workers [3] was the first to report on a simple procedure to synthesize TiO_2 derived nanotubes. He indicated that the removal of ions such as Na^+ or K^+ with distilled water is crucial if the resultant tubes are to be formed. Other factors included the pH and the acid treatment.

The metal substitution process occurs in a solution resulting in a chemical change and can be expedited by the introduction of a base and subsequently subjecting the mixture to autogenous pressure. The effects of temperature and pressure changes in

the process can also result in the material transformation (substitution). The chemistry occurring during the process also depends on the metal oxide and base ratios (concentration).

Nanotubes, especially titania derived, are generally produced by sol-gel procedures. This procedure involves the use both a base and subsequently an acid in the washing stage. The advantage of the sol-gel method is higher purity resulting from acid treatment. Although widely used, the sol-gel method produces titania derived nanotubes with relatively lower specific surface areas.

In this thesis the nanosized supports synthesized were solely produced by the substitution route but the sol-gel pathway was only employed for comparison.

3.1.3. Catalyst preparation techniques

There are many routes or methods employed in the synthesis of supported catalysts. Impregnation and precipitation are two of the more commonly used pathways in the synthesis of these catalysts. The precipitation route involves the formation of a new solid from the addition of aqueous alkali to the aqueous solution of a metal salt. The impregnation route involves the coating of support with solution of a compound that contains the active component to form a supported catalyst.

Any change in the chemistry of the catalyst synthesis results in the change in catalytic and mechanical properties of the catalyst material. While the mechanical properties of the supported catalyst are associated with the support the catalytic properties are associated with the active component. However, in the case of precipitation route both the mechanical and catalytic properties depend on the new material formed.

In the case of precipitation the choice of the precursor is primarily informed by the cost. The morphology, texture and structure of the catalyst precipitated can be influenced by a number of factors such as temperature, concentration of the solution, pH and rate of stirring [4].

In this thesis a variant of the precipitation method was employed, namely deposition precipitation. This procedure was discovered in 1943 by Farben [5] and it involves the deposition of the active component onto a support through a chemical reaction at a controlled and elevated pH.

In the impregnation technique an already-prepared support is coated with an aqueous solution that contains the active component. This is often achieved by covering the entire surface of the support material with an active component containing solution and this is sometimes referred to as soaking. Moreover, the impregnation may also be achieved by using a volume of solution containing the active component that is equal or less than the pore volume of the support. This is then referred to as incipient wetness. Impregnation is often carried out in the presence of water as a solvent primarily because of its ability to penetrate the pores due to capillary action.

3.1.4. Catalyst shaping

Catalyst supports may have various shapes depending on the preparation method, i.e. fine powder, granular, monolithic, tubular or fibrous. However, a catalyst support may be shaped to a desired shape by using various preparation routes [6]. Depending on the catalyst preparation pathway taken the shaping can be done before or after the addition of the active component.

3.1.5. Catalyst drying and calcination

Fundamentally important is the drying of the catalyst prior to calcination because it modifies the pore structure that is essentially formed during this process and is

expedited by capillary forces. Calcination is often carried out at high temperatures and it effectively removes the unwanted component that is often incorporated during the addition of the active component (e.g. nitrate ions). Both drying and calcination steps influence the mechanical strength of the catalyst.

3.1.6. Catalyst activation

This process is often carried out in the reactor system (in-situ) and it involves the heating of the catalyst at temperatures higher than the reaction temperature. This process can either be carried out under reductive, oxidative or inert conditions.

3.2. Actual catalyst preparation

3.2.1. Support preparation

All the synthesized supports were prepared from commercial P25 Degussa titania. P25 Degussa titania powder (~10 g) was placed in a 1L Teflon container together with 200 grams of either potassium hydroxide or sodium hydroxide pellets. Water (200 ml) was added to the mixture [6]. The mixture was heated for 20 hours at 120 °C in an autoclave with constant stirring at a rate of 500 rpm. The solution was allowed to cool and then aged for a few hours before it was washed with deionised water. Subsequently the solid product was separated from the mixture by centrifugation at a stirring rate of 10 000 rpm for 30 minutes at 4 °C. The washing was repeated until the conductivity of the solution was below 100 µS/cm and constant. The removal of the base is rather a lengthy process which may take a few weeks or even months. The pH was also monitored. This was achieved by measuring the pH of the liquid extract during the washing process. The solid was dried in an oven at 120 °C for 12 hours and then allowed to cool to room temperature. The material was then sieved to a desired size depending on the reaction to be carried out.

Other support powders were shaped and used as received. The shaping of these materials was achieved by mixing each powder with water and then compressing the slurry into a moist paste. This material was then dried in an oven at 120°C for 48 hours and after cooling it was crushed into fragments, and the particles of desired size were sieved out. The larger particles were recycled and re-sieved while the smaller ones (fine powder formed as a result of crushing) were mixed with water again to form a moist paste.

3.2.2. Preparation of supported catalyst

The loading of the most active phases of the various supports was achieved via the impregnation route. In the impregnation procedure a certain volume of the solution containing the precursor of the active phase was brought into contact with the solid support. Excess solvent was then removed by drying at room temperature for a few hours and subsequently in an oven at 120°C. The concentration profile of the impregnated compound depends largely on the mass transfer conditions within the pores during impregnation and drying [7,8]. Therefore, the concentration of the active phase may vary depending on the nature of the support used.

In addition, different catalysts for different reactions were also prepared from precursors with different loadings of the active phase. The precursors used included nitrate, acetate, chloride and tetrachloroauric acid. The solvent was chosen according to the solubility of the metal salt used. The solvents used included water, acetonitrile, toluene and ammonium hydroxide solution (see **Table 3.1**). Catalysts were calcined at temperatures ranging from 300 to 500°C for a few hours and then used for specific reactions. The details of catalyst preparation methods and conditions will be described in later chapters.

Table 3.1: Solvent used in the preparation of catalyst chosen according to the metal salt solubility

Catalyst	Precursor	Precursor formula	Solvent
Pd/TiO ₂	Palladium acetate	Pd(CH ₃ COO) ₂	Toluene
Pd/TNT	Palladium acetate	Pd(CH ₃ COO) ₂	Acetonitrile
Pd/TNT	Palladium chloride	PdCl ₂	Acetonitrile
Pd/TNT	Palladium nitrate	Pd(NO ₃) ₂	Acetonitrile
Au/TNT	Gold tetrachloroauric acid	HAuCl ₄	Water/Ammonium hydroxide
Li/TiO ₂	Lithium nitrate	LiNO ₃	Water
Na/TiO ₂	Sodium nitrate	NaNO ₃	Water
K/TiO ₂	Potassium nitrate	KNO ₃	Water
Cs/TiO ₂	Cesium nitrate	CsNO ₃	Water

Key: TNT = titania derived nanotubes

The deposition precipitation (DP) procedure was used to prepare gold-based supported catalysts by: (1) precipitation from bulk solutions and (2) interaction of gold particles with support surface. A slurry was formed using a powder of the appropriate salt in an amount that was sufficient to give the desired loading. The pH was controlled by the addition of 15 % NH₄OH thereby expediting precipitation where necessary. A well-dispersed and homogeneous active phase is achieved when the support interacts directly with the ions that are present in the solution and this determines the nature of the phase formed. This interaction provides a uniform

distribution of the active component over the support surface even at high loadings [7,9]. A specific description of the procedure and conditions employed will be discussed in Chapter 7.

3.3. Catalyst testing apparatus

A glass tube reactor (1.4 cm id x 34.5 cm) was constructed. This was equipped with a J-type thermocouple. The tube was then inserted into the heating jacket which was built from a coiled heating element with the exterior covered in stainless steel. The stainless steel exterior was further covered in glass fibre wool. The catalyst bed, which was placed at the centre of the reactor tube, was firmly held vertically at the centre of the heating jacket.

The hydrogen inlet was covered with a heating tape and glass fibre wool. The heating of both heating jacket and tape was regulated by a temperature controller with the aid of a J-type thermocouple.

The reactants were fed from the top to bottom of the reactor at controlled feed rates by means of a 50 ml liquid syringe using a Sage syringe pump. Before the liquid reactant was brought to contact with the catalyst it was brought into contact with heated hydrogen gas. The hydrogen flow rate was controlled by means of a needle valve and a calibrated rotameter. The reaction products were passed through a water condenser to ensure condensation of the trace amount of gaseous products. The products were subsequently collected for further analysis (**Fig. 3.1**). **Fig. 3.2** shows a schematic diagram of the catalyst testing apparatus.

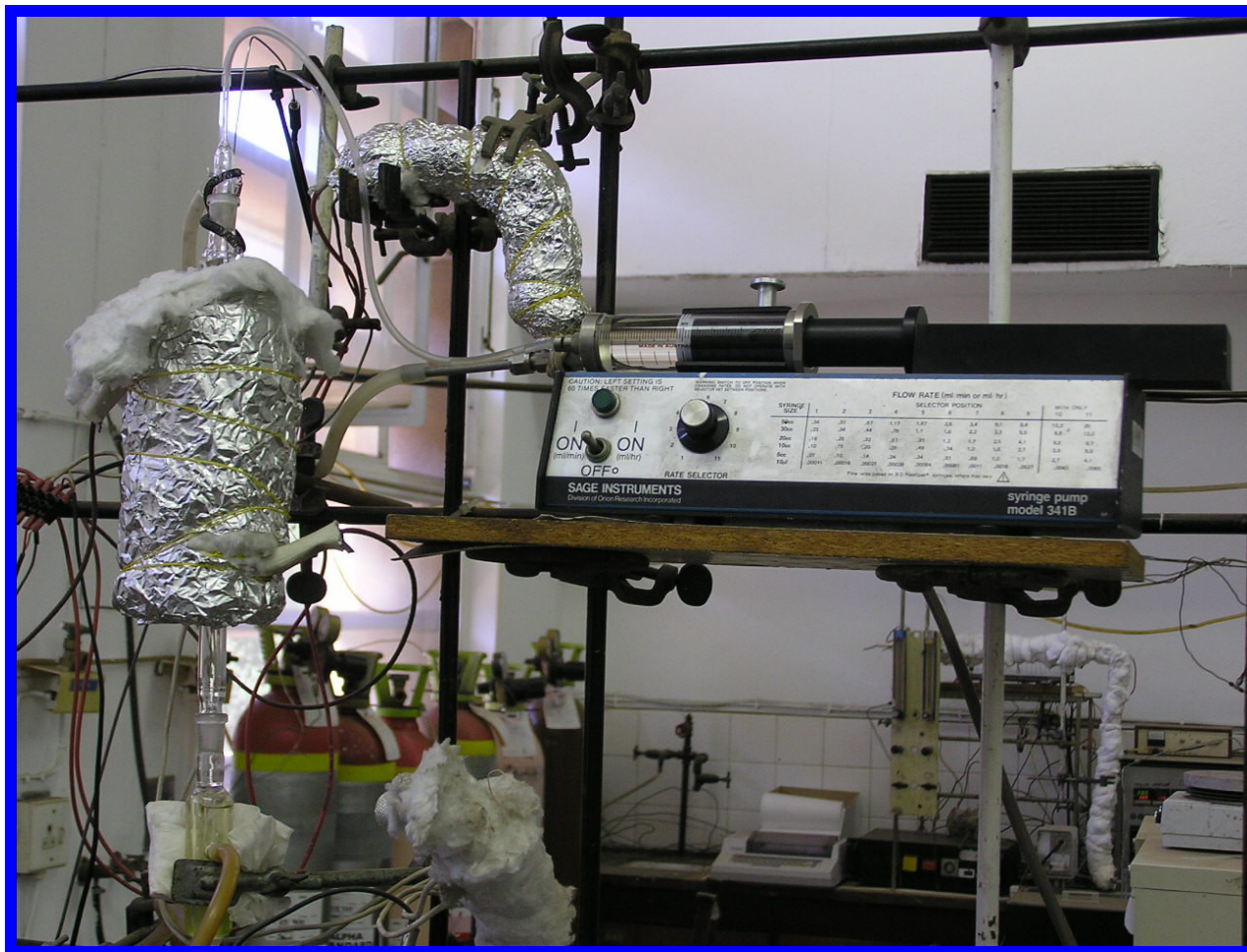
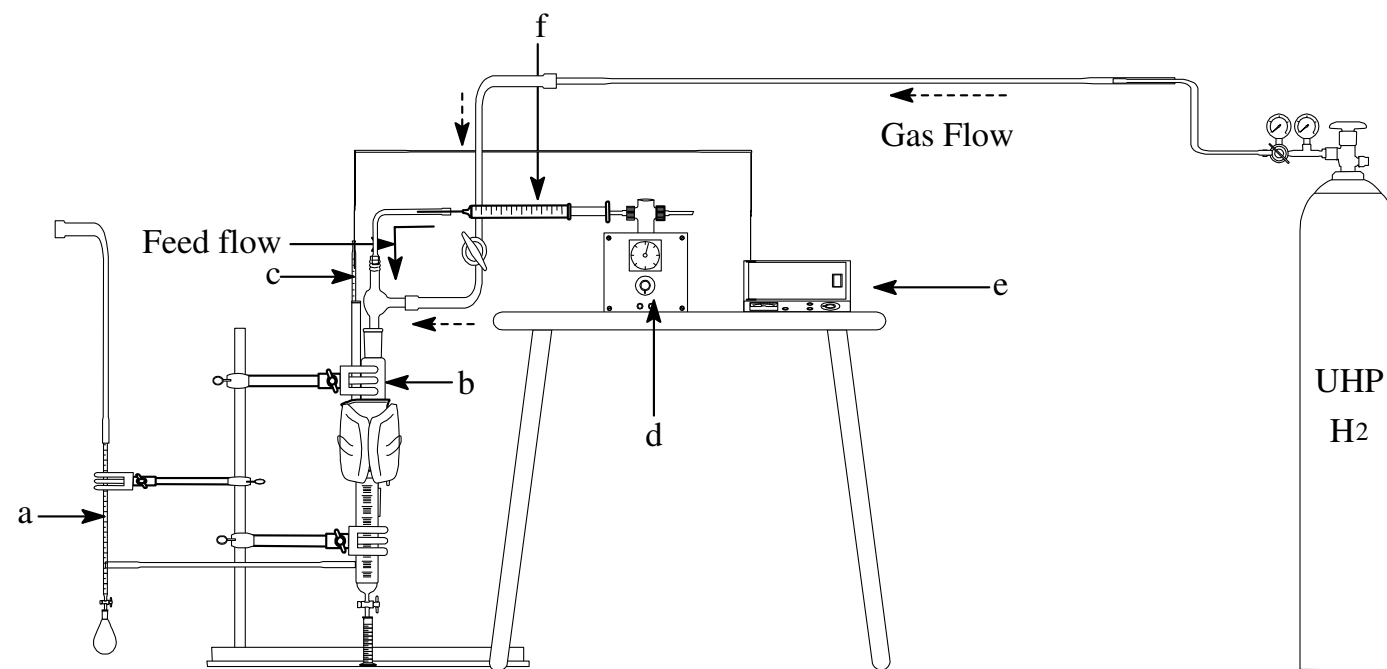


Figure 3.1: A digital image of catalyst testing apparatus. 1. Heating jacket; 2. Glass reactor; 3. Phenol/EtOH feed; 4. H_2 feed inlet covered with heating tape and glass fibre wool; 5. Syringe containing phenol/EtOH mixture; 6. Sage syringe pump; 7. Water condenser.



Key: (a) Bubble meter; (b) Fixed bed reactor equipped with a tubular furnace; (c) J-type thermocouple; (d) Syringe pump; (e) Temperature controller; (f) Syringe.

Figure 3.2: A Schematic diagram of catalyst testing apparatus

The effluent collected into a collector was periodically extracted and analysed by means of an off-line FID-GC (**Fig. 3.3**) equipped with a packed ZB wax capillary column (30 m long) at temperatures controlled from 30 to 220°C at a heating rate of about 5.33 Kmin⁻¹. The GC output was obtained by means of an integrator (**Fig. 3.4**).

The reaction products were further identified and confirmed by GC-MS, using a VG-11-250 data system, equipped by Hewlett Packard. This instrument was equipped with a Finnigan MAT GCQ gas Chromatograph and GCQ Quadrupole ion trap mass analyser. The advantage associated with the use of this instrument is that samples to be analysed can be gas, liquid, or solid. Gas and liquid samples can be injected through the gas chromatograph while liquid and solid samples can be introduced into the system through a direct sample probe.

Furthermore, the reaction product identification was achieved by injecting into a GC a mixture of the product sample and pure commercial products as identified by GC-MS. This process is sometimes referred to as spiking [10].



Figure 3.3: A picture of an off-line GC apparatus equipped with a capillary column and used to separate reaction products.



Figure 3.4: A picture of an integrator apparatus used for GC output.

3.4. Catalyst characterisation

3.4.1. BET

Surface areas were determined by the physical adsorption of a monolayer of nitrogen gas (area = 0.162 nm^2) at -196°C from Brunauer-Emmett-Teller (BET) adsorption isotherm measurements. The BET surface area determinations were achieved using either ASAP 2010 porosimeter or a Micromeritics TRISTAR 3000 analyser. Adsorption and desorption of a nitrogen was repeated until two consistent values for desorption were obtained.

The surface areas and pore diameters of the catalysts analysed are given in later chapters.

3.4.2. Scanning electron microscopy (SEM)

The scanning electron microscope provided information on sub-micrometer particle sizes and shapes. SEM is used to study topography, texture and surface features of powders. Furthermore, the SEM has a wide magnification range and produces images in the range of 10 to 10^5 times their normal size. The SEM produces a three dimensional view of a specimen and this is very useful in examining the shape and structure of a specimen.

Sample preparation is crucial in order for the sample to withstand the vacuum in the microscope. Samples that are poor conductors in nature are usually coated with a thin layer of a metal to prevent the accumulation of charge on the surface of the sample.

In SEM analysis an electron gun emits a beam of electrons which then interacts with the surface leading to the emission of electrons from the surface of the specimen during the scanning with the electron beam. The electrons from the beam interact

with the sample resulting in the deflection of secondary particles to a detector which subsequently converts the signal to voltage and amplifies it.

For the analysis, all samples were mounted on aluminium stubs and then coated with gold. The analysis was then carried out using a JEOL JSM-840 scanning electron microscope.

3.4.3. Transmission electron microscopy (TEM)

TEM is a useful technique in determining crystal morphology and particle size of materials. It can also be used for the assessment of particle agglomeration and sintering. TEM has become a very useful technique for various applications in nanotechnology.

In TEM a beam of electrons is propagated through a solid sample in a vacuum. Electrons transmitted through the sample are then detected to produce three-dimensional images which represent the relative extent of penetration of electrons in a specific sample. As in the case of SEM, when electrons interact with a specimen there are also emissions associated with the spacing of energy levels in the atoms. TEM can be coupled with energy-dispersive X-ray (EDX) analysis to obtain information about the chemical nature and composition of the sample. This is achieved by bombarding a region in the sample with an electron beam which leads to the emission of characteristic X-rays and subsequently gives information about the spatial distribution and concentration of elements in the sample.

High resolution TEM (HRTEM) allows for the determination of lattice spacings and direction of particles.

Samples were analysed either with a low resolution transmission electron microscope (JEOL 100S) or with a high resolution transmission electron microscope (JEOL 2010). Samples were mounted on hollow copper grids coated with carbon

film made in the electron microscopy laboratory at the University of the Witwatersrand.

3.4.4. Temperature programmed techniques

Temperature programmed techniques involve a number of catalyst characterisation methods that entail thermal transient analysis. In most temperature programmed techniques a sample is subjected to different gaseous environments while the temperature of the sample is systematically and linearly increased with time. The system response to the thermal transient is monitored by way of measuring the concentration of the gas desorbed by temperature programmed desorption (TPD), the concentration of gas consumed by temperature programmed reduction (TPR), a change in sample weight by thermogravimetric analysis (TGA), the heat of reaction at constant temperature by differential scanning calorimetry (DSC) and the change in temperature for constant heating by differential thermal analysis (DTA).

TPD was used to obtain information about the strength and number of basic sites while TPR was used for the reduction kinetics of metal oxides. CO₂ was used as a probe gas for TPD while H₂ was used in TPR studies. The number of total basic sites was obtained by the amount of total desorbed CO₂ as determined from the area under the curve. On the other hand TPR peaks give information about the reduction profile of metallic catalyst and the nature of the interaction between the metallic catalyst (active phase) and support. The extent of reduction can be calculated from the area under the curve.

TPR and TPD reaction setups were similar and operated similarly. With either technique a sample was placed on the sintered frit of a reactor chamber positioned midway along the upright arm of the Pyrex U-shaped tube. The modified U-tube was of singular construction thus restricting sample access to the top opening of an upright arm. An all glass external thermocouple well extended to just above the

sintered frit of the reaction chamber and provided a means of maintaining a sample temperature via a type J thermocouple probe linked to a digital readout.

Generally about 0.2 g of calcined catalyst was placed in the Pyrex U-shaped tube. The sample was heated in situ at 150 to 500°C under a He (in TPD) or N₂ (in TPR) gas to remove any residual H₂O and CO₂ adsorbed in the transfer of sample to the reactor. After cooling to room temperature, CO₂ (in TPD) or H₂ (in TPR) was passed over the system for 0.5 to 2 hours at a rate of 30 ml/min. The TPD system was then purged for 30 minutes using H₂ to remove gaseous CO₂ not adsorbed on the catalyst. The system was out-gassed until the detector maintained a constant output signal. The adsorbed CO₂ was then desorbed by increasing the temperature at a rate of 10°C min⁻¹ up to 300 or 800°C. The TPR signal was measured on a low temperature dual filament TCD and recorded using a PC equipped with an I/O card while the TPD signal was measured on an FID (CO₂ was converted to CH₄ using a methanation device and then the signal was measured with an FID).

TGA, DSC and DTA measurements provide information about the nature of solid compounds. TGA was used to measure weight changes in a material as a function of temperature under a controlled atmosphere using N₂ as a purge gas. This was achieved by placing about 20 mg of solid sample in a platinum pan which was then placed in a heating jacket. The sample was heated from room temperature to 800°C at a heating rate of 5°C/min. The analysis was carried out using a Perkin Elmer Pyris 1 thermogravimetric analyser (TGA). Information about the material thermal stability and composition was gathered from the analysis.

Differential scanning calorimetry (DSC) also provides information about the heat of reaction and was used to study the material's thermal transitions that occurred when the material was heated by measuring the heat flow with temperature. Phase transitions were determined. The phase transitions may be of either endothermic (heat absorption) or exothermic (heat evolution) in nature. Information on the

material purity can also be obtained from this technique. Data was gathered using a Mettler Toledo DSC822 instrument.

Both DSC and DTA techniques provide similar information.

3.4.5. X-ray diffraction (XRD)

Bulk catalysts can be subjected to analysis by X-ray diffraction. Comprehensive libraries of available characteristic d-spacings and intensities of previously studied solids are available for comparative purposes.

In XRD, a beam of X-rays with a wavelength ranging from 0.5 to 2 Å, incident on a specimen is diffracted by the crystalline phases in a specimen according to Bragg's law:

$$\lambda = 2d\sin\theta$$

where d is the spacing between atomic planes in the crystalline phase and λ is the X-ray wavelength. The intensity of the diffracted X-rays is measured as a function of the diffraction angle 2θ and the specimen orientation.

X-ray diffraction patterns from a Phillips PW1830 Generator Diffractometer were used to determine the phase and crystallite size of various catalysts. This apparatus utilizes nickel filtered $\text{CuK}\alpha$ -radiation. The diffraction patterns were collected with an X-ray gun operated at 40 kV and 20 mA. Samples were run as powders mounted on an aluminium sample holder. Compound identification was accomplished by comparison of measured spectra with the spectra of pure samples.

3.4.6. Raman spectroscopy

Raman spectroscopy can be thought of as a means to measure the inelastic light scattering which results from the excitation of the vibrations in molecular and crystalline materials all as a function of wavenumber. Raman scattering of monochromatic light is usually from a laser in the visible, near infrared or near ultraviolet region. Excitations in the system are absorbed or emitted by the laser light, resulting in the energy of the laser photons being shifted up or down. The shift in energy gives information about the photon modes in the system. Raman spectroscopy is very sensitive to lengths, strengths and arrangements of chemical bonds in a material, but less sensitive to the chemical composition. Raman spectroscopy was used for the identification of polymorphic phases in the support materials. It was also used to identify the crystal structure of supports. The in-situ temperature Raman studies were also carried out to investigate the phase changes that occurred with increasing temperature.

Raman spectra were acquired with the micro-Raman attachment of a Jobin-Yvon T64000 Raman spectrometer operated in triple subtractive mode. The excitation wavelength was the 514.5nm line from a Coherent Innova 308 argon ion laser. Using a 20x objective, the laser beam diameter at the sample was approximately 1.5 micron. The power at the sample was kept below 1mW to minimise local heating. Plasma lines were removed from the incident light using a narrow bandpass laser line filter. The dispersed spectra were detected with a liquid nitrogen cooled CCD detector, and the data was recorded using Labspec 3.03 software.

3.4.7. Infrared spectroscopy (IR)

In infrared spectroscopy molecules are thought of as systems of balls (atoms or ions) that are connected by springs (chemical bonds). These systems can be set into vibration, and vibrate with frequencies that are determined by the mass of the balls

(or atomic weight) and by the stiffness of the springs (bond strengths). The mechanical molecular vibrations are within the infrared region in the electromagnetic spectrum.

Photon energies that are associated with an infrared region are used to induce vibrational excitations of covalently bonded atoms and groups. The covalent bonds in molecules are like stiff springs and they bend and stretch causing various vibrational motions that are characteristic of specific atoms within a molecule. As a result compounds will absorb infrared radiation that corresponds in energy to these vibrations. An infrared spectrometer gives absorption spectra of compounds that are a reflection of their molecular structure. Data was collected using a Bruker Tensor 27 spectrometer.

3.4.8. Malvern analysis

A Malvern Mastersizer 2000 was used for particle size analysis. This utilises Fraunhofer diffraction of light formed by particles with a diameter larger than the incident laser beam wavelength. A combination of an optical filter, lens, and photodetector coupled with a computer with Mastersizer software enables computation of the particle size distribution from the diffraction data. The dispersant is prepared by adding an ammonium polyacrylate deflocculant to ~ pH8.30 using a water medium (dispersant) in a 1000ml container and delivered to the optical unit. The mastersizer was then used to capture the scattering pattern from the prepared sample which was then displayed and stored as volume% against the particle size.

3.5. References

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4

Nanotubular titanate supported palladium catalysts: the influence of structure and morphology on phenol hydrogenation activity

4.1. Introduction

The discovery of carbon nanotubes has directed research activities involving catalyst supports towards the structure and morphology of nanotubes and fibres and their mechanism of formation [1]. Recently, nanotubular materials based on titanium dioxide has attracted much attention due to the versatile applications shown by these materials in environmental purification, gas sensors, high effect solar cells, and in photocatalysis [2-4]. The ever-growing interest in titania derived nanotubes is driven mainly by the large surface area, chemical stability, non-toxicity, and the modest production costs of the tubular materials [5].

Conventionally the sol-gel method has been widely used to synthesize TiO_2 derived nanotubes using templates such as organogels or porous anodic alumina [6-9]. These methods are relatively inexpensive and offer numerous advantages since the final products are pure and homogeneous [10-12]. However, the removal of the homogeneously mixed template is invariably a challenging task [13].

Early studies on the synthesis of nanotubular titanate suggested that tube formation is underpinned by an acid-treatment step [14-16]. However, in investigations by ourselves and others, a simple and cheap methodology was employed to synthesize the nanotubes in the absence of both a template and an acid treatment. The influence of synthesis conditions such as ageing time, morphology, crystallinity on the surface properties of the tubular material was investigated.

In our present study, we report on the use of nanotubular titanate, as *catalyst support*, for use in the hydrogenation of phenol. It is known that the activity of a supported metal catalyst is determined by the extent of interaction between the metal component and the support. The formation of small metal particles in a catalyst system is expedited by the use of a support on which the particles are relatively well anchored and dispersed [17]. Studies have shown that the performance of the catalyst may be influenced by several factors such as method of synthesis, nature of support, metal loading, pre-treatment and reduction conditions [18-27].

Hydrogenation of phenol is an industrially important reaction required for the production of nylon 6 and numerous methods are used to produce cyclohexanone [28]. The industrial production is achieved either by the oxidation of cyclohexane or hydrogenation of phenol. However, high temperature and pressure are essential for the reaction and the generation of by-products is inevitable. In the hydrogenation of phenol a one- or two-step process is employed to produce cyclohexanone. The two-step process involves the hydrogenation of phenol to cyclohexanol and subsequently the dehydrogenation of cyclohexanol to cyclohexanone. The one-step process is a direct method for the synthesis of cyclohexanone from phenol and it provides economical advantages in terms of capital costs and energy savings [13,29].

The development of a suitable catalyst for such a process is still an area of active research in catalysis. Typically metals such as Pd, Pt, Ni, Cr, V, and Zr supported on Al_2O_3 , MgO , SiO_2 , TiO_2 have been used as catalysts for the hydrogenation of phenol to give cyclohexanone and cyclohexanol [2,30,31]. Although the preparation of Pd nanoparticles supported on TiO_2 derived nanotubes has been reported elsewhere [44] there have been no reports on the use of Pd supported on nanotubes derived from titanium dioxide, as a catalyst, for this gas-phase reaction. In this report, both the synthesis and the application of Pd supported on TiO_2 derived nanotubes for hydrogenation of phenol are reported. The objective is to study the effect of morphological features, structural composition and the high surface area of the nanotubes of titanate supported Pd catalysts on the overall catalytic activity, selectivity and stability of the reaction. Some reports have suggested that supports with acidic properties are imperative for the selective formation of cyclohexanone while other reports have in contradiction suggested that the basic nature of the support is essential [28]. The understanding of these contradictions remains a challenge. Thus, the need for further studies to resolve this puzzle is crucial. The influence of the basic properties of the titanium dioxide derived nanotubes is thus reported.

4.2. Experimental

4.2.1. Catalyst preparation and activation

Two types of TiO_2 , referred to as commercial and synthetic, were generated from '*as-received*' TiO_2 powder (P-25 Degussa, containing anatase and rutile phases). In the case of the commercial TiO_2 support, '*as received*' TiO_2 powder was mixed with water and compressed into a moist paste. The solid material was dried in an oven at 120°C for 48 h. After cooling, it was crushed and sieved to the desired size (800 to 1000 μm in diameter) and designated as $\text{TiO}_2\text{-D}$.

Synthetic TiO_2 samples were prepared by a similar route to that described elsewhere in the literature [32]. 'As received' TiO_2 powder (~10 g) was placed in a 1L teflon container together with 200 g of KOH pellets. Water (200 ml) was added to the mixture. The mixture was heated for 20 h at 120°C in the autoclave with constant stirring at the rate of 500 rpm. Three reactions were performed. In each case the solution was allowed to cool and then aged at room temperature without stirring. The aging time for the three solutions was varied (0, 2 or 61 days). After aging each sample was washed with deionised water. Subsequently the solid product was separated from the mixture by centrifugation at a stirring rate of 10,000 rpm for 30 minutes at -4°C . The washing was repeated until the conductivity of the solution was below $100\ \mu\text{S}/\text{cm}$ and constant. The removal of the basic ions is rather a lengthy process which may take many weeks. The pH of the solution during washing was also monitored. The solid was dried in an oven at 120°C for 12 h. Each sample was sieved to give particles with a size of 800 – 1000 μm in diameter. These synthetic samples of TiO_2 were designated according to the ageing time as $\text{TiO}_2\text{-A}$ (0 day), **-B** (2 days) and **-C** (61 days) respectively. The addition of Pd (1 wt%) to the supports ($\text{TiO}_2\text{-A}$, **-B**, and **-C**) as well as the reference sample ($\text{TiO}_2\text{-D}$) was carried out by a simple wet impregnation method where an appropriate amount of $\text{Pd}(\text{CH}_3\text{COO})_2$ was dissolved in acetonitrile and added to each support sample. The mixtures were dried at room temperature for 5 h and then placed in an oven at 120°C for 12 h. The catalysts were then calcined at 300°C for 5 h and designated as **CAT-A**, **-B**, **-C** and **-D**.

4.2.2. Catalyst characterisation

XRD analysis of the samples was carried out using a Phillips PW1830 Generator Diffractometer. The apparatus utilizes nickel filtered $\text{CuK}\alpha$ -radiation ($1.54\ \text{\AA}$). The diffraction patterns were collected with an X-ray gun operated at 40 kV and 20 mA.

The surface area of the catalysts was determined by the physical adsorption of a monolayer of nitrogen gas (cross-sectional area = 0.162 nm^2) at -195°C from BET adsorption measurements using an ASAP 2010 porosimeter.

The reducibility of the catalysts was tested by temperature programmed reduction (TPR) by passing a stream of 5% H_2 balanced in argon (FR= 8 ml/min) through a sample contained in a glass tube reactor. This was achieved by heating 0.3-0.4 g of the sample in a reactor up to 800°C at a heating rate of $5^\circ\text{C} / \text{min}$. The system was equipped with a thermal conductivity detector (TCD).

Surface basicity was determined by CO_2 adsorption at room temperature. The amount of catalyst utilized was $\sim 0.2 \text{ g}$. The catalysts were degassed at 150°C for 30 minutes and then cooled to room temperature. CO_2 gas was adsorbed at ambient temperature. Desorption of the probe gas was carried out over a range of temperatures (RT to 300°C) and the isotherm was recorded.

Raman spectra were acquired with the micro-Raman attachment of a Jobin-Yvon T64000 Raman spectrometer operated in triple subtractive mode. The excitation wavelength was the 514.5 nm line from a Coherent Innova 308 argon ion laser. Using a 20x objective, the laser beam diameter at the sample was approximately 1.5 microns. The power at the sample was kept below 1 mW to minimise local heating. Plasma lines were removed from the incident light using a narrow bandpass laser line filter. The dispersed spectra were detected with a liquid nitrogen cooled CCD detector, and the data was recorded using Labspec 3.03 software.

The morphological analysis was carried out using transmission electron microscopy (TEM on a JEOL 100S microscope; at high resolution (HR) on a JEOL 2010 microscope). Samples for both TEM and HRTEM analysis were prepared by adding about 1 mg of each sample to 1 ml of ethanol followed by sonication for 10 minutes. A few drops of suspension were placed on a hollow copper grid coated with a carbon film made in the laboratory.

The morphological analysis was further carried out using scanning electron microscopy (SEM) on a JEOL JSM-840 scanning electron microscope.

Thermal analysis studies were carried out using a Perkin Elmer thermogravimetric analyser (TGA). Samples were purged with nitrogen and heated from room temperature to 800°C at a heating rate of 5°C per minute.

4.2.3. Hydrogenation of Phenol

A fixed-bed microcatalytic reactor (1.4 cm id x 34.5 cm) was employed to carry out the gas phase phenol hydrogenation reaction. About 0.5 g of the catalyst sample (particle diameter of 800-1000 μm) was placed in the reactor and kept between two quartz wool plugs. The sample was pre-treated in hydrogen at 300°C for 1 h and cooled to the reaction temperature ($165 < T/^{\circ}\text{C} < 300$). The reactant feed consisting of phenol dissolved in ethanol (1:1 w/w) and the reaction mixture (hydrogen to phenol mole ratio ranging from 2 to 12) was fed into the reactor at a calculated rate from the top of the reactor using a calibrated motorized syringe pump (Sage). The products were periodically collected and analysed by means of a flame ionisation detector (FID) GC equipped with a packed capillary column (ZB wax). The reaction products were further identified and confirmed by GC-MS, using a VG-11-250 data system, equipped by Hewlett Packard.

4.3. Results and discussion

Nanotubular titanate materials have been synthesized from NaOH [32,33]. However, previous attempts to prepare the tubes using KOH have either been unsuccessful or led to the synthesis of titanate nanobelts (sheets) [34]. We have found that by using an 18 M solution the tubes can be reproducibly synthesized in large and small amounts. The procedure for making 1-20 g from KOH is described in the experimental section.

4.3.1. BET surface area

The physico-chemical properties of synthetic TiO_2 and Pd (1 wt%) impregnated on synthetic TiO_2 are reported in **Table 4.1**. The BET surface areas of the new materials (TiO_2 -**A**, -**B** and -**C**) along with reference TiO_2 -**D** were measured both before and after the addition of palladium (**Table 4.1**). It is evident that the surface area of TiO_2 -**D** and -**A** do not vary much. This shows that when the raw material is not aged (TiO_2 -**D**) prior to the removal of KOH that the surface area is not significantly altered. However, ageing of '*as received*' TiO_2 for 2 days in KOH, resulted in TiO_2 -**B** having a surface area of $270 \text{ m}^2/\text{g}$. Further, ageing for 61 days, resulted in preparation of TiO_2 -**C** with a low surface area of $33 \text{ m}^2/\text{g}$, lower than that of the '*as received*' TiO_2 (TiO_2 -**D**). This implies that ageing in an alkali solution (KOH) for a long time promotes agglomeration of TiO_2 by way of inducing charge accumulation on the surface resulting in the particles sticking together to form bigger particles. Thus, an appropriate ageing time is important to produce a TiO_2 derived material with high surface area. The addition of Pd to either the reference or synthetic support does not have any significant influence on the surface area. The slight decrease in surface area for TiO_2 -**A** and -**B** after the addition of Pd may be due to the effect of calcination temperatures used. The average pore diameters of TiO_2 -**D** and the synthetic TiO_2 -**A**, and -**B**, are comparable (**Table 4.1**). This shows that the surface enlargement phenomenon was not affected by the base (KOH) treatment.

However, a different kind of behaviour was noticed with TiO_2 -**C**. The average pore diameter was found to be bigger (8.8 nm) than TiO_2 -**D** (5.9 nm) and both TiO_2 -**A** and -**B**. The addition of Pd to TiO_2 -**C** increased the pore diameter (9.4 nm) and decreased the surface area to $25 \text{ m}^2/\text{g}$. Thus, a longer ageing time results in a less porous TiO_2 (pore volume = $0.23 \text{ cm}^3/\text{g}$). The conductivity and pH values are also reported in **Table 4.1**. It is noteworthy that with an increase in ageing time, both conductivity and pH values increase. It appears that long ageing time enhances KOH surface binding resulting in a high pH value leading to the high level of basicity.

Table 4.1: Physical and chemical properties of reference and synthetic TiO₂ and the corresponding Pd (1 wt%) supported catalysts

Catalyst	Designation	AT (days)	S _{BET} (m ² /g)	PD (nm)	pH value	Conduct. (μS/cm)
TiO ₂ -D		-	50	5.9	-	-
Pd/TiO ₂ -D	CAT-D	-	46	6.3	-	-
TiO ₂ -A		0	52	5.4	7.76	15.0
Pd/TiO ₂ -A	CAT-A	-	46	5.4	-	-
TiO ₂ -B		2	270	6.4	9.98	36.2
Pd/TiO ₂ -B	CAT-B	-	225	7.4	-	-
TiO ₂ -C		61	33	8.8	10.40	95.0
Pd /TiO ₂ -C	CAT-C	-	25	9.4	-	-

Key: AT = Ageing time; S_{BET} = BET surface area; PD = Pore diameter;
Conduct. = Conductivity.

4.3.2. SEM and TEM analysis

The morphology of the TiO_2 samples was investigated by electron microscopy (TEM and SEM) and the results are shown in **Fig. 4.1**. The TEM image of TiO_2 -**D** (**Fig. 4.1a**) shows that the sample is composed of clusters of particles or agglomerates that have an average diameter of 75 nm. The TEM image of TiO_2 -**B** is shown in **Fig. 4.2a** and shows the presence of 100% tubes (randomly distributed). These tubes have a diameter of 8 to 11 nm and are one hundred to several hundred nanometers in length. The tubes are open-ended on both sides and are thin walled. The TEM image of TiO_2 -**C** (**Fig. 4.1b**) reveals the formation of a lesser proportion of tubes and larger amounts of amorphous material. Though the presence of tubes is small in quantity, they are still fully developed with thick walls. The presence of amorphous TiO_2 suggests that longer ageing re-dissolves the tubes giving back the amorphous form. This shows that the formation of amorphous material is thermodynamically favoured even at a high KOH concentration.

The low magnification TEM image of TiO_2 -**A** (**Fig. 4.1c**) shows the presence of some tube-like structures. Attached to these structures is some amorphous material that has formed agglomerates. The SEM image of TiO_2 -**A** (**Fig. 4.1d**) confirms the presence of unrolled sheets of tube-like structures. It is believed that sheet formation may be the first step towards tube formation [35]. The reason for TiO_2 -**A** not being fully developed into a tubular structure is ascribed to the absence of ageing. The addition of Pd to TiO_2 -**A** (**CAT-A**) did not alter the morphology of the material.

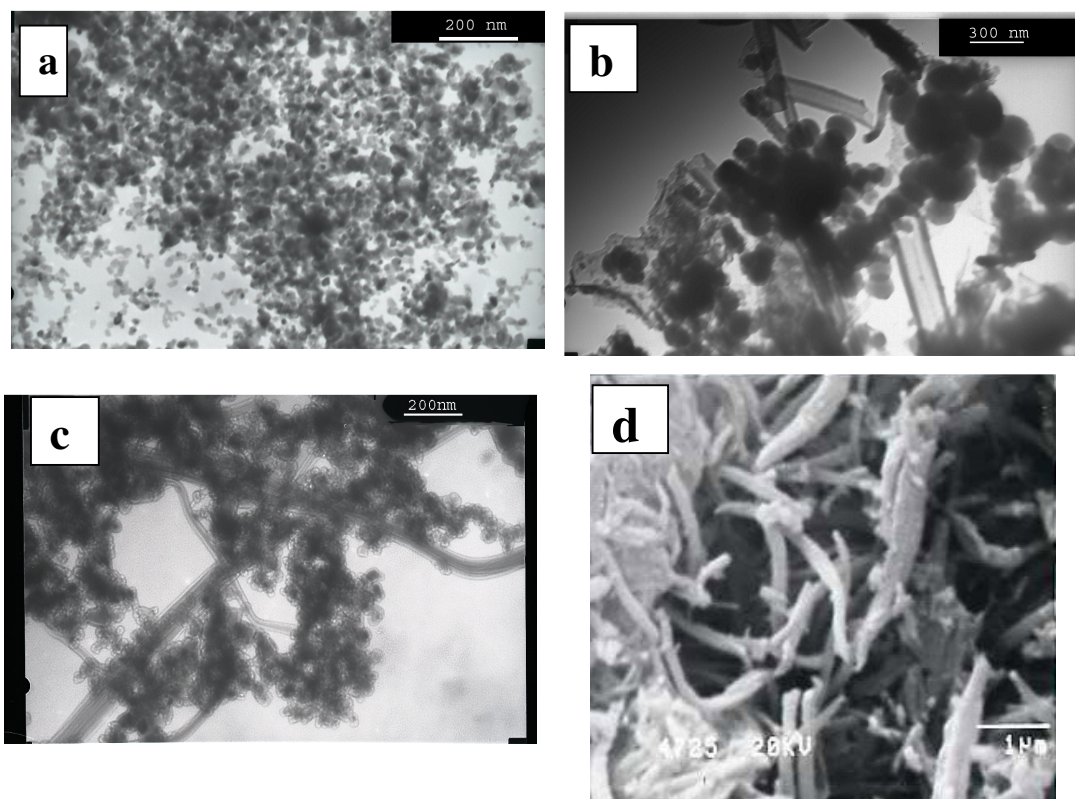


Figure 4.1: TEM images of (a) $\text{TiO}_2\text{-D}$; (b) $\text{TiO}_2\text{-C}$; (c) $\text{TiO}_2\text{-A}$; and SEM image of (d) $\text{TiO}_2\text{-A}$.

High resolution TEM images of **CAT-B (Fig. 4.2b)** shows a parallel arrangement of tubes after Pd treatment. HRTEM revealed that the tubes are multi-walled with the lattice spacing of about 3 nm. The tubes occur in bundles [33]. The formation of tubular structures by acid treatment has been reported [14, 36] but the mechanism of formation of tubes is still not fully understood. Further, in our investigation, treatment with acid was omitted and tubes with good quality were successfully synthesized under our reaction conditions. Therefore, the tube formation is largely dependent on the formation of a disordered intermediate phase facilitated by base treatment. Thus, when the raw material crystallites are treated in KOH solution, the crystallites are exfoliated into layered crystalline sheets. This is in agreement with observations made by Chen and co-workers [32]. Based on our observation, it is suggested that a chemical interaction

between TiO_2 and KOH will primarily form Ti-O-K and Ti-OH bonds. On ageing, the sheet-like TiO_2 rolls into tubes. It must be emphasized that the ageing process alone gives tube formation since a sample with no ageing ($\text{TiO}_2\text{-A}$) shows only minimal tube formation. The basicity of the solution is crucial since in a strong base ($\text{pH} > 10$), the tubes are not stable [37] and they gradually become amorphous with ageing time (see above).

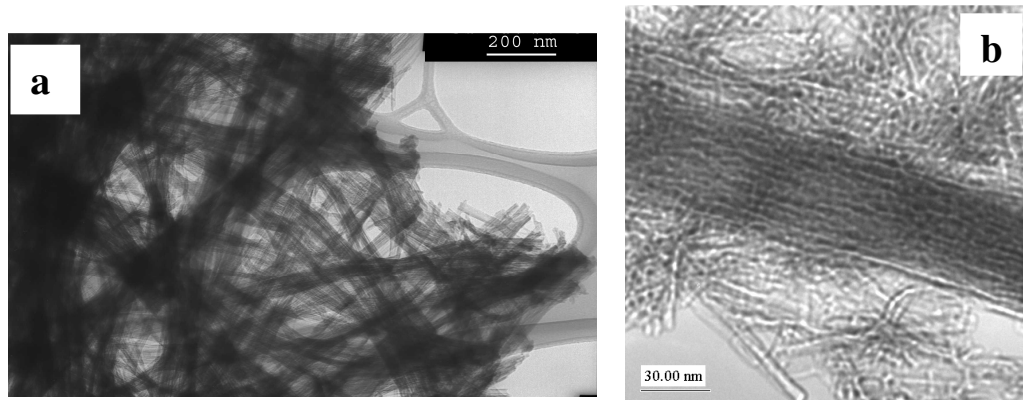


Figure 4.2: (a) TEM image of $\text{TiO}_2\text{-B}$ and (b) HRTEM image of CAT-B

4.3.3. XRD and Raman studies

The X-ray diffraction (XRD) patterns of $\text{TiO}_2\text{-D}$ and $\text{TiO}_2\text{-B}$ are shown in **Fig. 4.3a**. $\text{TiO}_2\text{-D}$ is crystalline and consists of 80% anatase and 20% rutile. The broad peaks and low intensities of $\text{TiO}_2\text{-B}$ (**Fig. 4.3b**) reveal that the sample has no well defined periodicity (i.e. is amorphous) and a poor crystallinity was observed after calcination at low temperatures. $\text{TiO}_2\text{-A}$, though not aged, was found to be crystalline and showed 100% anatase phase (**Fig 4.4a**). This suggests that treating titanium dioxide with KOH followed by its removal without ageing removes the rutile phase. Further, ageing for 61 days, resulted in the formation of an even more amorphous sample, $\text{TiO}_2\text{-C}$ (**Fig. 4.4b**).

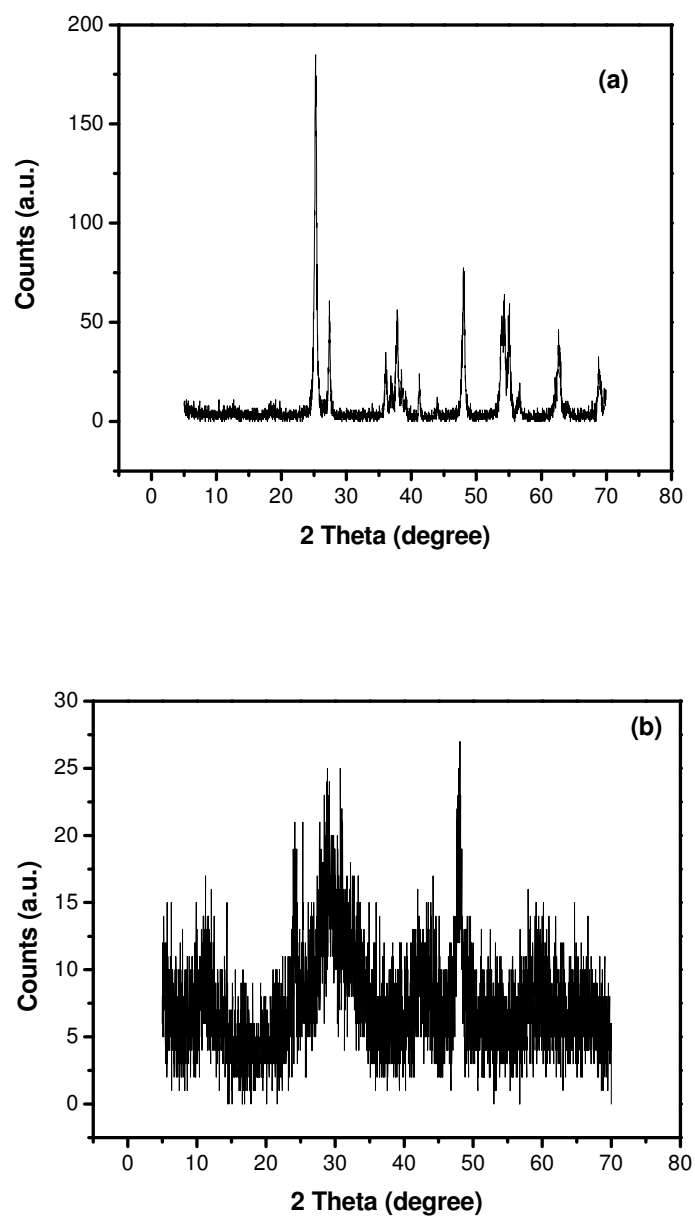


Figure 4.3: XRD patterns of (a) $\text{TiO}_2\text{-D}$ and (b) $\text{TiO}_2\text{-B}$

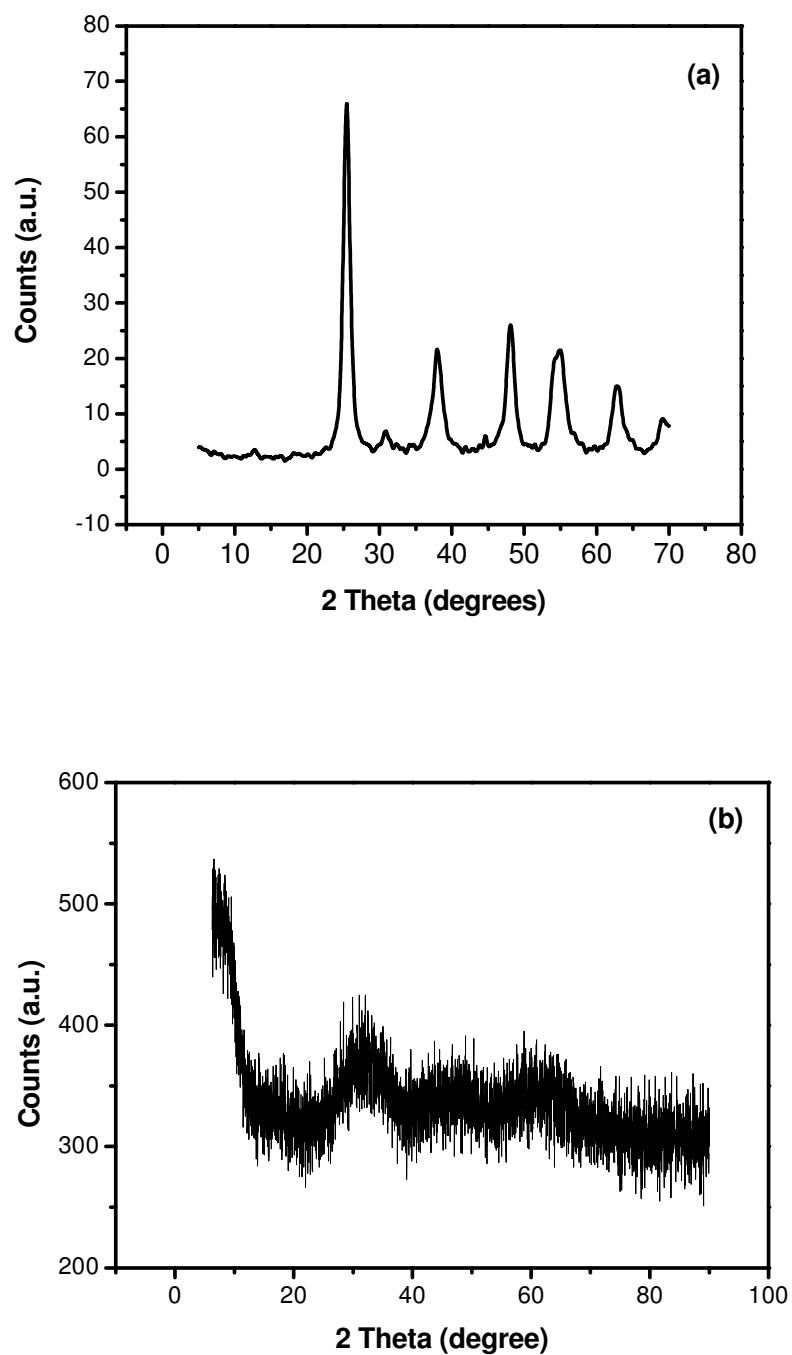


Figure 4.4: XRD patterns of (a) TiO₂-A and (b) TiO₂-C

The Raman spectrum of TiO₂-A is shown in **Fig. 4.5**. The sharp bands indicate that the material is crystalline and composed of anatase phase. Although, the

absence of ageing time proves to be useful for the synthesis of phase-pure TiO_2 , the corresponding surface area observed is still relatively low (**Table 4.1**) and tube formation was not attained. The Raman spectrum of sample $\text{TiO}_2\text{-B}$ is shown in **Fig. 4.6a**. The sample shows broad peaks ascribed to small particle sizes implying that there is no ordered crystallinity in agreement with our XRD results. The peaks observed at 188, 271, 441 and 652 cm^{-1} are ascribed to titanate species. The 188, 271 cm^{-1} peaks are assigned to a pure framework Ti-O-Ti vibration whereas the 441 and 652 cm^{-1} peaks are assigned to Ti-O-K vibration [37,38]. An EDX study of sample $\text{TiO}_2\text{-B}$ revealed that 19% by mass of potassium ions were left in the sample after washing with deionised water and centrifugation until the conductivity was $\sim 15\text{ }\mu\text{S/cm}$. This suggests that the nanotubes are made from a potassium titanate structure, $\text{KTiO}_2(\text{OH})$ [39,40]. The results are reproducible in terms of material phase composition. The Raman spectrum of sample $\text{TiO}_2\text{-C}$ (**Fig. 4.6b**) shows the sample contains a mixture of tubes and amorphous material. The two peaks at 271 and 441 cm^{-1} are ascribed to titanate and the absence of other titanate peaks (188 and 652 cm^{-1}) to the presence of undeveloped material. This observation is again in agreement with TEM results where the presence of both tubes and amorphous material was observed.

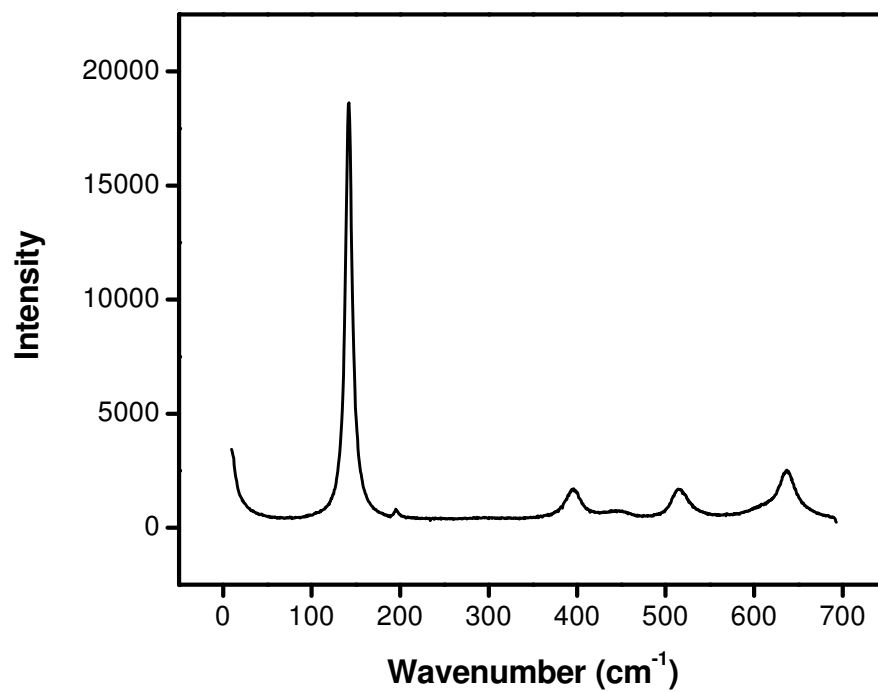


Figure 4.5: Raman spectrum of TiO₂-A

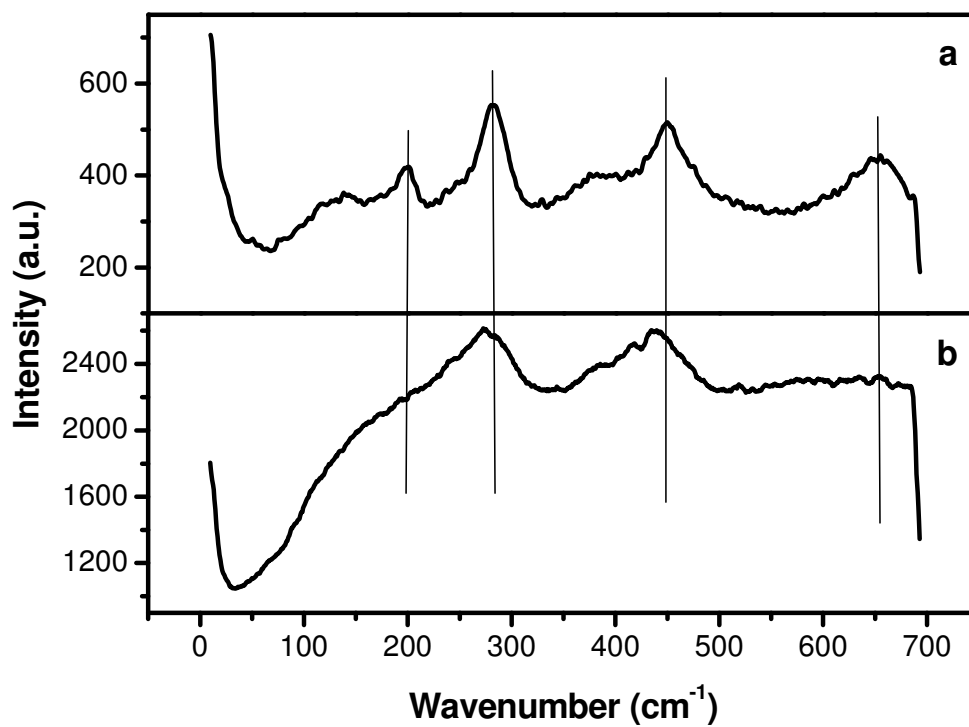


Figure 4.6: Raman spectra of (a) $\text{TiO}_2\text{-B}$ and (b) $\text{TiO}_2\text{-C}$.

4.3.4. Temperature programmed desorption (TPD) studies

CO₂ TPD was performed on the samples - from room temperature to 300°C - to determine the presence of basic sites as well as their strength on the material surface. It was observed that TiO₂-**D** showed a small desorption peak trace implying that there were few weak basic sites on the surface. However, addition of Pd to TiO₂-**D** (**CAT-D**), revealed the presence of two CO₂ desorption peaks at 215 and 265 °C, (**Fig. 4.7**). **Fig. 4.8** shows the TPD profiles of TiO₂-**C** and **CAT-C**. TiO₂-**C** reveals the presence of two desorption peaks at 120 and 215°C indicating two types of basic sites (weak) present on the surface. However, addition of Pd reduces the intensity of both peaks considerably. This suggests that Pd addition may have a neutralizing influence on the two surface basic sites. A similar observation was noticed with TiO₂-**A** as well as **CAT-A** (**Fig. 4.8, inset**). However, the TPD profiles of TiO₂-**B** and **CAT-B** showed an opposite effect from that shown by the profiles of **CAT-C** or **-A** (**Fig. 4.9**). The appearance of a lower temperature desorption peak at 120°C for TiO₂-**B** shows that these basic sites are moderately weak. On addition of Pd, peaks appeared at 75, 175 and 280°C. It is clear that the two peaks at 75 and 280°C were created by the presence of Pd while the peak at 175° C is believed to be due to KOH treatment. In summary, the TPD results reveal that TiO₂-**A**, **-B** and **-C** have weak basic sites which were less significant in reference TiO₂-**D**. It is evident that the sites are created by the base (KOH) treatment in the initial synthesis step. The sample containing tubular structures (**CAT-B**) showed an increasing trend in the number of adsorption sites while non-tubular structures (**CAT-A**) and a mixture of tubular and undeveloped material (**CAT-C**) showed a decline in the number of weak basic sites on the surface. This data shows that adsorption of CO₂ occurs on the support TiO₂ while Pd particles also have a structural influence on the surface of TiO₂.

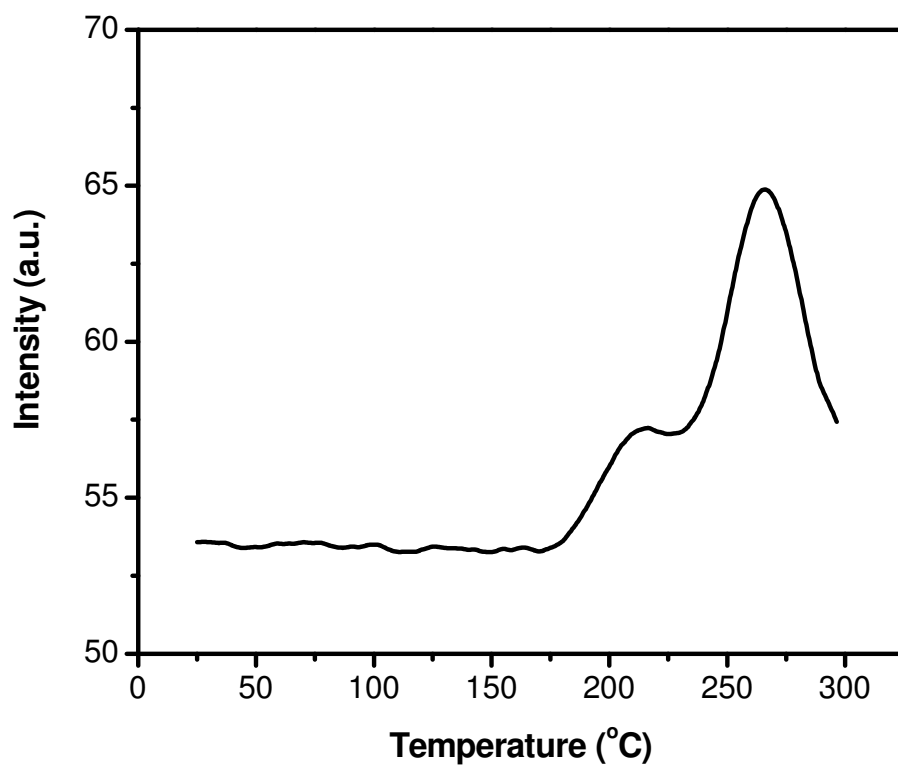


Figure 4.7: A CO₂ TPD profile of CAT-D.

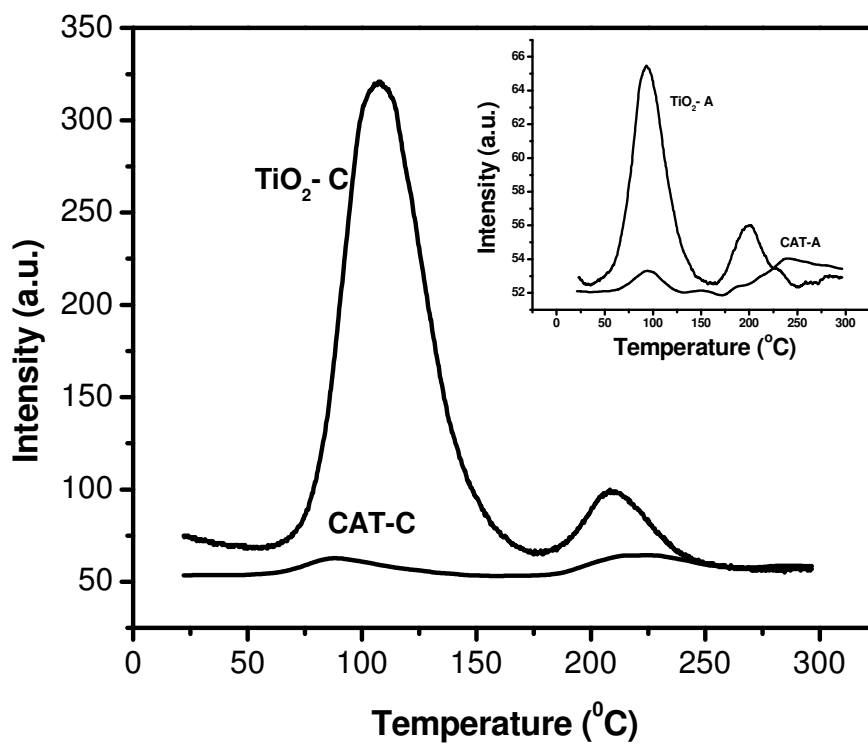


Figure 4.8: TPD profiles of TiO₂-C and CAT-C; and TiO₂-A and CAT-A (inset).

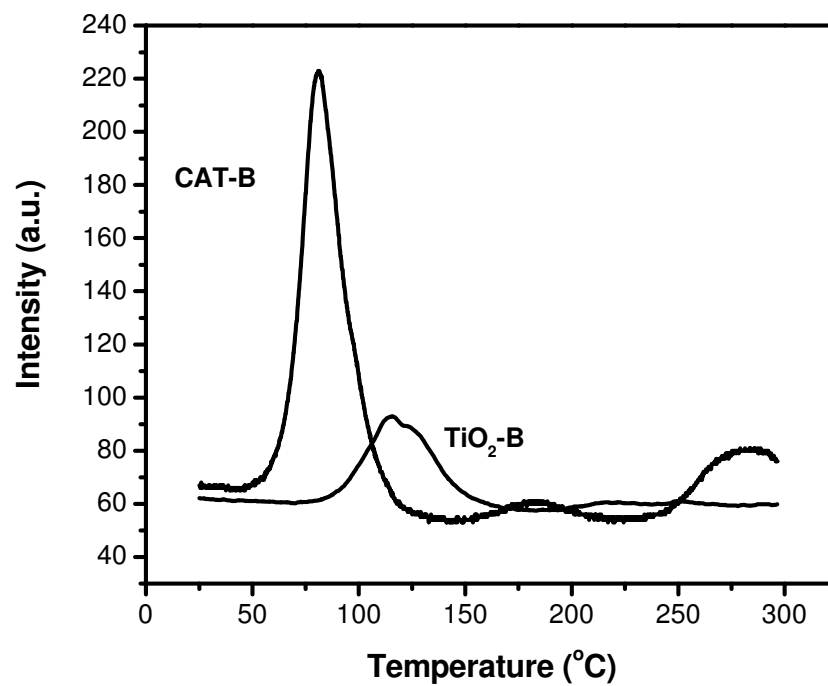


Figure 4.9: TPD profiles TiO₂-B and CAT-B

4.3.5 Temperature programmed reduction (TPR) and temperature programmed oxidation (TPO) studies

TPR was used to study the effects of reducibility of Pd on the catalyst supports [41]. TiO₂-D (P25 Degussa) is a reducible support as shown in **Fig. 4.10a**. **Fig. 4.10b** shows the TPR profile of **CAT-A** revealing two reduction peaks at 110 and 590°C. The low temperature peak (110°C) is attributed to the reduction of PdO species while the high temperature peak (590°C) is attributed to the reduction of bulk oxygen in the TiO₂ material (**Fig. 4.10a**). The low temperature reduction peak is smaller than the high temperature reduction peak. This indicates the ratio of PdO species to that of the bulk oxygen in the support. The shoulder peak at 750°C shows the reduction of more strongly bound oxygen in the support. The TPR profile of **CAT-C** was very similar to **CAT-A** but more easily reducible with two peaks at 90 and 545 °C (**Fig. 4.10c**). However, it is interesting to observe that the TPR profile of **CAT-B** did not show any reduction peaks. The XRD and XPS results (not shown) also did not show any Pd in **CAT-B**. The absence of Pd nanoparticles in HRTEM suggests that the Pd particles formed were too small to be detected (<1.5 nm). Though Pd particles were not detected by HRTEM its presence was noticed with EDX.

The TPO profile of fresh **CAT-B** (**Fig. 4.10d**) shows an oxidation peak at 284 °C suggesting that Pd was pre-reduced on contact with titania derived nanotubes prior to treatment with H₂ gas.

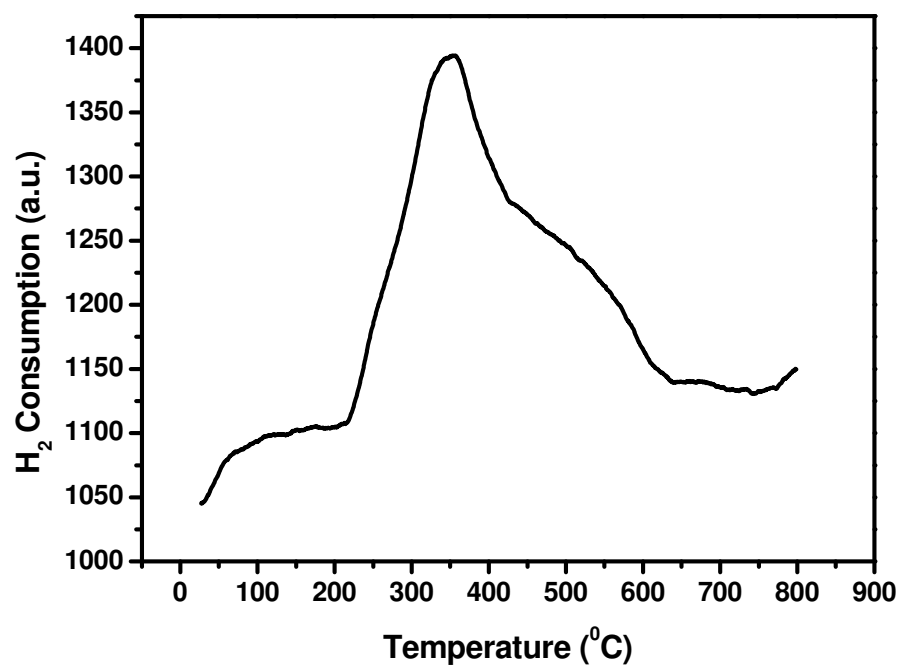


Figure 4.10a: A TPR profile of TiO₂-D

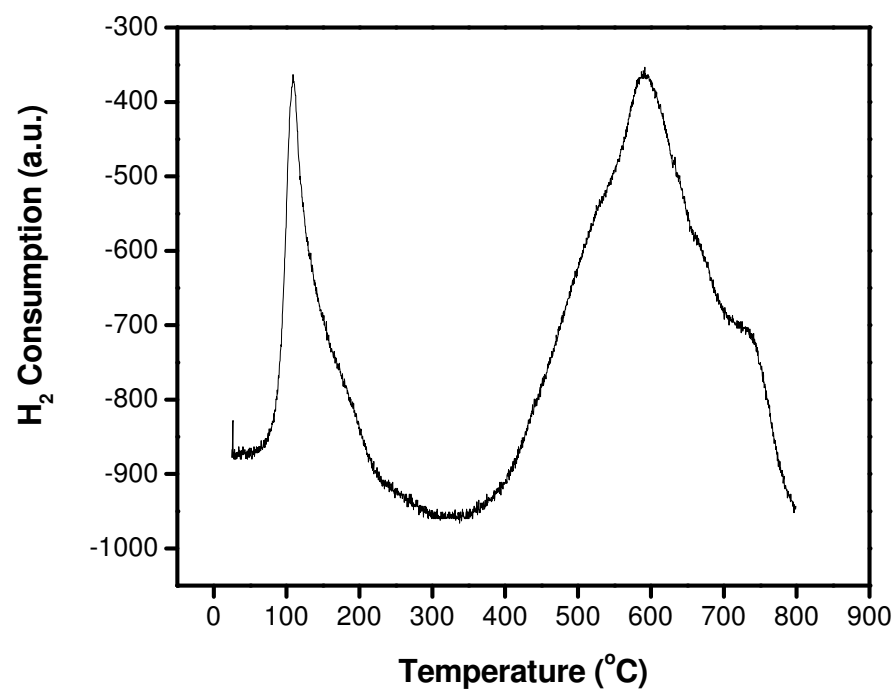


Figure 4.10b: A TPR profile of CAT-A

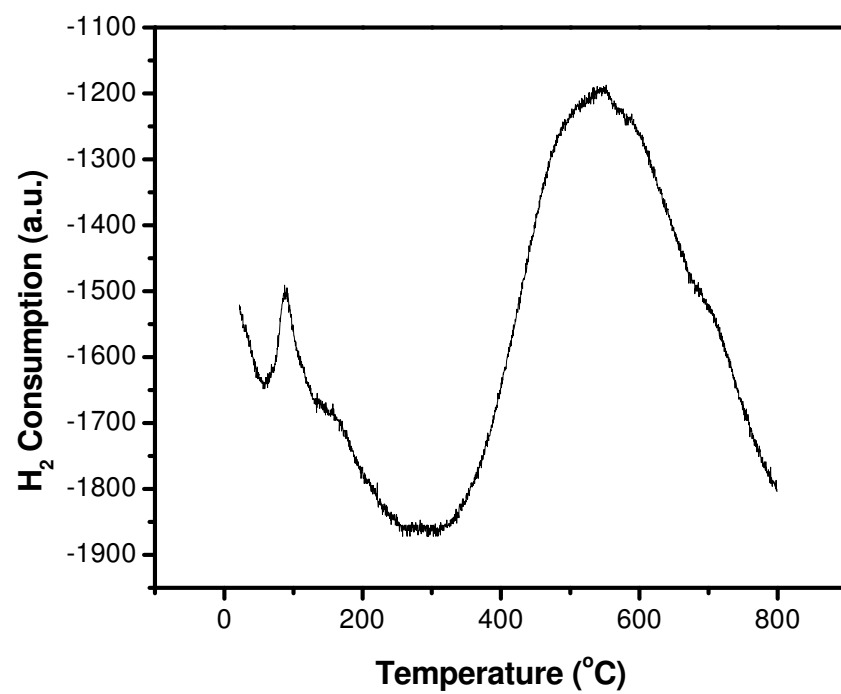


Figure 4.10c: A TPR profile of CAT-C

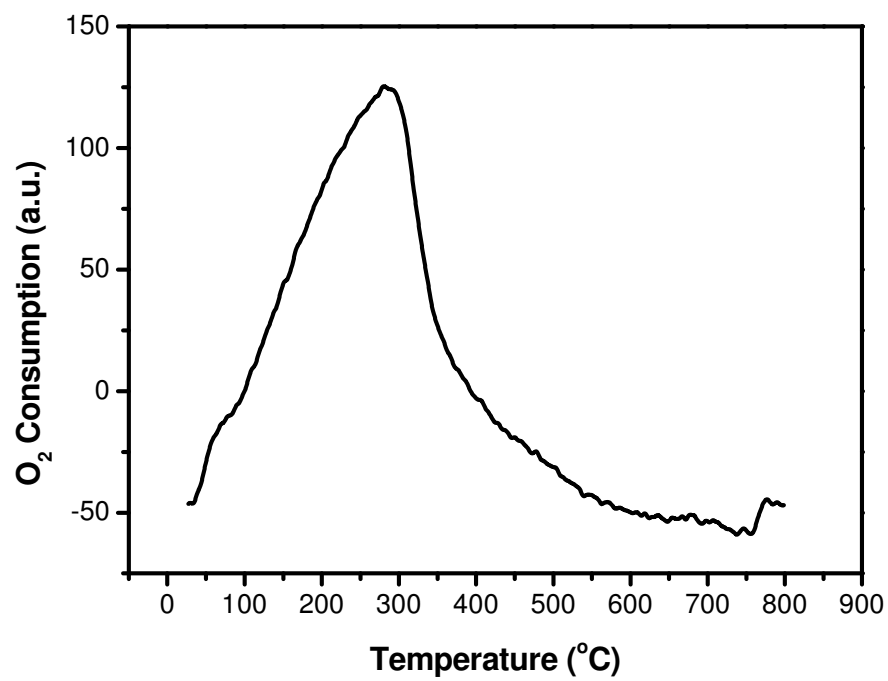


Figure 4.10d: A TPO profile of CAT-B

4.3.6. Phenol hydrogenation studies

The hydrogenation of phenol on 1 wt% Pd supported on synthetic TiO₂ catalysts, was carried out in a gas phase medium under atmospheric pressure. The results are shown in **Table 4.2**. Addition of Pd to TiO₂-**D** (**CAT-D**) showed a conversion of 10 % with high selectivity to cyclohexanone (~95 %). **CAT-A**, and **-B** gave a higher conversion of phenol and low selectivity to cyclohexanol. The selectivity to cyclohexanol was high for **CAT-C** and it thus appears that longer ageing time synthesis of catalyst promotes selectivity to cyclohexanol rather than cyclohexanone.

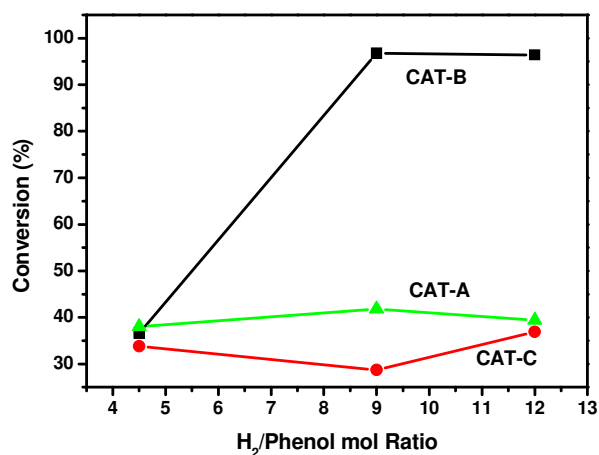
Table 4.2: Phenol hydrogenation data over Pd (1 wt%) supported on reference and synthetic TiO₂ catalysts¹

Catalyst	Conversion (%)	Selectivity (%) ²		
		C=O	C-OH	Others
CAT-D	10.2	95	4	1
CAT-A	31.6	96	4	-
CAT-B	79.6	99	<1	<1
CAT-C	27.0	56	44	-

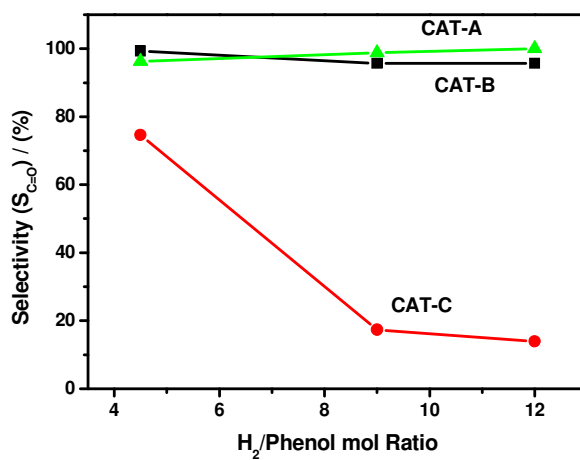
¹ Reaction conditions: T = 200°C; H₂/Phenol = 4.5; Wt. cat = 0.5g; Feed rate = 2.5 ml/h

² Key: Cyclohexanone (C=O) and Cyclohexanol (C-OH)

The influence of the hydrogen to phenol mole ratio on conversion as well as selectivity for cyclohexanone is shown in **Fig. 4.11**. The conversion of phenol over **CAT-A** (42 %) and **-C** (37 %) remained more or less constant while **CAT-B** conversion increased with increase in hydrogen to phenol ratio until 9, beyond which it remains constant. The selectivity for cyclohexanone showed a drastic decrease with H₂/phenol ratio for **CAT-C** but remained constant (100 %) for **CAT-A** and **-B**, with increase in ratio. This variation in product selectivity can be ascribed to factors such as the morphology, surface area and the phase composition of the TiO₂ material.



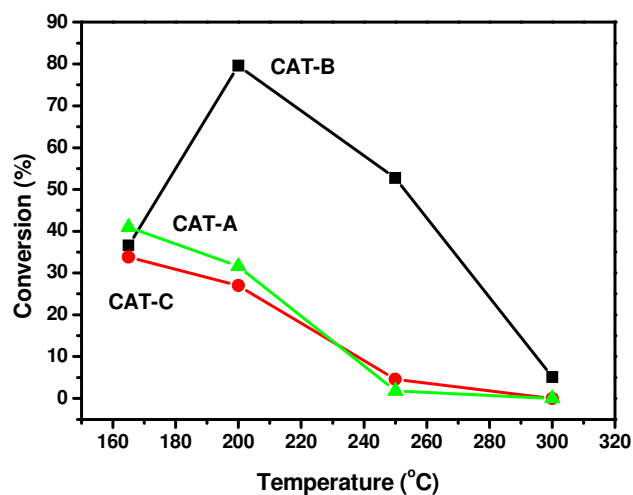
(a)



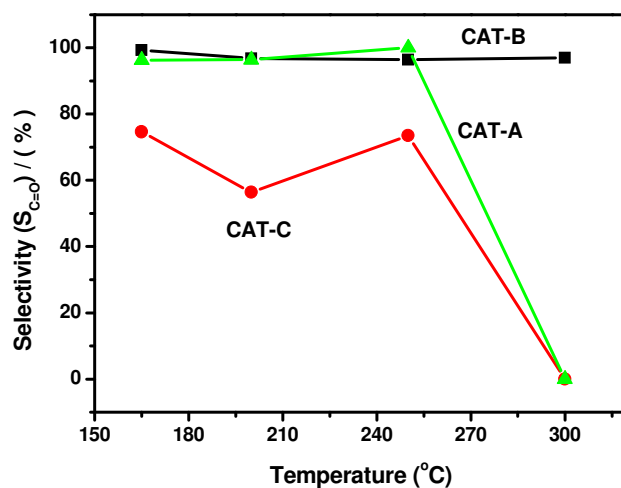
(b)

Figure 4.11: Effect of mole ratio on (a) phenol conversion and (b) selectivity to cyclohexanone ($S_{C=O}$) of CAT-A, -B, and -C. Reaction conditions: $T = 165^{\circ}\text{C}$; Wt. cat = 0.5g; Feed rate = 2.5 ml/h

The effect of temperature on phenol conversion and selectivity in the reaction to produce cyclohexanone is shown in **Fig. 4.12**. All three synthetic catalysts showed an initial conversion of around 40 % at 165°C. **CAT-A** and **-C** conversion decreased sharply from 40 to 0 % with increase in temperature from 165 to 300°C while **CAT-B** went through a maximum of 80 % at a reaction temperature of 200°C before decreasing. **CAT-A** and **-C** showed a constant selectivity for cyclohexanone to 250°C before decreasing while the selectivity to cyclohexanol increased. However, selectivity remained constant (100 %) for **CAT-B**, even though conversion decreased from 100 to almost 0 % beyond 200°C. The near ~0 % conversion with all three synthetic catalysts at 300°C suggests that severe deactivation takes place at higher temperature on the catalyst surface. It appears that **CAT-A** and **-C** are thermally less stable than **CAT-B**. It is noted that a catalyst with a large proportion of tubular structures (**CAT-B**) performs better at higher temperature than those without (**CAT-A**) or with a lower proportion of tubes (**CAT-C**). The variation in phenol conversion (**Table 4.2**) further shows that in **CAT-B**, the interaction between the active metal component and the support is rather different from the rest of the catalysts.



(a)



(b)

Figure 4.12: Effect of temperature on (a) phenol conversion and (b) selectivity to cyclohexanone ($S_{C=O}$) of CAT-A, -B, and -C. Reaction conditions: $H_2/Phenol = 4.5$; Wt. cat = 0.5g; Feed rate = 2.5 ml/h.

4.3.7. Deactivation studies

To examine the titanate stability, catalysts were subjected to an 8 h study on stream. **Fig. 4.13** shows the effect of time-on-stream (TOS) on phenol conversion and selectivity to cyclohexanone with **CAT-A** and **-B**. **CAT-A** showed a slow decline in activity with reaction time while **CAT-B** remained more or less constant with a high conversion level. The presence of hydrocarbons over a Pd metal surface is known to reduce the dissociative adsorption of hydrogen and hence limit the reactivity of surface hydrogen atoms [42]. Although, there was a decrease in conversion with **CAT-A** with TOS, both **CAT-A** and **-B**, showed a high selectivity to cyclohexanone over a long period of time. This high selectivity suggests that the tubular structure of **CAT-B** does not readily promote adsorption of hydrocarbons at low temperatures as compared to **CAT-A** thereby enhancing the stability of the catalyst.

It is evident from the foregoing results that **CAT-A** and **-C** did not show activity anywhere near as good as that obtained with **CAT-B** for hydrogenation of phenol. The absence of reduction peaks in the TPR profile of **CAT-B** is suggestive of Pd insertion into the titanate nanotubular structures. The presence of amorphous titanium dioxide (**CAT-C**) seems to promote a weak interaction between Pd and the TiO₂ support and consequently results in a decline in phenol activity as compared to that of samples made up of titanate structures (**CAT-B**).

Though there was no deactivation of **CAT-B** at lower reaction temperatures (**Fig. 4.12a**), deactivation of **CAT-B** was observed at elevated temperatures. An examination of the morphology and microstructure of the spent **CAT-B** (after reaction at 300°C) was carried out by TEM and the results indicate that there was no significant change in the morphology that occurred during the reaction. The spent **CAT-B** was very similar to that of the fresh catalyst. It must be realised that TiO₂ derived nanotubes were found to stick to each other (agglomerated) forming bundles after the reaction because they are numerous and lie close to each other as shown by the TEM image of spent **CAT-B** (**Fig. 4.14**).

Nevertheless, this process did not deform the morphology of the individual tubes. Furthermore, the TPD profile of the spent **CAT-B**, revealed the presence of two weak basic sites on the catalyst surface and the profile looked very similar to the fresh catalyst (**Fig. 4.15**). The difference in peak intensity is ascribed to the presence of hydrocarbons adsorbed on the catalyst during the reaction. However, the surface area of freshly calcined **CAT-B** ($225 \text{ m}^2/\text{g}$) decreased with reaction temperature (300°C) to $148 \text{ m}^2/\text{g}$.

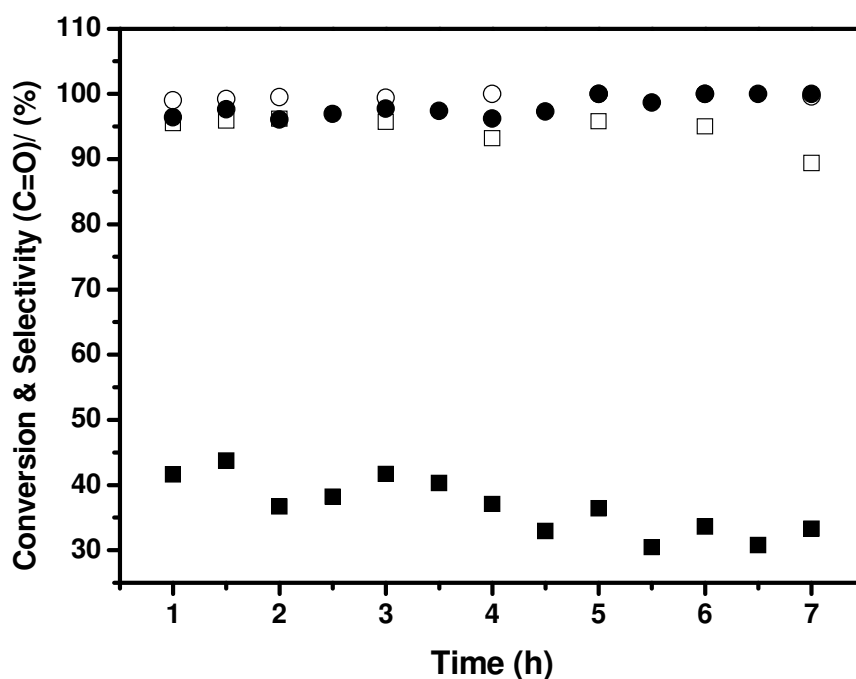


Figure 4.13: Effect of time-on-stream on conversion (■) and selectivity (□) of phenol for **CAT-A** and conversion (●) and selectivity (○) over **CAT-B**. Reaction conditions: $T = 200^\circ\text{C}$; $\text{H}_2/\text{Phenol} = 4.5$; Wt. cat = 0.5g; Feed rate = 2.5 ml/h

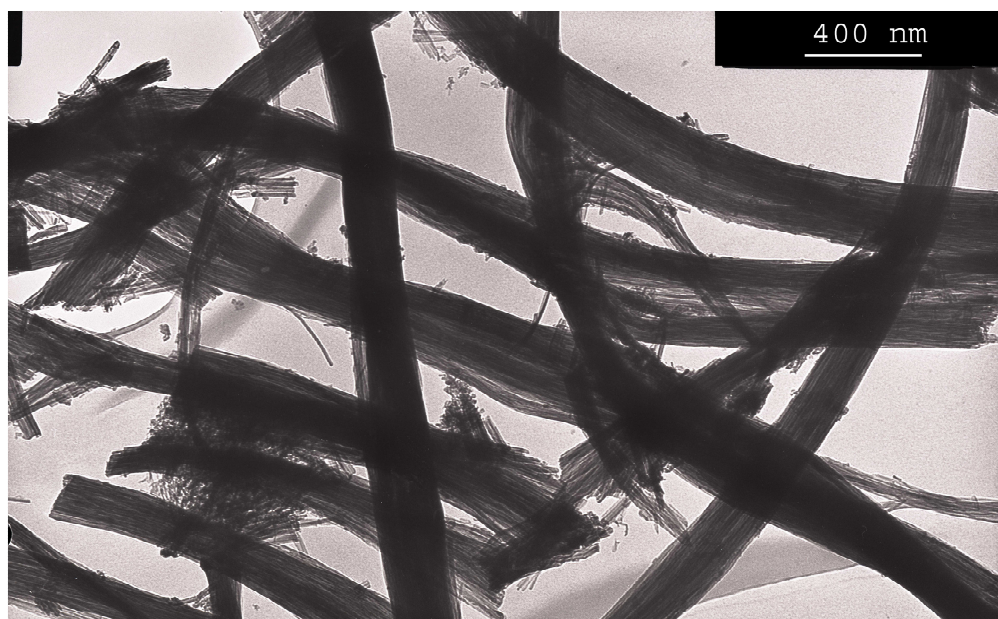


Figure 4.14: TEM image of spent **CAT-B** (Reaction T = 300 °C; H_2 /phenol = 4.5)

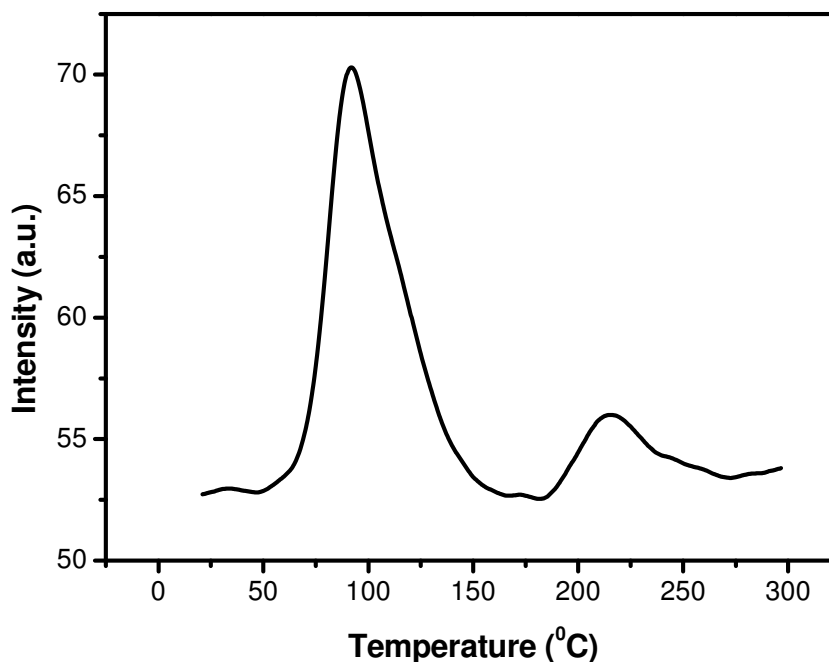


Figure 4.15: A CO₂ TPD profile of spent **CAT-B** (Reaction T = 300 °C; H₂/phenol = 4.5)

The TGA results obtained on spent **CAT-B** subjected to a reaction temperatures of 250 and 300°C are shown in **Fig. 4.16**. After the reaction was carried out at 250°C, the total weight loss was 16%. This is attributed to the removal of deposits of hydrocarbons on the catalyst surface (**Fig. 4.16, curve-a**). However, carrying out the reaction at 300°C, resulted in the total weight loss of 16%, of which 12% was ascribed to hydrocarbons (~450°C) and the rest to the deposition of carbonaceous material (500 to 750°C) formed as a result of hydrocarbon decomposition (**Fig. 4.16, curve-b**). Therefore, the deactivation of **CAT-B** at 250°C is caused by the deposition of hydrocarbons resulting in a reduced conversion of 53%, **Fig. 4.12a**. Further increase in the reaction temperature (300°C), also resulted in the remarkable decline in conversion to 5%. It is interesting to observe that hydrocarbons are weakly adsorbed on the surface and can be reversed by thermally treating the spent **CAT-B** in air at 300°C for 3 h, as

shown in **Fig. 4.16, curve-c**. The surface area of this regenerated **CAT-B** increased from 148 to 200 m²/g. These results show that deactivation arises from the blocking of pores on the surface by high molecular weight products formed as reaction by-products.

Both the high surface area and porosity of the nanotubular catalyst (**CAT-B**) promise to be advantageous for catalytic activity for hydrogenation of phenol just as is the case in photocatalysis. The gradual deactivation observed with **CAT-B** as the temperature increased is an indication that it takes longer periods of time to cover up all the reactive sites on the large surface. The presence of cylindrical structures in the form of tubes may also have played a role in the improved resistance to deactivation and the enhancement of activity. The addition of Pd may have led to a favourable orientation of tubes which in turn may lead to enhancement of the activity and selectivity.

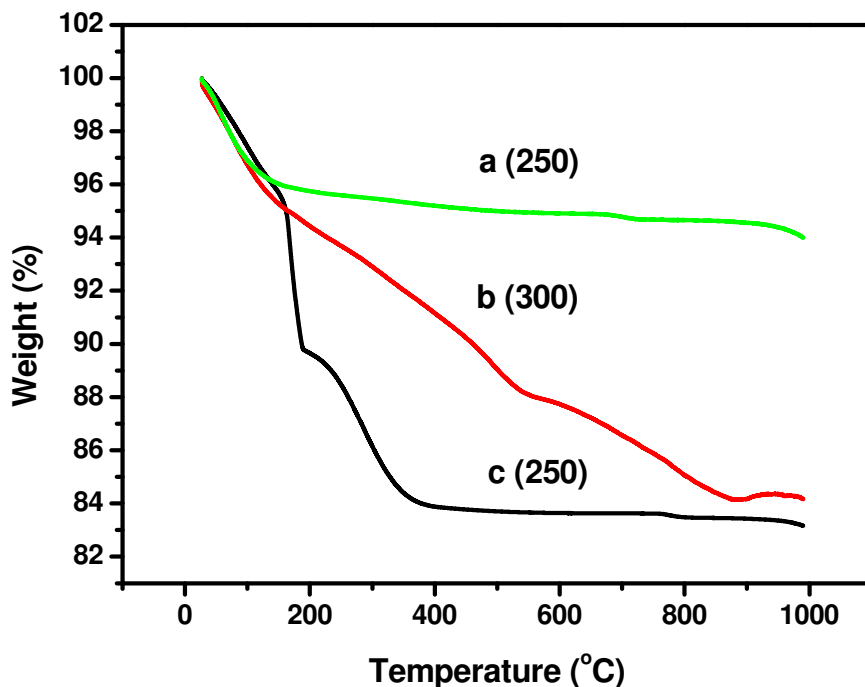


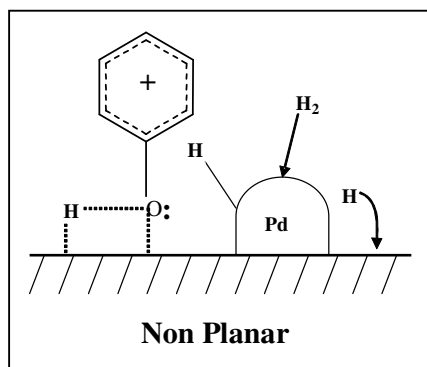
Figure 4.16: TGA profiles of the spent catalysts (**CAT-B**) after reaction at 250°C (curve-**c**) and 300°C (curve-**b**); and spent catalyst at 250°C regenerated in air at 300°C (curve-**a**).

4.3.8. Reaction mechanism

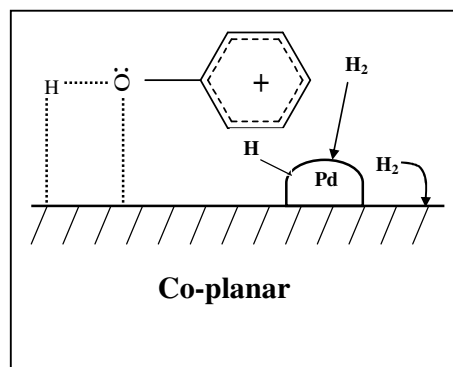
The reaction mechanism seems to vary as the reaction temperature is varied for the different catalysts. Cyclohexanone, formed over **CAT-A** and **-B** appears at the expense of cyclohexanol under the different reaction conditions. However, **CAT-C** showed a deviation in product preference at higher temperatures. With **CAT-C**, more cyclohexanol was formed as the temperature was increased. This effect on the product selectivity can be ascribed to the change in surface acid-base properties as reported by others [43, 44].

Based on our results a mechanism with a limited interaction of the support surface and the aromatic ring of the reactant molecule (phenol) is proposed. A

non planar approach of phenol with the basic sites of tubular supports (**Scheme 4.1**) is envisaged and this invariably favours cyclohexanone [13]. The constant selectivity to cyclohexanone at high temperature clearly shows that the relative adsorption modes are independent of temperature.



Scheme 4.1.



Scheme 4.2.

The data also suggest that a different pathway is needed to explain products generated for **CAT-C** when compared to that of **CAT-A** and **-B** as cyclohexanol is increasingly favoured as the temperature is elevated. This phenomenon is associated with a typical co-planar approach of phenol (**Scheme 4.2**) in which a strong interaction between the aromatic nucleus and the support surface is involved [13,45]. It is thus seen that different morphologies lead to different reaction mechanisms and subsequently different reaction products when the materials are used as catalyst.

4.4. Conclusions

1. It is evident that the ageing time of TiO₂ in a KOH solution is a key step in synthesising nanotubular titanium dioxide during the initial synthesis steps. In the absence of ageing, the formation of titanium dioxide (TiO₂-A) having a sheet-like structure with a high degree of crystallinity was found. However, ageing for two days resulted in 100% yield of nanotubes (as shown by TEM) with titanate

structure (TiO₂-**B**) while over-ageing resulted in a product with well developed tubes (TiO₂-**C**) in a pool of amorphous material.

2. The BET surface area of the synthetic TiO₂ varied with ageing time in KOH solution. The tubular material (TiO₂-**B**) showed a relatively high surface area of 270 m²/g with respect to the reference material (TiO₂-**D**, 50 m²/g). The synthetic TiO₂ found after longer ageing time (TiO₂-**C**) gave a low surface area of 33 m²/g, and confirmed the collapse of the tubular structure.

3. The TPR analysis of **CAT-B** revealed the absence of any reduction peaks due to palladium. HRTEM and EDX revealed that Pd is well dispersed. TPO analysis confirmed the existence of Pd nanoparticles, possibly too small to detect with HRTEM.

4. Of the three catalysts studied under a standard list of conditions (**Table 4.2**), **CAT-B** showed the best conversion (>79%) and selectivity (<99%) of cyclohexanone. Though **CAT-C** showed a moderate conversion, it favoured higher selectivity to cyclohexanol. This behaviour is attributed to the difference in acid-base properties on the surface of the two catalysts.

5. **CAT-B** showed higher resistance towards deactivation than observed with **CAT-A** or **CAT-C** and the selectivity for cyclohexanone remained fairly constant (~100%) throughout the reaction.

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5

Hydrogenation of phenol over Pd supported on high surface area mesoporous TiO₂ prepared from NaOH

5.1. Introduction

The somewhat neutral surface of TiO₂ makes it very different from other acidic, neutral or basic supports in that its surface can be modified in various ways rendering the material a promising catalyst support [1]. Recently the surface structure and catalytic properties of TiO₂ have attracted research interest since the material has been reported to show an improved photocatalytic activity when its surface area is enlarged [2-4]. The improved basicity of some forms of titania has also been reported to improve the activity for some chemical processes. An important research direction is thus the development of methods to prepare TiO₂ with high surface area by making the crystal size smaller (e.g. nanocrystals) or the titania more porous.

Antonelli and co-workers first reported, in 1995, the synthesis of mesoporous amorphous TiO₂ using phosphorous containing surfactant templating procedures. Since then many different methods have been developed and used to synthesize TiO₂

nanoparticles at relatively low temperatures [5]. These methods include ultrasonic irradiation, UV light assistance, solvent evaporation-induced crystallisation, sol-gel, etc. [6-9]. However, each method has its own limitation when it comes to the properties of the final product. For example, the sol-gel method is the most commonly used method. But the products obtained using this method are amorphous in nature and temperatures higher than 350 °C are essential to achieve the transition from an amorphous to a crystalline anatase phase [10-11]. The major drawback with heating the material is that it leads to nanocrystalline particle growth which subsequently leads to a decrease in surface area.

The use of a high surface area mesoporous oxide as catalyst support is more desirable than the low surface area commercial material because it, especially, enhances the catalytic performance of noble metals or transition metals [12]. This is because the mesoporous support promotes a good dispersion of the active component leading to stable metal particles on the surface especially after thermal treatments. This subsequently results in improved catalytic efficiency of the material supported on the oxide [13-14]. The high surface area and controlled crystalline framework of modified TiO₂ have made it one of the most attractive semiconductors for use by photocatalytic reactions [15-19].

In this chapter we have investigated the use of mesoporous TiO₂ as a support for Pd metal ions for the hydrogenation of phenol.

Phenol is known to be environmentally unfriendly because it is a toxin emanating from various industrial sources that are associated with petrochemical synthesis and polymer manufacture [20,21]. A catalytic conversion of such chemical waste to an environmentally friendlier material should be more favourable than the conventional destructive route by incineration [22]. Hydrogenation of phenol could be more viable than conventional methods (i.e. incineration) in terms of fuel and chemical recovery [23].

Hydrogenation of phenol in liquid [24,25] and gaseous [25-35] phases has been reported over platinum[31,32,35], nickel [36-39] and palladium [26-28,38,40-42] catalysts. From the literature it has been established that the selectivity towards cyclohexanone largely depends on the reaction conditions and that selectivity as high as 95 % can be attained [26,28,36,42-44]. It is noteworthy that both the conversion and selectivity are known to be greatly influenced by factors such as the morphology of the support or catalyst, structural properties, surface acidity or basicity and the presence of promoters [34,36,40,41,45]. It is generally accepted that the hydrogenation of phenol to give cyclohexanone occurs on basic sites [43]. Although higher selectivity to cyclohexanol is attainable the inevitable production of cyclohexanol and high selectivity to cyclohexanone at higher conversions of phenol continues to prove to be a challenge for chemists.

In this study we examine the effect of modification of the support on the dispersion of the active phase and how the surface area of the catalyst affects the catalyst performance.

5.2. Experimental

5.2.1. Preparation of mesoporous TiO₂ based support

P25 Degussa titania was used as raw material for the synthesis of high surface area materials. P25 TiO₂ (~10 g) was mixed with 200 ml of aqueous NaOH solution (18 M). The mixture was hydrothermally treated at 120 °C in an autoclave lined with Teflon for either 10 or 20 hours with constant stirring at the rate of 10 000 rpm. The material was allowed to cool and then washed immediately, without ageing, with deionised water. The treated solid materials were separated from the mixture by centrifugation and the procedure was repeated until the conductivity of the washing solution was lower than 100 µS/cm. The solid was dried in an oven at 120 °C for 12 hours. The samples were labelled according to the autoclave processing time of 10 or 20 hours as TiO₂-B and TiO₂-C respectively.

5.2.2. Metal loading

Pd loaded (1 % w/w) samples were prepared by a standard incipient wetness impregnation procedure using acetonitrile to prepare a metal salt solution (palladium acetate). An appropriate amount of Pd acetate solution was added to the commercial (P25 Degussa TiO₂) and modified titania supports. The samples were dried in air for 5 hours and then dried in an oven at 120 °C for 12 hours. Catalysts were then calcined in air at 300 °C for 5 hours. The catalysts were designated Pd/TiO₂-B and Pd/TiO₂-C.

5.2.3. Catalyst characterisation

A Malvern Mastersizer 2000 version 5.22 analyser was used for particle size measurements. The general procedure entails the measurement of background in order to account for any particles that may be present in the dispersant prior to the actual measurements. The sample suspension is prepared using an appropriate dispersant (in this case water was used). The pH of the final dispersant solution is controlled at ~pH 8. The sample is added until the obscuration is between 10-20 %. The solution is then placed on an ultrasonic sonicator for about 3 minutes to produce a good suspension. Then the measurement is carried out using the Malvern analyser. The data collection is done by means of a computer.

Nitrogen adsorption and desorption isotherms were collected using a Micromeritics Tristar 3000 system. The samples were degassed at 120 °C for 5 hours followed by the analysis carried out at liquid nitrogen temperature (-196 °C) over a range of relative pressures from 0.01-0.995. The specific surface area was determined by the Brunauer-Emmett-Teller (BET) analysis method and the pore size distribution was obtained from the nitrogen adsorption branch of isotherms using the Barrett-Joyner-Halenda (BJH) method.

TEM, SEM, TPR, TPD, Raman spectroscopy and XRD measurements were carried out using procedures described in Chapter 4 (ref. 51).

5.2.4. Hydrogenation of phenol

The gas phase hydrogenation of phenol to give cyclohexanone was carried out in a vertical fixed-bed reactor at atmospheric pressure and at temperatures ranging from 165 to 300 °C. Details of the reaction procedure and conditions are described in ref. 51 and Chapter 4 of this thesis.

5.3. Results and discussion

Hydrothermal treatment of TiO₂ with concentrated solution of NaOH is known to yield nanotubular sodium titanate materials [46,47]. The preparation technique is based on the use of 10 M NaOH aqueous solution. We have found that by using 25 M solution of NaOH the non-tubular nanoparticles can be synthesized instead.

5.3.1. Textural characterization of the samples

The Pd-based catalysts used in this study are listed in **Table 5.1**, which shows the BET surface areas and average pore diameters of the materials used. Both TiO₂-B (90 m²/g) and TiO₂-C (146 m²/g) showed higher surface areas than that of the “as prepared” TiO₂ (49 m²/g) material. The addition of Pd to both TiO₂-B and TiO₂-C followed by calcination at 300 °C for 5 hours resulted in the decrease in the surface areas by almost half of the original surface areas (**Table 5.1**). This reveals that the materials are thermally unstable after the NaOH treatment.

Table 5.1: BET surface areas and pore diameters.

Catalyst	Designation	S_{BET} (m ² /g)	Pore diameter (nm)
TiO ₂ (P25)	TiO ₂ -A	49.4	5.9
Pd/TiO ₂ (P25)	Pd/TiO ₂ -A	46.2	6.3
TiO ₂ (sample 1)	TiO ₂ -B	90.1	4.6
Pd/TiO ₂ (sample 1)	Pd/TiO ₂ -B	44.7	6.8
TiO ₂ (sample 2)	TiO ₂ -C	146.1	6.9
Pd/TiO ₂ (sample2)	Pd/TiO ₂ -C	89.2	7.6

Fig. 5.1 shows the nitrogen adsorption-desorption isotherms of Pd/TiO₂-C. The isotherms of both Pd/TiO₂-B (not shown) and -C are similar. The isotherm is a classical type IV type isotherm which is characteristic of mesoporous materials according to the IUPAC classification [48]. A hysteresis loop with a clear slope is observed in the high relative pressure (P/P_0) range of 0.6 to 0.9. It is a well known fact that a distribution of various sized cavities but with the same entrance diameter would give rise to this type of hysteresis loop [49]. The hysteresis loop was of type H1 which is expected of open-ended cylindrical pores. The pore size distribution plot, calculated using the BJH (Barrett-Joyner-Halenda) equation from the adsorption branch of the isotherm, is shown in **Fig. 5.1** (inset). The material showed pores with most diameters between 5–40 nm. The pore size distribution suggests reasonable homogeneity of the pores.

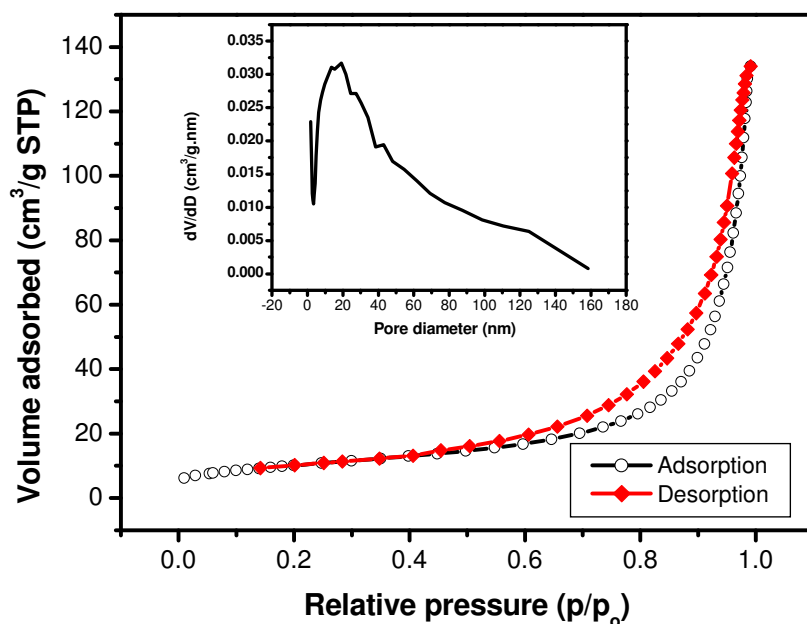


Figure 5.1: Nitrogen adsorption-desorption isotherms and corresponding pore size distribution (inset) of Pd/TiO₂-C.

5.3.2. Structural properties

5.3.2.1. Scanning electron microscopy (SEM)

The SEM images of the prepared samples (TiO₂-B and -C) are shown **Fig. 5.2(a)** and **(b)**. The micrographs show similar microstructures for TiO₂-B and -C. Both TiO₂-B and -C samples are comparable in terms of particle shape and size. They both exhibited a regular spherical morphology. It is interesting to note that although TiO₂-B and -C have similar morphology they have different surface areas (90 and 146 m²/g respectively). The surface areas are also different to that of TiO₂-A (P25 Degussa TiO₂). Furthermore, the material pore diameters are also comparable. The

similar particulate morphology suggests that the larger surface areas of modified samples (TiO₂-B and -C) are probably due to both intra- and inter-particle porosity.

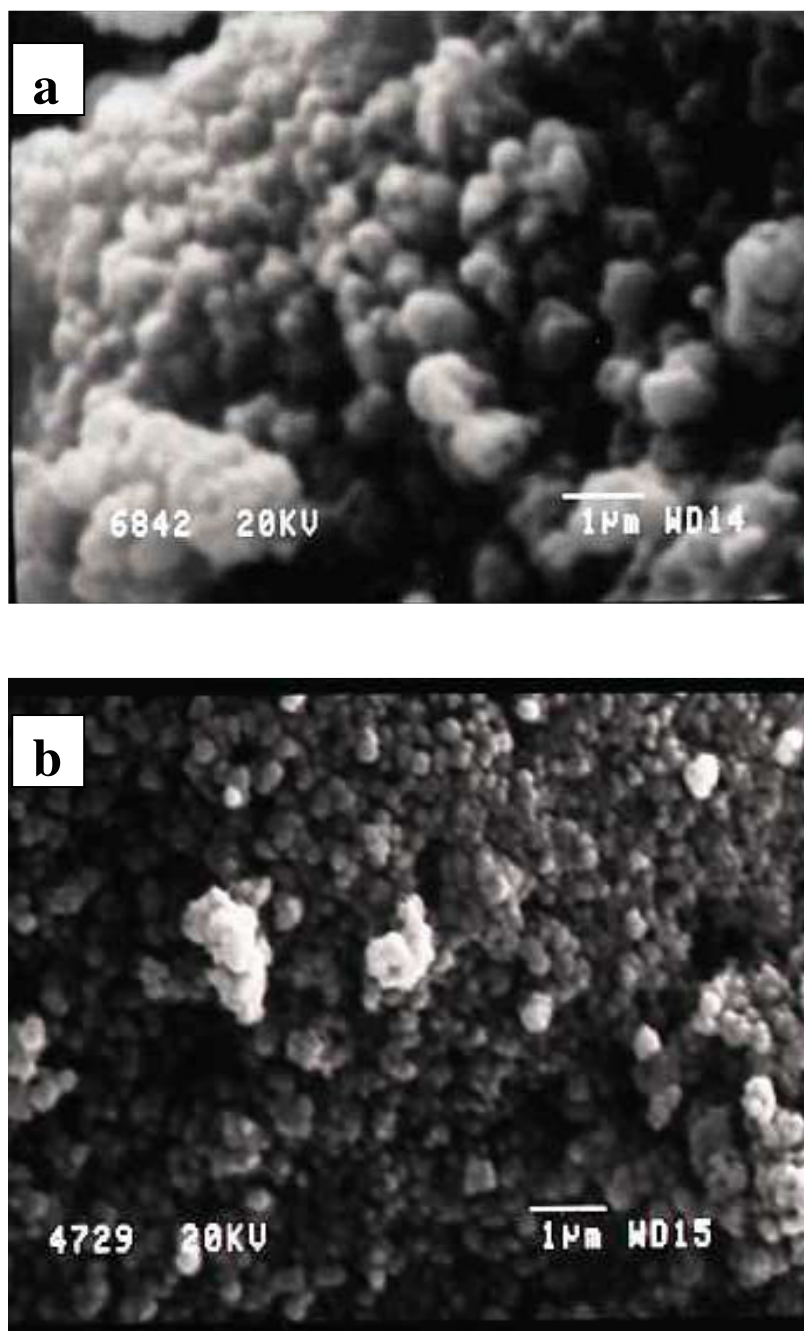


Figure 5.2: SEM images of (a) TiO₂-B of (b) TiO₂-C

5.3.2.2. Malvern analysis

Malvern analysis is widely used to measure the particle size of a material. It is an analytical system for characterisation of a wide variety of materials ranging from bulk materials to nanomaterials. The Malvern analysis results are recorded in **Fig. 5.3** and show that both TiO₂-B and TiO₂-C samples have similar particle size distributions. Both samples gave rise to a bimodal particle size distribution with similar peak maxima. The Malvern analysis results show that the TiO₂-B material has particles ranging from 28 to 73 μm and from 405 to 738 μm in size. It appears that the amount of finer particles is comparable to that of coarser ones. TiO₂-C has more particles within the diameter range of 34 to 70 μm . A small amount of particles are in the size range of 389 to 725 μm . A shift to coarser particles is observed for TiO₂-B (**Fig. 5.3**). This is in agreement with the BET results. The higher surface area observed in TiO₂-C is ascribed to the presence of smaller particles of the material.

The Malvern data shows a high degree of precision while the accuracy of the data is underpinned by a number of factors. The data obtained with Malvern analysis did not reveal a numerical comparison when compared with SEM results. The particle sizes obtained from the Malvern analysis were larger than those obtained from SEM. The disparity is attributed to the nature of the support and its behaviour in a solvent (H₂O). For example, the particles can absorb water which may result in particle agglomeration via accumulation of charges on the material. Although Malvern analysis is deemed one of the most reliable methods in determining particle size it has limitations with certain materials. For example, some materials undergo agglomeration due to the interaction of solvent with materials of different polarity.

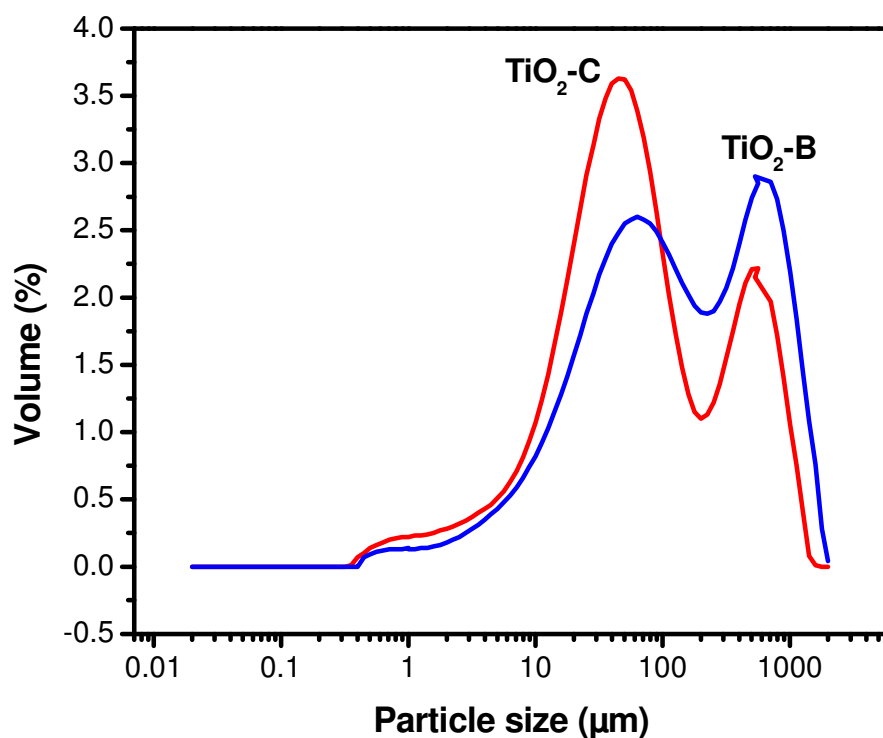


Figure 5.3: Particle size distribution plots as obtained by Malvern analysis

5.3.2.3. X-ray diffraction (XRD)

The XRD patterns of TiO₂-B and TiO₂-C are shown in **Fig. 5.4**. The figure shows similar patterns for both materials (TiO₂-B and TiO₂-C). In both instances the diffraction peaks are broad. Consequently, the assignment of these few peaks to any of the known crystal structures is not possible. The TiO₂-C sample appears to be more amorphous than TiO₂-B and the peak broadening is indicative of nanocrystals.

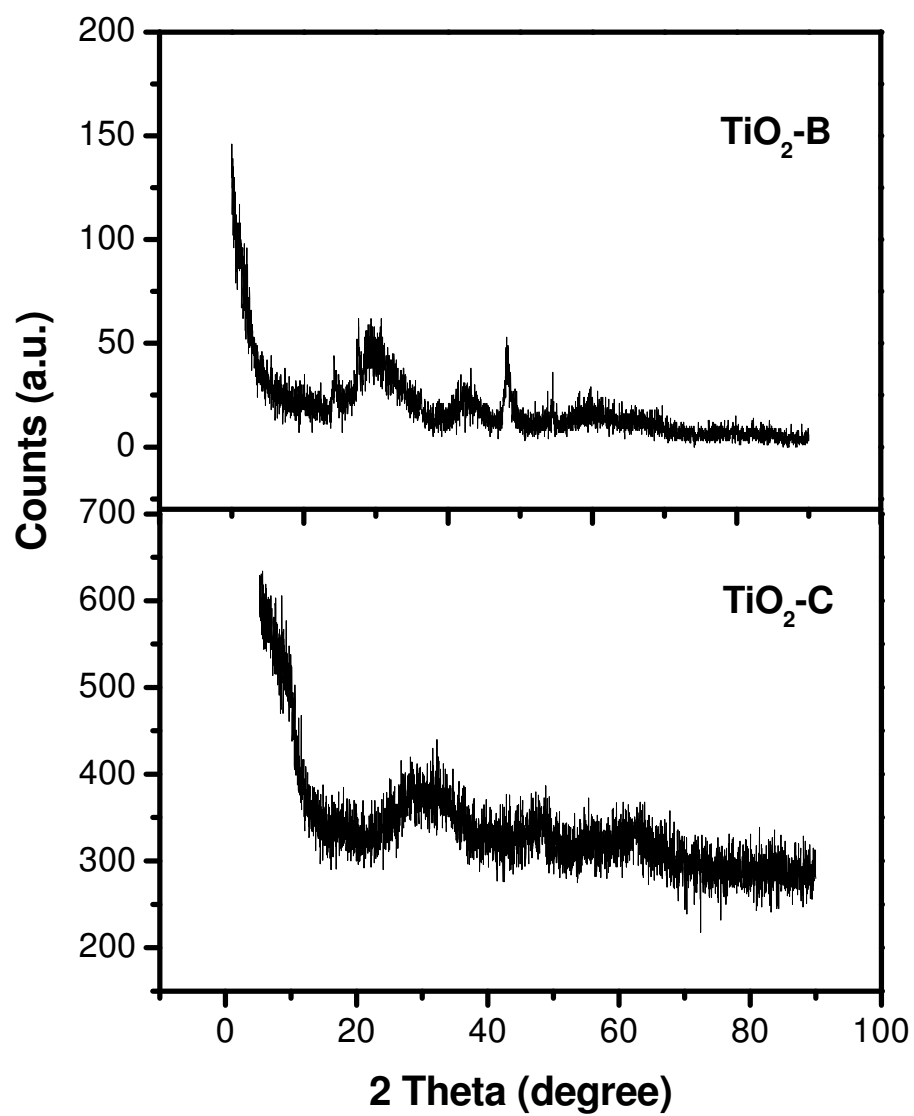


Figure 5.4: XRD patterns of TiO₂-B and TiO₂-C

5.3.2.4. Raman spectroscopy

Figure 5.5 shows the Raman spectra of TiO₂-B and TiO₂-C. The spectra of the two samples are basically similar. The peaks are broad and not well resolved rendering it impossible to assign them to known crystal structures. The spectrum of the higher surface area sample (TiO₂-C) shows an up-field peak shift analogous to those of TiO₂-B. This suggests that TiO₂-C has a slightly smaller particle size than TiO₂-B [50] and this is consistent with the XRD results.

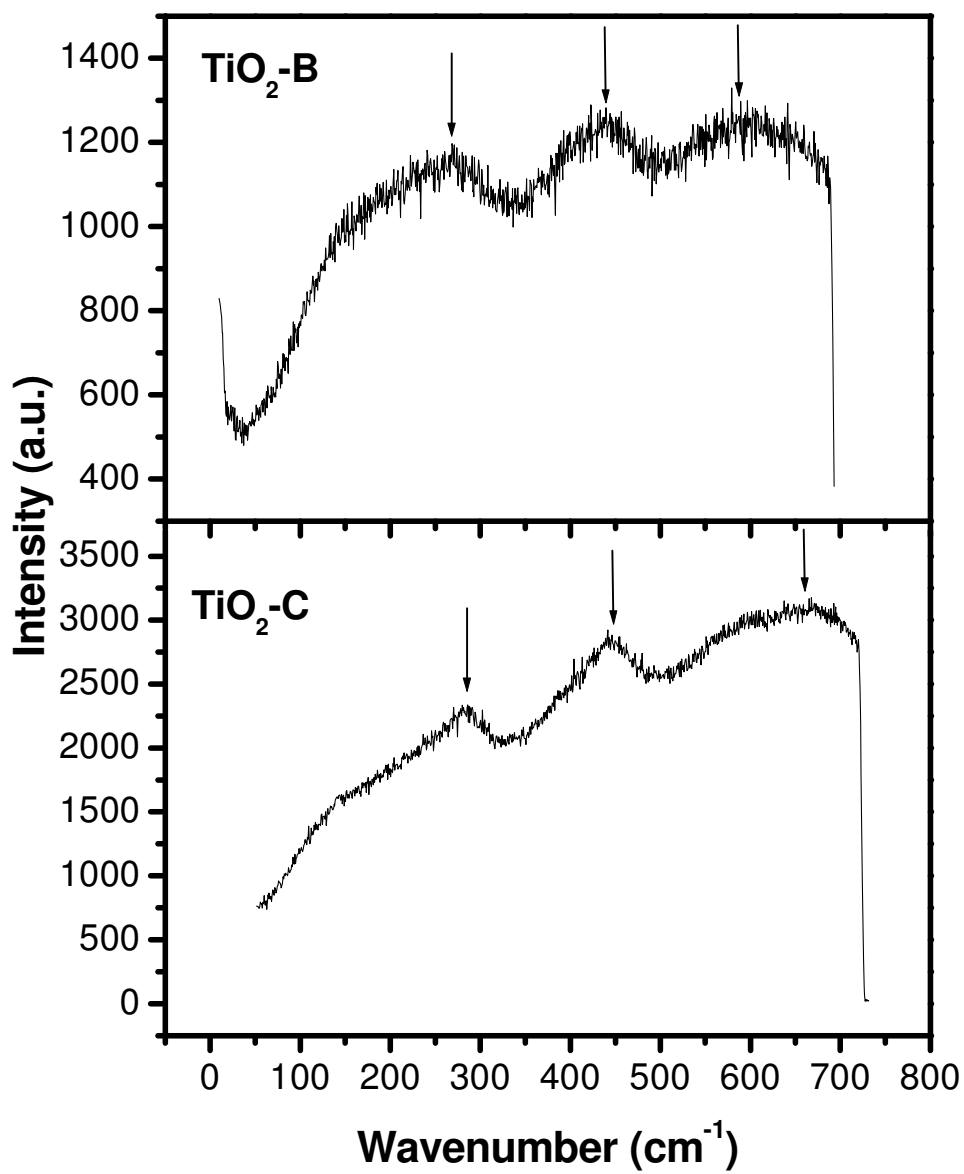


Figure 5.5: Raman spectra of TiO₂-B and TiO₂-C

5.3.2.5. CO₂ TPD

TPD profiles of TiO₂-B and Pd/TiO₂-B are shown in **Fig. 5.6**. The TPD profile of TiO₂-B reveals two desorption peaks at 128 and 258 °C. Both peaks have low intensity. However, the addition of Pd resulted in a peak shift to lower temperatures (i.e. 98 and 170 °C respectively). It is noteworthy that the lower temperature peak intensity increased suggesting an increase in the amount of weak basic sites. This implies that the addition of Pd further provides adsorption sites.

Fig. 5.7 shows the TPD profiles of TiO₂-C and Pd/TiO₂-C. Two peaks are observed in the profile of TiO₂-C at 130 and 288 °C. The addition of Pd also resulted in the peak shift to lower temperatures of desorption (i.e. 80 and 270 °C). As evidenced by the TPD profiles in **Figs. 5.6** and **5.7**, Pd increases the number of basic sites and promotes a weak adsorption of CO₂ molecules on the surface. Although the intensity in both **Figs. 5.6** and **5.7** is generally low with respect to data obtained for nanotubular materials, this data is consistent with our earlier findings in Chapter 4 (ref. 51).

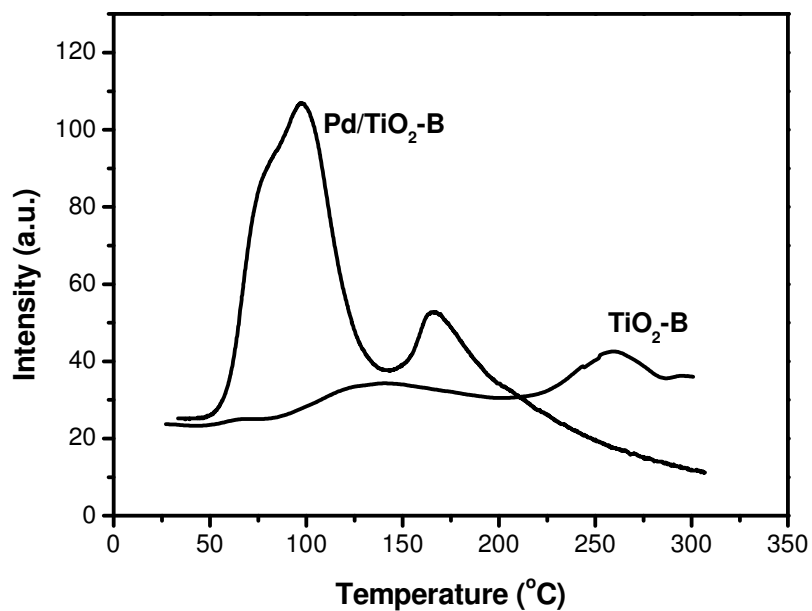


Figure 5.6: CO₂ profiles of TiO₂-B and Pd/TiO₂-B.

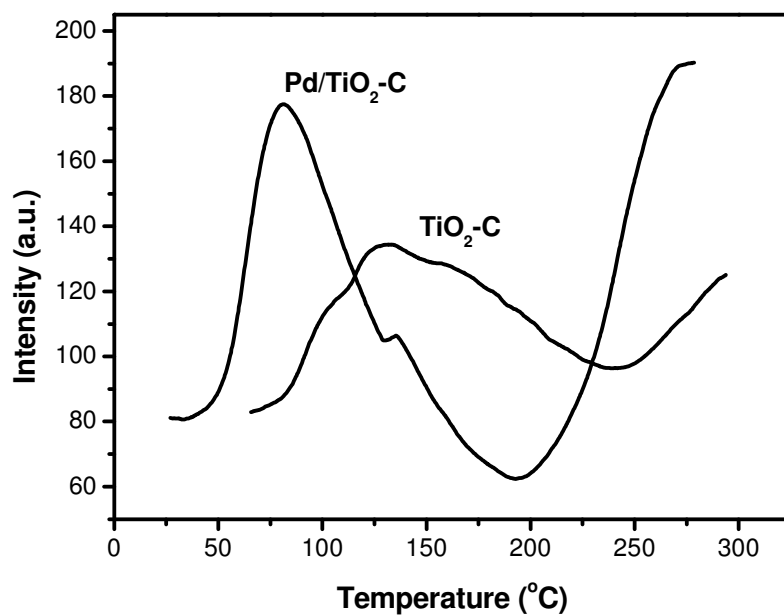


Figure 5.7: CO₂ profiles of TiO₂-C and Pd/TiO₂-C.

5.3.3. Hydrogenation of phenol

The effect of the H₂/phenol mole ratio was investigated and the results are summarised in **Fig. 5.8**. The conversion of the phenol to cyclohexanone over both Pd/TiO₂-B and Pd/TiO₂-C increases gradually with an increase in H₂/phenol ratio. The Pd/TiO₂-C catalyst gave better conversion of the phenol at different H₂/phenol ratios than did Pd/TiO₂-B. The conversion of phenol over Pd/TiO₂-B increased from 5 to 18 % as the H₂/phenol ratio increased from 4 to 12. Furthermore, the conversion increased from 40 to 48 % over Pd/TiO₂-C under similar conditions. The higher conversion obtained with Pd/TiO₂-C is presumed to be a consequence of higher surface area. The lower conversion obtained with Pd/TiO₂-B (~5 %) is lower than that obtained with Pd/TiO₂-A (~10 %) as reported in Chapter 4 or ref. [51]. This is because the surface area of Pd/TiO₂-B decreased from 90 to 44 m²/g which is lower than that of Pd/TiO₂-A (46 m²/g) after the addition of Pd and calcination at 300 °C. The summary of these results is presented in **Fig. 5.9a** and in the histograms given in **Fig. 5.9b**. On the basis of the above facts it is clear that the activity or conversion is dependent on the dispersion on the support. This is illustrated by a plot of conversion and selectivity versus dispersion (expressed as a function of surface area) in **Fig. 5.9a** where conversion increases with an increase in surface area.

The product compositions obtained with both catalysts were similar. Cyclohexanone and cyclohexanol were the only products obtained with Pd/TiO₂-C while trace amounts of ethanaldehyde (<1 %) were obtained with Pd/TiO₂-B. The selectivity to cyclohexanone decreased with increasing H₂/phenol ratio over both catalysts. The selectivity decreased from 100 to 94 % over Pd/TiO₂-B and from 39 to 18 % over Pd/TiO₂-C (**Fig. 5.9b**). The decrease in selectivity is more severe with Pd/TiO₂-C than Pd/TiO₂-B. The observed decrease in selectivity with increasing conversion is characteristic of sequential hydrogenation (cyclohexanone serves as a reactive intermediate and cyclohexanol is the ultimate product) where a complete hydrogenation is favoured at relatively higher conversions [52].

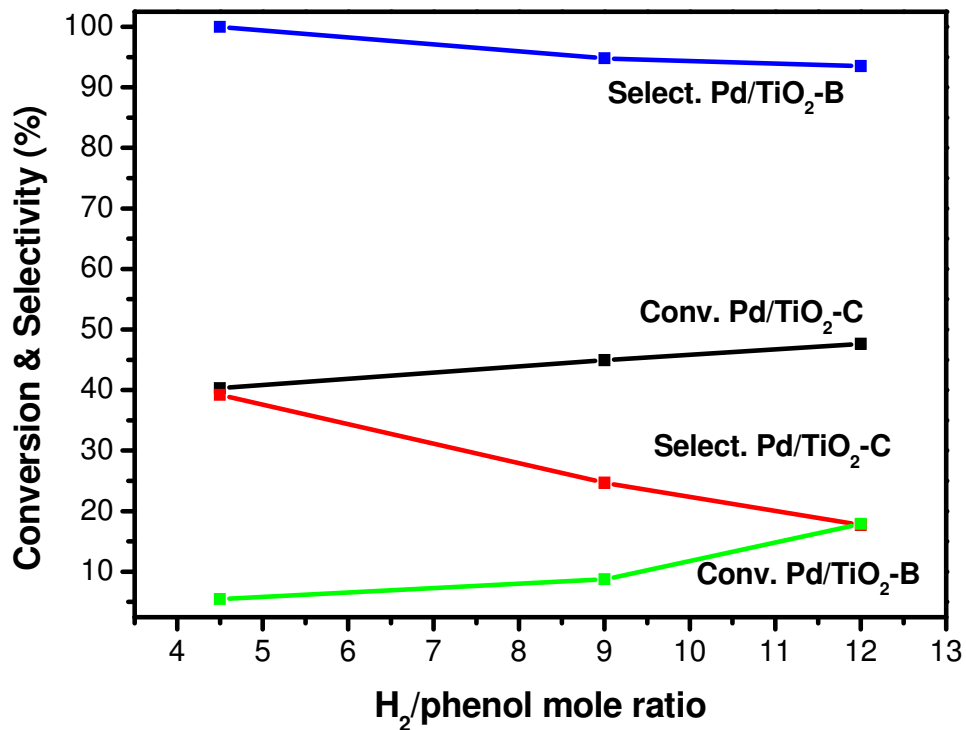


Figure 5.8: The effect of H₂/phenol mole ratio on conversion and selectivity of Pd/TiO₂-B and Pd/TiO₂-C. T = 165°C; Phenol/ethanol FR = 2.5 ml/h; Cat. wt. = 0.5 g; t = 1h.

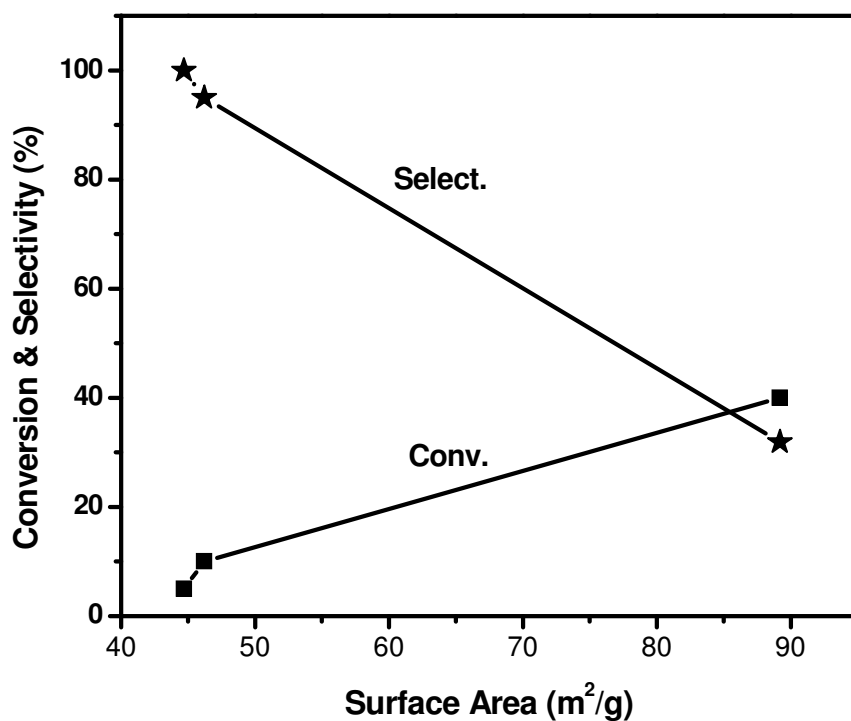


Figure 5.9a: A plot of conversion and selectivity against dispersion (expressed as a function of surface area). T = 165°C; Phenol/ethanol FR = 2.5 ml/h; H₂/phenol mole ratio = 4.5; Cat. wt. = 0.5 g; t = 1h.

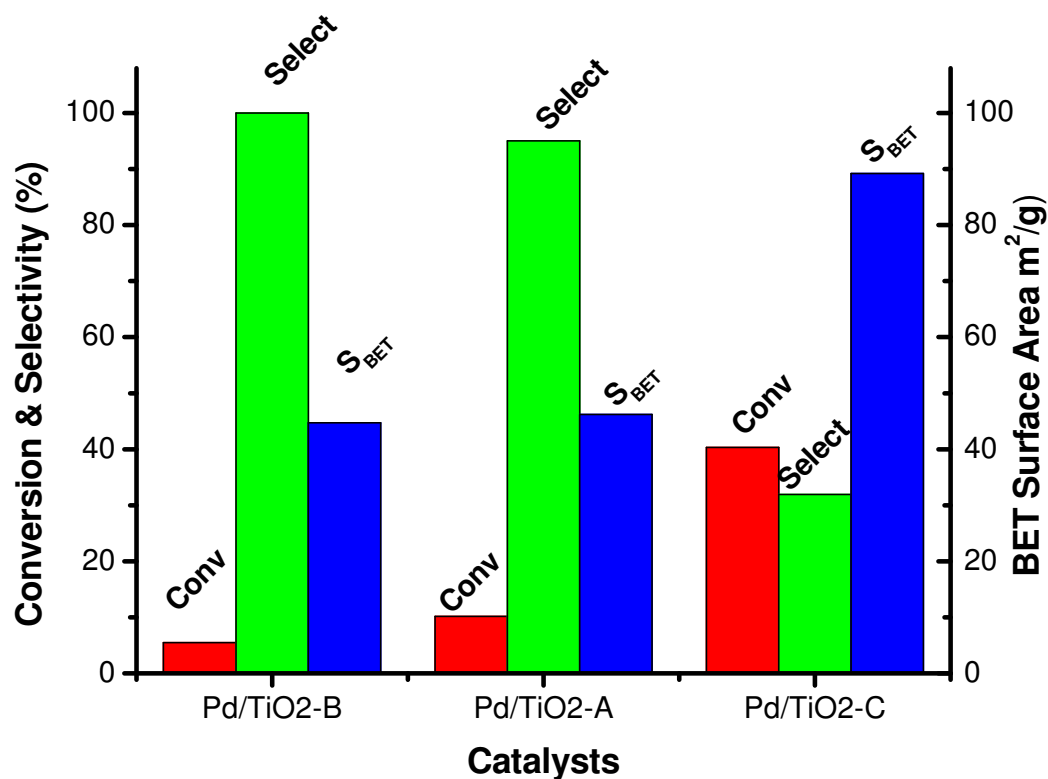


Figure 5.9b: The effect of BET surface area on both conversion and selectivity.

T = 165 °C; H₂/phenol = 4.5; Phenol/ethanol FR = 2.5 ml/h; Cat.
wt. = 0.5g; t = 1h.

The effect of temperature on both conversion and selectivity was also investigated and the results are shown in **Fig. 5.10**. The conversion of phenol over Pd/TiO₂-B increased with temperature variation from 5 % at 165 °C and reached a maximum conversion of 27 % at 250 °C. When the temperature was increased further (to 300 °C) a sharp decrease in conversion was observed (8 %). Pd/TiO₂-C showed a different behaviour as the temperature was systematically varied. The conversion decreased constantly from 40 to 2 % as the temperature was increased from 165 to 300 °C. Based on these results it can be inferred that Pd/TiO₂-B is more thermally

stable than Pd/TiO₂-C. The change in conversion as a result of temperature variation is attributed to the loss of the surface area [52].

The selectivity to cyclohexanone over Pd/TiO₂-B decreased from 100 to 87 % with increasing temperature (165-300 °C). The decrease in selectivity is attributed to the increase in conversion. The formation of by-products is facilitated by the amount of the reactant (phenol) converted. Furthermore, Pd/TiO₂-C showed an increase in selectivity from 39 to 100 % with temperature variation. The increase was related to surface coverage as well as changed conversion and loss of surface area.

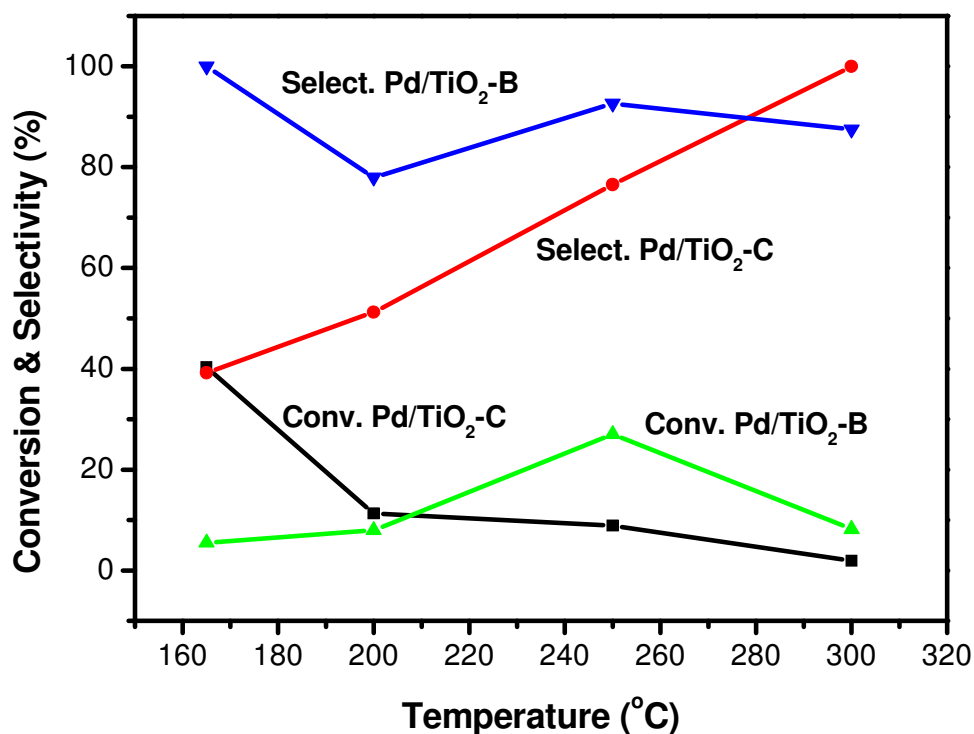


Figure 5.10: The effect of temperature on conversion and selectivity of Pd/TiO₂-B and Pd/TiO₂-C. H₂/phenol = 4.5; Phenol/ethanol FR = 2.5; Cat. wt. = 0.5 g; t = 1h.

The catalytic performance over Pd/TiO₂-C was investigated as a function of time on stream and both conversion and selectivity data are shown in **Fig. 5.11**. The conversion of phenol gradually decreased from 55 to 43 % over a period of 7 hours. The decrease in conversion is believed to be because of catalyst poisoning as a result of the deposition of hydrocarbons on the catalyst. The presence of the hydrocarbons on the metal surface is known to reduce the dissociative adsorption of hydrogen thereby limiting the reactivity of surface hydrogen atoms [53]. The selectivity to cyclohexanone increased from 18 to 28 % with time. It is clear that the conversion and selectivity are interdependent. This observed relationship between the conversion and selectivity is a typical anti-sympathetic one that leads to a sequential hydrogenation where complete hydrogenation is improved at higher conversion [53]. It is interesting to note that although Pd/TiO₂-C gave relatively higher conversions it generated a significant amount of cyclohexanol at 165 °C, with selectivity in excess of 82 %.

A comparison of selectivity data with that obtained in Chapter 4 [51] suggests that the selectivity is largely influenced by the morphology of the support. In Chapter 4 titania derived tubular supports were used and they gave high selectivity to cyclohexanol at low temperature and H₂/phenol ratio. In the present work cyclohexanone was the preferred product. This clearly shows that the nature of the support used for the hydrogenation of phenol is crucial.

The TPD data suggest that the participation of weak basic sites is imperative for the hydrogenation of phenol to give cyclohexanone.

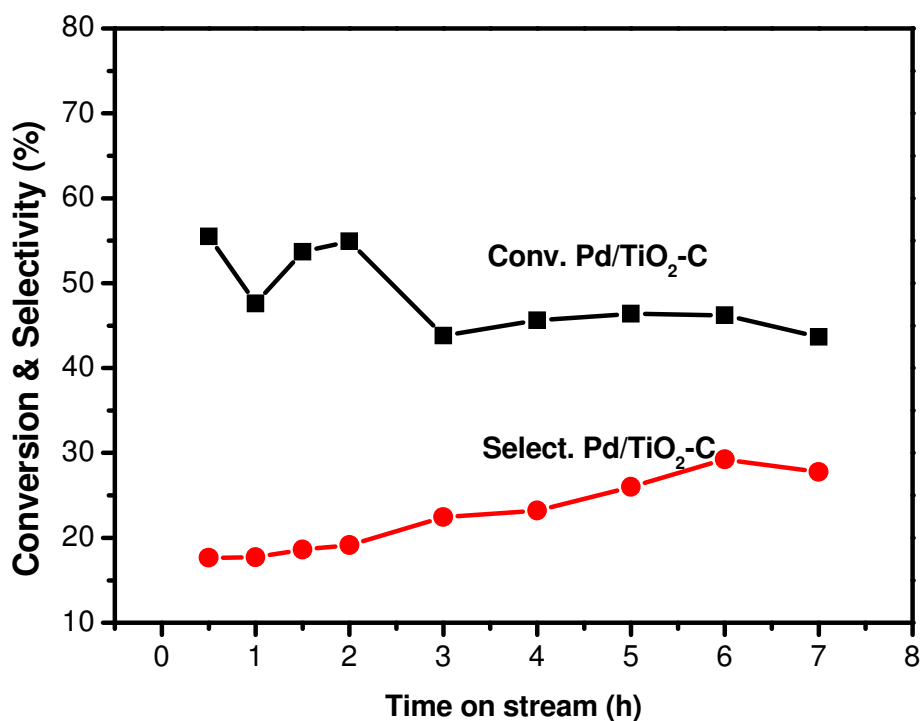


Figure 5.11: The effect of time on stream (TOS) on conversion and selectivity over Pd/TiO₂-C. T = 165 °C; H₂/phenol = 12; Phenol/ethanol FR = 2.5, Cat. Wt % = 0.5 g.

5.3.4. Mechanism

It is known that phenol can interact with a surface either via use of an aromatic ring or a hydroxyl substituent, depending on the nature of the catalyst [54]. The route involving the interaction via the aromatic ring often leads to complete hydrogenation to form cyclohexanol while the interaction via the hydroxyl substituent leads to partial hydrogenation to form cyclohexanone. Depending on the basicity of the surface the phenol ring may be perpendicular to or co-planar with the surface [54,55]. It has been established elsewhere that the strong interaction between phenol

and the surface is more likely to result in complete hydrogenation to give cyclohexanol [37]. Our data suggest the existence of a strong interaction of phenol with the surface and hence the formation of cyclohexanol.

5.4. Conclusions

1. Pd/TiO₂-C is a better catalyst than Pd/TiO₂-B for the gas phase hydrogenation of phenol (higher conversion of 55 %) under different conditions.
2. Treatment of TiO₂ with NaOH in an autoclave for longer times leads to a larger surface area which is required for enhanced activity of the catalyst. Pd/TiO₂-C, with a larger surface area of 89 m²/g, gave a higher conversion than Pd/TiO₂-B, under similar conditions.
3. The addition of Pd increases the number of basic sites which are required for the selective hydrogenation of phenol to give cyclohexanone.

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6

Hydrogenation of o-chloronitrobenzene over Pd supported on TiO₂ derived nanotubes

6.1. Introduction

Aromatic chloroamines are important chemical intermediates in the production of dyes, drugs, herbicides and pesticides. The conventional synthesis method involves the reduction of the corresponding chloronitro compounds, either with a metal-acid system or with hydrogen and a noble metal supported catalyst. The catalytic process of reduction is non trivial because extensive dehalogenation takes place during the reaction. Hence, in the hydrogenation of o-chloronitrobenzene (O-CNB), it is desirable to achieve a high selectivity to o-chloroaniline (O-CAN) by reducing the primary side reaction, namely, dehalogenation. Reviews on this subject have been published by Kosak [1], Bond [2] and Greenfield et. al. [3]. The reviews reveal that most of the catalysts reported have some limitation in their application. The reaction product depends mainly on the type of catalysts being used and the reaction conditions.

Supported noble metal catalysts such as Pd/C [4], Ru/SnO₂ [5], Pt/ γ -Fe₂O₃ [6], Pt/TiO₂ [7], Pt/PVP-Ni [8] and Pt/ γ -Al₂O₃ [9] have been used with varying degree of

success for this reaction. Coq and co-workers [10] have reported that the type of support material and the nature of the metal precursors influence the selectivity towards O-CAN rather than aniline (AN). The reason for this behaviour is not due to the decrease in reactivity of C-Cl bond in chloroaniline but due to the lower adsorption strength of chloroaniline with respect to chloronitrobenzene on the support surface of the catalyst [5].

Nanotubular materials based on titanium dioxide have many applications as revealed by their use as gas sensors, in environmental purification, in photocatalysis etc. [11-13]. The on-going interest in titanium dioxide derived nanotubes is driven mainly by the large surface area and chemical stability of the material [14]. Conventionally the sol-gel method is used to synthesise nanotubular titanium dioxide using templates such as organo-gels or porous acidic aluminas [15-17]. These methods are relatively inexpensive and the final products are pure [18,19]. An alternative method involves base treatment of commercial TiO₂ which generates tubular materials. In the present investigation a simple and cost-effective methodology was employed to synthesise the nanotubular titanium dioxide [20,21]. The literature shows that hydrothermal treatment of TiO₂ with 10 M NaOH solution yields nanotubular sodium titanate materials [22,23]. However, previous attempts to synthesize tubes using KOH have either been unsuccessful or led to the synthesis of titanate nanobelts (sheets) [24]. In the present study it was found that by using 18 M solution, instead of 10 M solution, the tubes can be synthesized in large and small amounts with good reproducibility.

There are no reports available on the use of Pd supported on titanium dioxide derived nanotubes for the gas phase selective hydrogenation of ortho-chloronitrobenzene (O-CNB). Herein we report a detailed study on such a novel catalytic system for the title reaction. The overall catalytic activity of the reaction was compared with the performance of Pd supported on a commercial TiO₂ (Degussa P-25) catalyst under similar conditions.

6.2. Experimental methods

6.2.1. Synthesis [25]

Commercial titanium dioxide powder, Degussa P-25, designated as TiO₂-C, was used as a starting material to synthesise the nanotubes derived from titanium dioxide, designated as TiO₂-M. In a typical procedure, TiO₂-C (ca. 20 g) was placed in a 1 L teflon container along with KOH pellets (300 g) and distilled water (300 ml). The mixture was heated for 20 h at 120°C in an autoclave with constant stirring at a rate of 500 rpm. The solution was allowed to cool and then aged for 2 days. Subsequently, the solid product was separated from the mixture by centrifugation. The washing was repeated until the conductivity of the solution was below 100 uS/cm and remained constant. The sample was dried at 120°C for 12 h and sieved (800-1000 um) to prepare a material referred to as TiO₂-M. The addition of Pd (1 wt%) to TiO₂-M as well as the reference support TiO₂-C was carried out by a simple wet impregnation method where an appropriate amount of Pd(CH₃COO)₂ was dissolved in acetonitrile and subsequently added to the TiO₂ supports. The samples were dried and calcined at 300°C for 5 h and designated as either Pd/TiO₂-M or Pd/TiO₂-C respectively. In another experiment, two more Pd (1 wt%)/TiO₂-M catalysts were prepared from two different precursor salts of palladium, namely, Pd(NO₃)₂ and PdCl₂ using the same above mentioned procedure. The catalysts are designated as Pd-N/TiO₂-M and Pd-Cl/TiO₂-M, respectively.

6.2.2. Characterisation

The BET surface area of the catalysts was determined by the physical adsorption of a monolayer of nitrogen gas at –195°C using a Micromeritics ASAP 2010 porosimeter.

The surface morphology analysis was carried out using transmission electron microscopy (TEM) on a JEOL 100S microscope. High resolution (HR) studies were

carried out on a JEOL 2010 microscope. Samples for both TEM and high resolution TEM were prepared by adding about 1 mg of each sample to 1 ml of ethanol followed by sonication for 10 minutes. A few drops of suspension were placed on a hollow copper grid coated with carbon film made in our electron microscopy laboratories.

X-ray diffraction analysis of the samples was carried out using a Philips PW 1830 Diffractometer. The apparatus utilizes nickel filtered CuK α -radiation (1.54 Å).

Raman spectra were collected using a J-Y T64000 spectrometer. The measurements were done at room temperature at ambient conditions.

Temperature programmed desorption (TPD) of CO₂ was used to measure the surface basicity of the catalysts at room temperature. A small amount of catalyst (~0.2 g) was degassed at 150°C for 30 minutes and then cooled to room temperature. CO₂ was adsorbed at ambient temperature. The desorption of the probe gas was carried out over a range of temperatures (RT to 300°C) and the isotherm was recorded.

Temperature programmed reduction (TPR) was used to study the reducibility of the catalysts by passing a stream of 5 % H₂ and balanced with argon (FR = 8 ml/min) through a sample (0.3 g) placed in a glass reactor. The reduction was monitored from RT to 800°C at a heating rate of 5°C/min. The system was equipped with a thermal conductivity detector (TCD).

6.2.3. Hydrogenation reaction

Gas phase hydrogenation of o-chloronitrobenzene (O-CNB) was studied in a vertical fixed-bed reactor under normal atmospheric pressure. Prior to each experiment, the catalyst (ca. 0.5 g) was reduced in a hydrogen flow at 300°C for 3 h. The reactant feed consisting of O-CNB dissolved in ethanol (1:2 w/w) was fed into the reactor

using a calibrated motorized SAGE syringe pump. The reaction was carried out at 250°C and the reaction products were analysed by means of a flame ionization detector (FID) equipped with a packed capillary column (HP-5).

6.3. Results and discussion

6.3.1 Characterisation studies

The TiO₂ samples were prepared by procedures reported in an earlier paper [25]. However, in this study a larger quantity (20 g) of material was prepared and subsequently characterized. The results reported in **Table 6.1** show the surface area and pore diameter data obtained from the BET measurement of the new materials. The specific BET surface areas of TiO₂-C and Pd/TiO₂-C were found to be 50 and 46 m²/g respectively. The pore diameters are comparable. The surface areas of TiO₂-M and Pd/TiO₂-M were also determined and found to be 174 and 149 m²/g respectively. These values are similar to data obtained in our earlier study [25].

The pore volumes of TiO₂-C and -M were found to be 0.47 and 0.85 cm³/g respectively. It is therefore suggested that the increase in surface area is not necessarily influenced by an enlargement of particle size but by the increase in pore volume. The synthetic TiO₂-M is more porous than the TiO₂-C.

Figure 6.1 shows the nitrogen adsorption-desorption isotherms of TiO₂-M. The isotherm was of type IV classification which is typical of mesoporous materials according to the IUPAC classification [26]. The hysteresis loop observed at relative pressures (P/P₀) between 0.6 - 1.0 was of type H1 associated with tubular particles giving rise to open-ended cylindrical pores. It is a well known fact that a distribution of various sized cavities but with the same entrance diameter would give rise to this type of hysteresis loop [27]. This implies that the mesopores formed by the assembly of TiO₂ derived nanoparticles have entrances that are equal sized. This is consistent with the small-angle diffraction peak seen in **Fig. 6.3**. The pore size distribution plot

calculated using the BJH (Barrette-Joyner-Halenda) equation from the adsorption branch of the isotherm is shown in **Fig. 6.1** (inset). The material showed a narrow pore size distribution suggesting good homogeneity of the pores.

It is clear that the nanotubular support (TiO₂-M) has a higher surface area than the commercial support (TiO₂-C). The tubular material has larger pores and a larger surface area. The incorporation of Pd into either support resulted in a decrease in the specific BET surface area and an increase in average pore diameter. The decrease in surface area is more noticeable when Pd is added to the nanotubular support. This is mainly thought to be due to the penetration of the dispersed Pd oxide into the pores of the support. The solid state reactions between the dispersed Pd oxide and the support are also known to cause a decrease in surface area [28]. A comparison with our previously reported results [25] suggests that the surface area of TiO₂ derived nanotubes decreases with an increase in the amount of TiO₂ used per unit volume of KOH. Thus, increasing the amount TiO₂ at fixed volume and concentration of KOH enlarges the BET surface area of the material. The insertion of metal ions such as K and Na into the structural framework of TiO₂ is known to enlarge the BET surface area of the material [29].

Table 6.1: The specific surface area and average pore diameter of TiO₂-C, Pd/TiO₂-C, TiO₂-M and Pd/TiO₂-M obtained from BET measurements. Catalysts calcined at 300 °C.

Catalyst	Ageing Time (days)	BET Surface Area (m ² /g)	Average Pore Diameter (nm)
TiO ₂ -C	-	49.5	5.9
Pd/TiO ₂ -C	-	46.2	6.3
TiO ₂ M	2	174	9.8
Pd/TiO ₂ -M	2	149	10.4

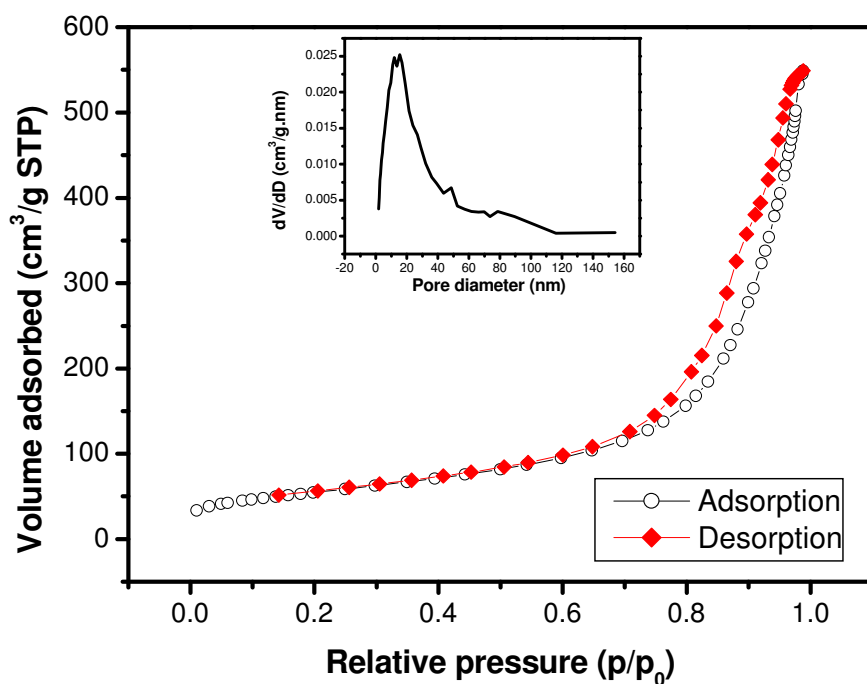


Figure 6.1: Nitrogen adsorption-desorption isotherms and corresponding pore size distribution (inset) of TiO₂-M.

The surface morphology of the modified titanium dioxide (TiO₂-M) was studied under the electron microscope and typical TEM images are shown in **Fig. 6.2**. The TEM image of TiO₂-M shows a large number of randomly distributed tubes (**Fig. 6.2-a**). The tubes are agglomeration free and have a diameter range of 8-11 nm. The tube length ranges from one hundred to several hundreds of nanometers. The analysis of the microstructure was also carried out by high resolution TEM (HRTEM) and the results are shown in **Fig. 6.1-b**. The HRTEM picture shows bundles of tubes. The shape and size of the TiO₂ derived nanotubes were not altered by the addition of Pd nor calcination at 300 °C (not shown). Our results suggest that tube formation was preceded by the formation of a sheet of the material which ultimately rolled up into a scroll-like structure (tubular form). Kasuga and others

[30,31] have proposed that the tube formation is mainly underpinned by acid treatment step whereas Chen and co-workers [32] have demonstrated that the acid step treatment is not required for the formation of tubes. These contradictory reports are an indication that the mechanism of formation is still not understood. Our results suggest that the tube formation does not require acid treatment and was mainly expedited by ageing [25].

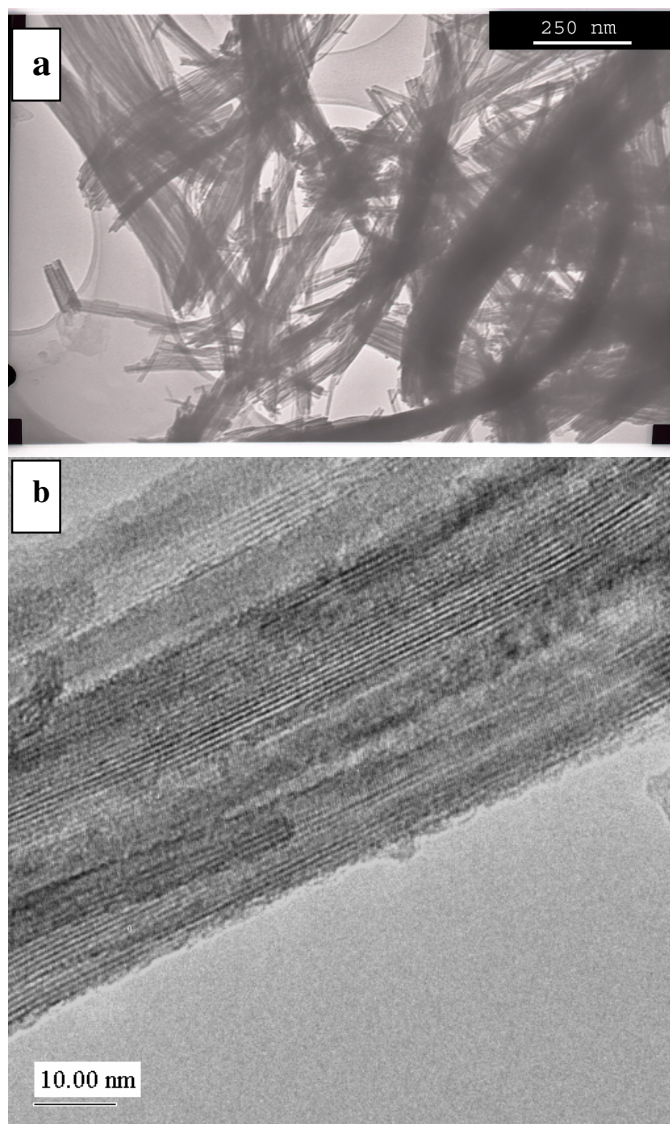


Figure 6.2: TEM images of (a) TiO₂-C and (b) TiO₂-M and HRTEM image of (c) TiO₂-M

The X-ray diffraction patterns of TiO₂-M and TiO₂-C are shown in **Fig 6.3**. The X-ray diffraction data was collected to compare the structure of titania derived nanotubes (TiO₂-M) to that of commercial support (TiO₂-C). The XRD pattern of TiO₂-C (**Fig. 6.3**, inset) shows that the material is crystalline and consists of a mixture of anatase and rutile phases in different proportions. **Figure 6.3** shows the XRD pattern of TiO₂-M and suggests that the material is amorphous and that the pattern cannot be assigned to either crystal phase of TiO₂ (anatase or rutile). The broadening of the diffraction peaks is ascribed to the small nanometer size of the nanotubes and possible bending of some planes of atoms of the tubes [33]. Again it appears that the use of large amounts of reactants used to produce the tubes is not influenced by the scale up procedure employed in the study.

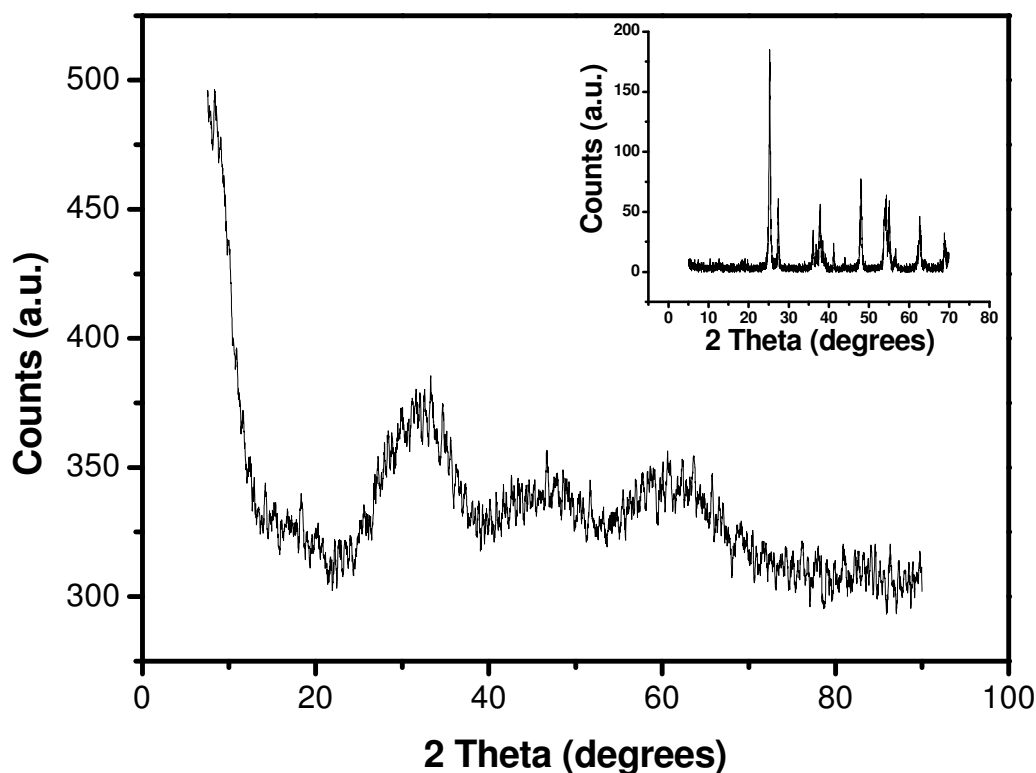


Figure 6.3: XRD patterns of TiO₂-M and TiO₂-C (inset)

The Raman spectra of TiO₂-M and TiO₂-C (inset) are shown in **Fig. 6.4**. The Raman spectrum of the commercial material (TiO₂-C) shows the presence of sharp and strong bands which are attributed to both anatase and rutile. The band proportions are also consistent with the phase weight ratio of 4:1 (anatase : rutile) expected for TiO₂-C. The characteristic titanate bands are observed for the nanotubular support (TiO₂-M) at 188, 271, 441 and 652 cm⁻¹. The broad and relatively weak bands are due to the poor crystallinity of the support. The peaks at 278 and 660 cm⁻¹ are assigned to Ti-O-K bonding in the titanate structure [30]. This shows that a complete removal of K ions was not possible even after weeks of washing. This was also confirmed by means of energy dispersive X-ray (EDX) spectroscopy which revealed the presence of K ions. The data are consistent with a potassium titanate structure with the formula KTiO₂(OH) [34,35].

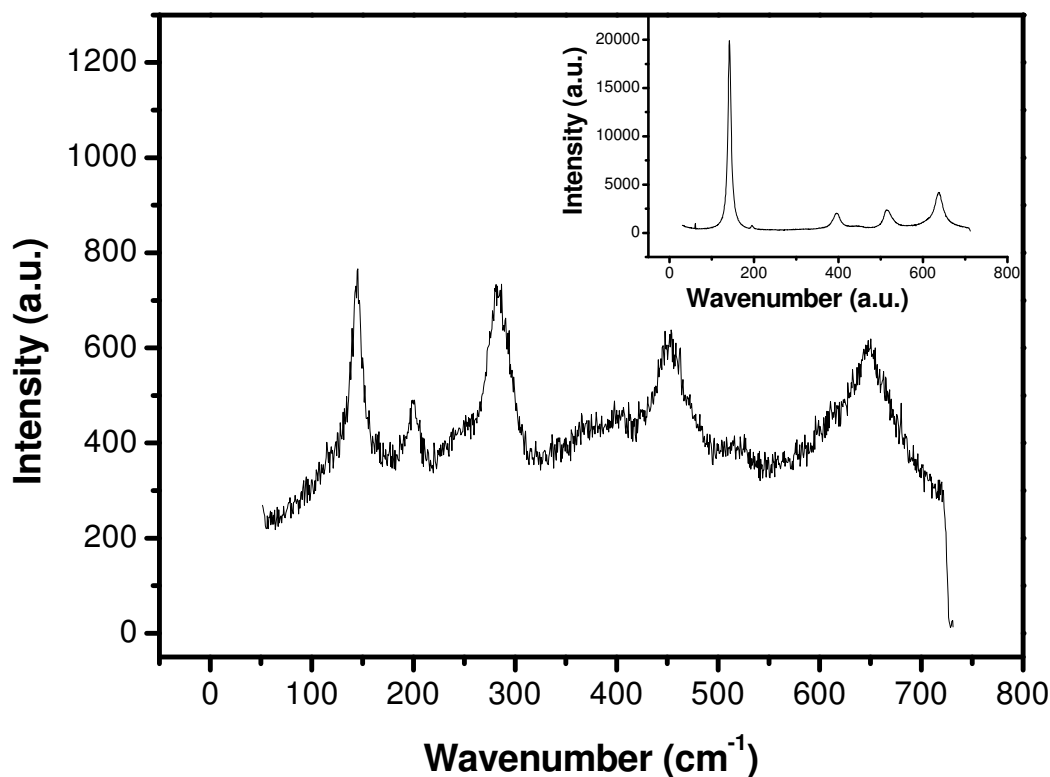


Figure 6.4: Raman spectra of TiO₂-M and TiO₂-C (inset)

Temperature programmed desorption (TPD) of CO₂ was used to study the adsorption/desorption on Pd/TiO₂-M catalyst. The study was carried out from room temperature to 300 °C to determine the presence of basic site and their strength on the surface. While the commercial material (TiO₂-C) showed the presence of insignificantly small amount of basic sites, Pd/TiO₂-C showed a different pattern with a small peak at 210 °C and a broad peak at 264 °C (**Fig. 6.5**, inset). The generation of these two peaks is attributed to the addition of Pd. The TPD profile of TiO₂-M (**Fig. 6.5**) shows the presence of moderately weak basic sites at 116 °C. This is an indication that the treatment of TiO₂-C with KOH suppresses the high temperature peaks and generates relatively weaker basic sites. The number of basic

sites also increased as a result of KOH treatment. Pd/TiO₂-M showed the presence of weak and moderate basic sites as evident from the two peaks at 61 and 228 °C. It is clear that the addition of Pd not only increased the amount of basic sites but also expedited the peak shift to lower temperature. Since the effect of the addition of Pd to both supports yielded different results, it was noted that the influence of Pd addition depends on the nature and properties of TiO₂ support under investigation. Titania derived nanotubular catalyst (Pd/TiO₂-M) showed more basic sites than commercial based catalyst (Pd/TiO₂-C). These data clearly demonstrate that Pd particles have a structural influence on the surface of TiO₂ [22].

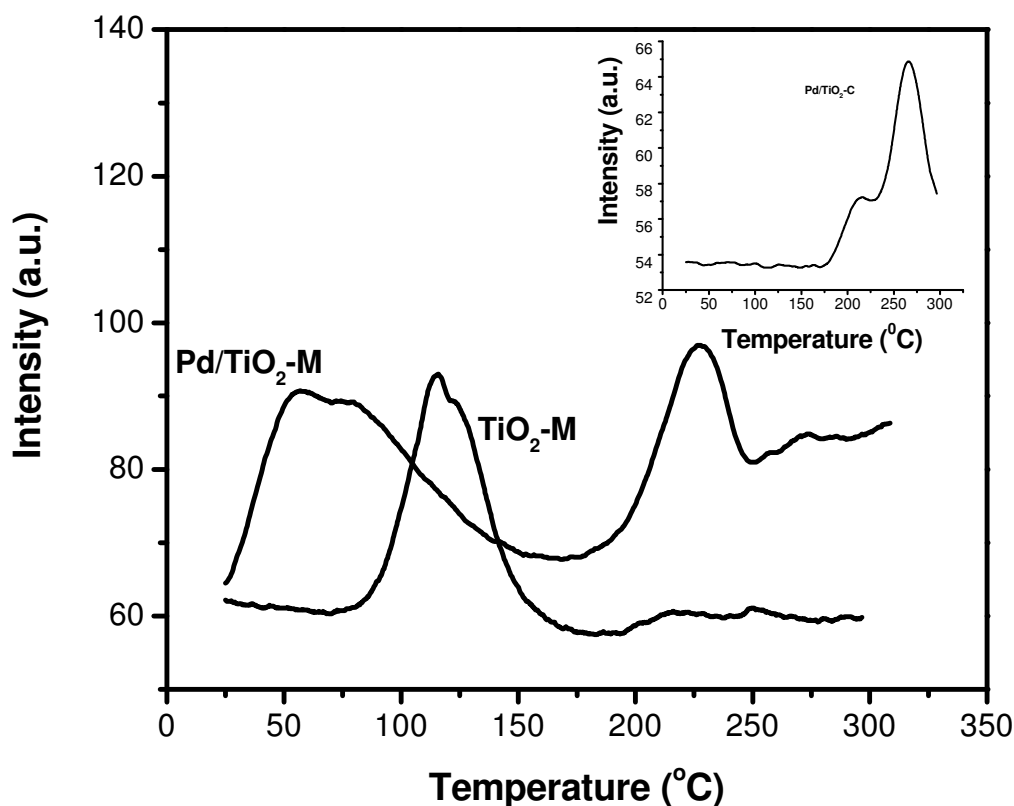


Figure 6.5: TPD profiles of TiO₂-M and Pd/TiO₂-M and Pd/TiO₂-C (inset)

The temperature programmed reduction (TPR) profile of TiO₂-C is shown in **Fig. 6.6**. The technique was employed to study the influence of Pd reducibility on the catalyst support. The commercial support (TiO₂-C) did not show any reduction peak in the absence of PdO. The weak low temperature peak observed at 96 °C is assigned to the reduction of PdO species weakly bound to the support. A broad high temperature peak consisting of two overlapping peaks at high temperature (462 and 570 °C) was observed. The hydrogen consumption is believed to be due to the reduction of bulk oxygen in the TiO₂ support. Interesting to note is that titania derived nanotubular catalyst (Pd/TiO₂-M) did not show any reduction peak within the analysis temperature range. The absence of the reduction peak was attributed to the existence of very small reduced Pd nanoparticles [25].

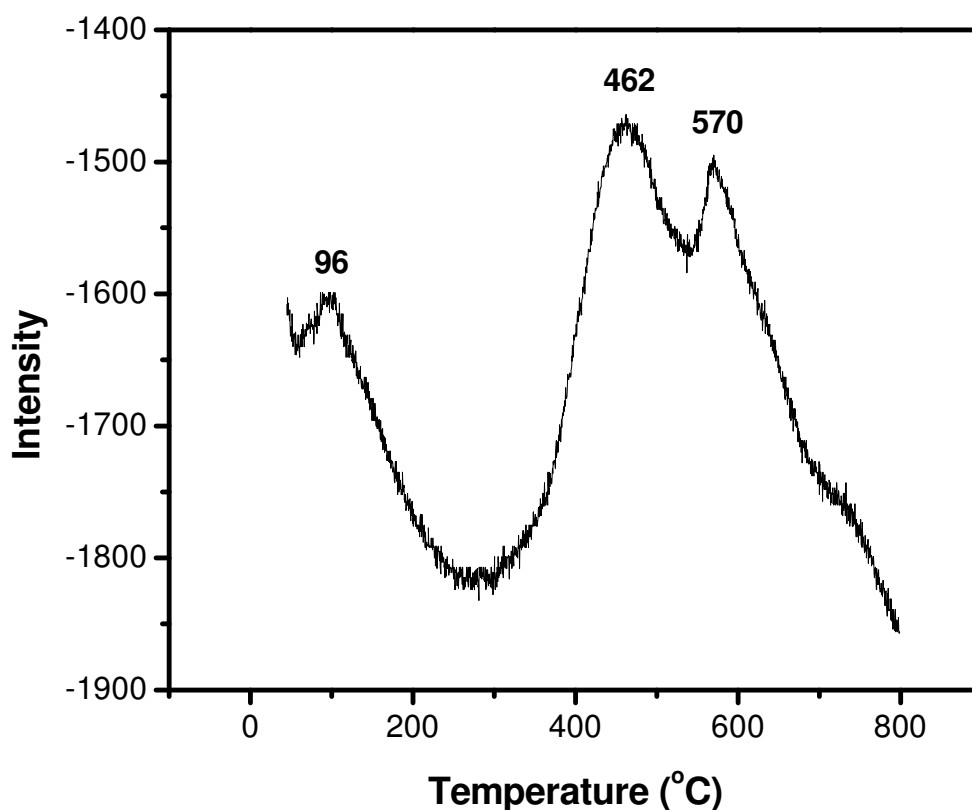
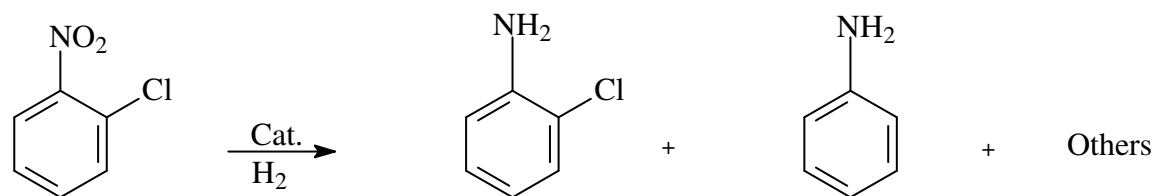


Figure 6.6: A TPR profile of Pd/TiO₂-C.

6.3.2. O-CNB hydrogenation (O-CNB) studies

The vapour phase hydrogenation of O-CNB over Pd (1 wt%) on TiO₂ catalysts was carried out under normal atmospheric pressure. Neither of the support materials, TiO₂-C or TiO₂-M, showed any hydrogenation activity. Addition of Pd to TiO₂-C showed a conversion of O-CNB of 63 % and selectivity to O-CAN of 59 %. The hydrogenation of O-CNB to give ortho-chloroaniline and aniline as the main products is shown in **Scheme 6.1**. Other detectable by-products included nitrobenzene (NB), orthochloronitrosobenzene (O-CNSB) and azobenzene. The results are shown in **Table 6.2**. Pd/TiO₂-C catalyst also showed a significant amount of aniline (AN) formation (38%). On the other hand, Pd/TiO₂-M catalyst gave complete conversion (100 %) of O-CNB with high selectivity to O-CAN (84 %). Further, the selectivity to the secondary product aniline was observed to be much lower (14%) than that obtained with Pd/TiO₂-C catalyst. This implies that Pd/TiO₂-C promotes more hydrogenolysis of C-Cl than does the Pd/TiO₂-M catalyst.

It is known that the Pd counterion plays an important role in the dispersion of palladium and hence the hydrogenation activity [36]. The influence of different precursor salts of palladium on the conversion of O-CNB as well as selectivity towards O-CAN over TiO₂-M supported catalysts is shown in **Table 6.2**. Among the three precursor salts of palladium used, the acetate salt shows the best conversion of O-CNB (100 %) while the nitrate salt showed the least conversion of O-CNB of 56 %. The selectivity to O-CAN remained almost constant (~85 %) irrespective of the nature of the Pd anions used. This implies that the type of anion of the Pd precursor salts only has an influence on Pd dispersion.



Scheme 6.1.

Table 6.2: Comparison between reaction data of TiO₂ supported Pd (1 wt%) catalysts and effect of precursor salts of Pd supported on TiO₂-M catalysts (Pd : TiO₂-M = 1: 37 mol/mol) on O-CNB hydrogenation

	Catalyst/ Precursor	Conversion (%)	Product selectivity (%)		
			O-CAN	AN	Others
Catalyst	Pd/TiO ₂ -C	63	59	38	3
	Pd/TiO ₂ -M	100	84	14	2
Precursor	Pd(CH ₃ COO) ₂	100	84	14	2
	PdCl ₂	90	86	13	1
	Pd(NO ₃) ₂	56	85	13	2

Key: O-CAN = ortho-Chloroaniline; AN=Aniline

Reaction conditions : T = 250°C; H₂/O-CNB = 3; Feed rate = 4.5 ml/h;

Wt. cat = 0.5 g; t = 1h.

Table 6.3 shows the effect of Pd loading on both conversion and selectivity of TiO₂-M supported catalysts. The conversion of O-CNB remained relatively high, almost 100 %, irrespective of the Pd content. The selectivity to O-CAN decreased while selectivity to AN increased with increasing Pd content. It was observed that addition of Pd to TiO₂-M increased the basicity on the surface of the support (**Fig. 6.5**). Hence, with increase in Pd content on TiO₂-M, an increase in the basicity on the TiO₂-M surface is expected. The high basicity on the surface of the catalytic support is known to facilitate hydrogenolysis of a C-Cl bond [36,37] rather than hydrogenation of O-CNB and this will give rise to aniline formation.

The decrease in selectivity with increasing Pd loading could be related to the effect of Pd particle size. An average Pd particle size of 2.3 nm was attained when 5 % Pd was added to TiO₂-M support (**Fig. 6.7**). Moreover, the addition of 7 % Pd resulted in an increase in Pd particle size to 3.1 nm as shown in **Fig. 6.8**. Pd/TiO₂-M (7 % w/w) also showed a slightly wider Pd particle size distributions than Pd/TiO₂-M (5 % w/w) (**Fig. 6.9**).

Table 6.3: The effect of Pd loading on TiO₂-M supported catalysts for O-CNB hydrogenation.

Catalyst	Pd Loading (Wt %)	Conversion	Selectivity %		
			O-CAN	AN	Others
Pd/TiO ₂ -M	1	100	84	14	2
Pd/TiO ₂ -M	3	100	30	56	14
Pd/TiO ₂ -M	5	96	23	64	13
Pd/TiO ₂ -M	7	94	14	62	24

Reaction conditions: T = 250 °C; H₂/O-CNB = 3; Wt cat. = 0.5g; Feed Rate = 4.5 ml/h; t=1h.

Key: O-CAN = ortho-Chloroaniline; AN=Aniline

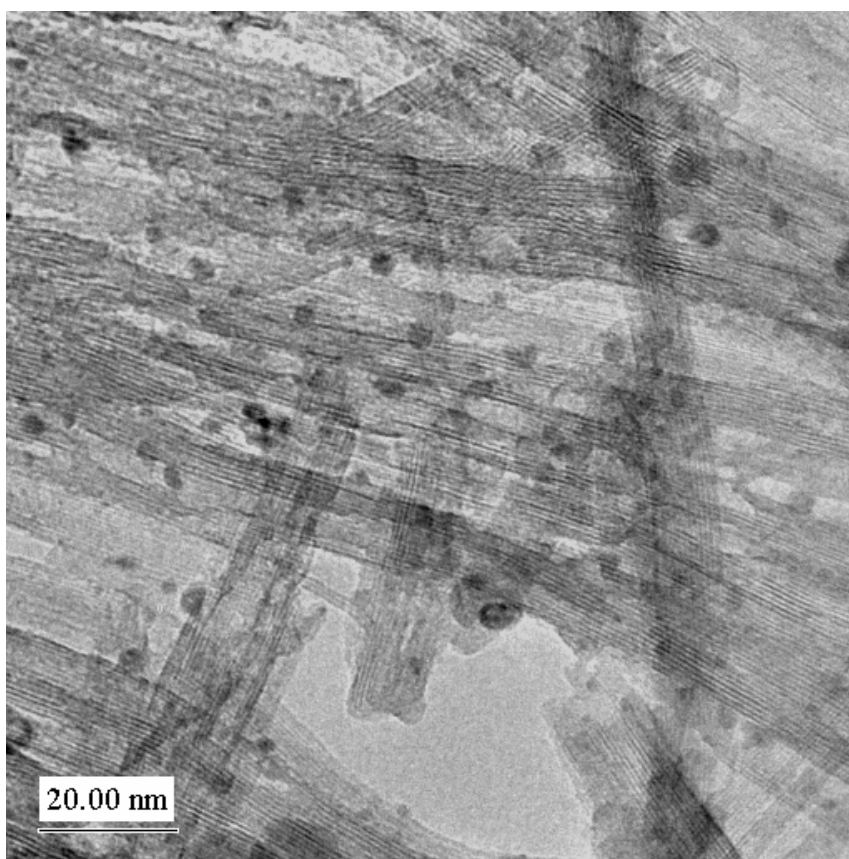


Figure 6.7: HRTEM image of Pd/TiO₂-M (5 % w/w).

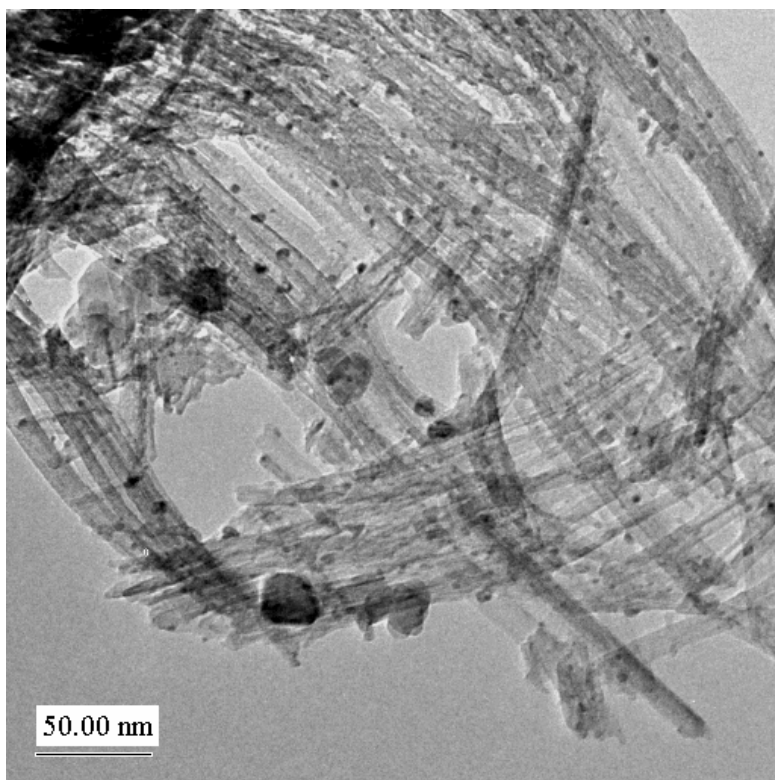


Figure 6.8: HRTEM image of Pd/TiO₂-M (7 % w/w).

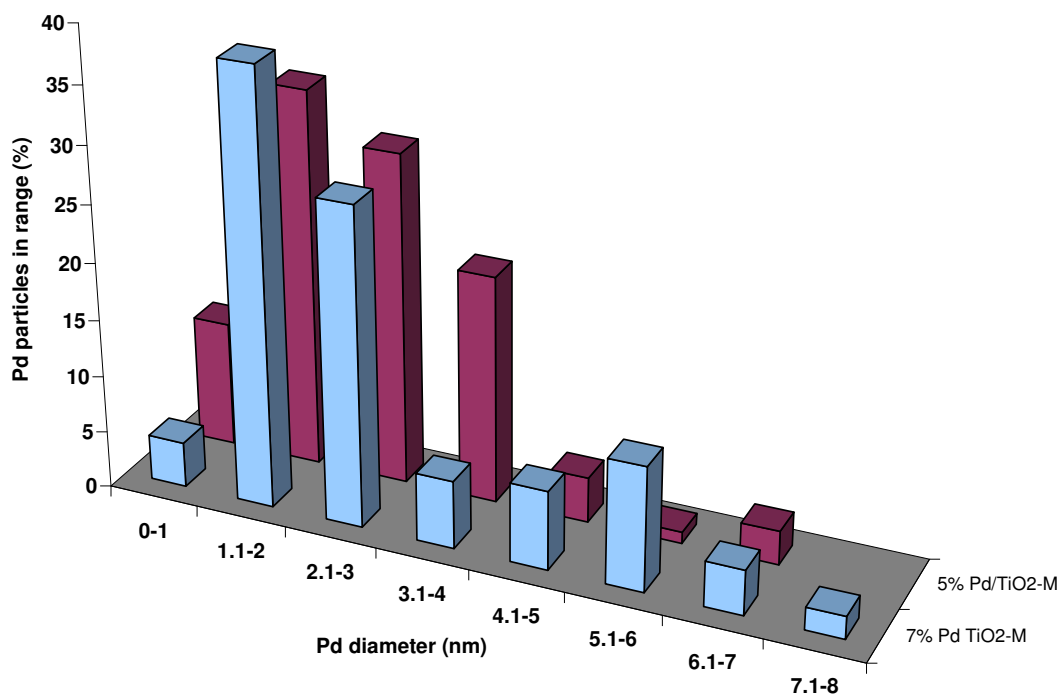


Figure 6.9: Palladium particle size distributions showing 5 and 7 % loadings on TiO₂-M

The effect of reaction temperature and the hydrogen to O-CNB mole ratio on conversion as well as selectivity to O-CAN is shown in **Figs. 6.10 and 6.11**. The conversion of O-CNB remains almost 100 % with increasing temperature. This suggests that the Pd/TiO₂-M catalyst is thermally stable even at high reaction temperature and this may be attributed to the morphology of TiO₂ and the material composition. The selectivity to O-CAN decreased while the selectivity to AN increased from 46 to 77 %.

There was a small decrease in conversion of O-CNB from 100 to 92 % with increase in mole ratio of H₂/O-CNB. The selectivity to O-CAN and AN changed dramatically. This shows that the extent of hydrogenation is partly influenced by the amount of H₂ in the system with AN more favoured at higher H₂/O-CNB mole ratio.

The results suggest that variation in product preference (O-CAN or AN) also depends on the surface morphology and phase composition of the TiO₂ support of Pd/TiO₂ catalysts.

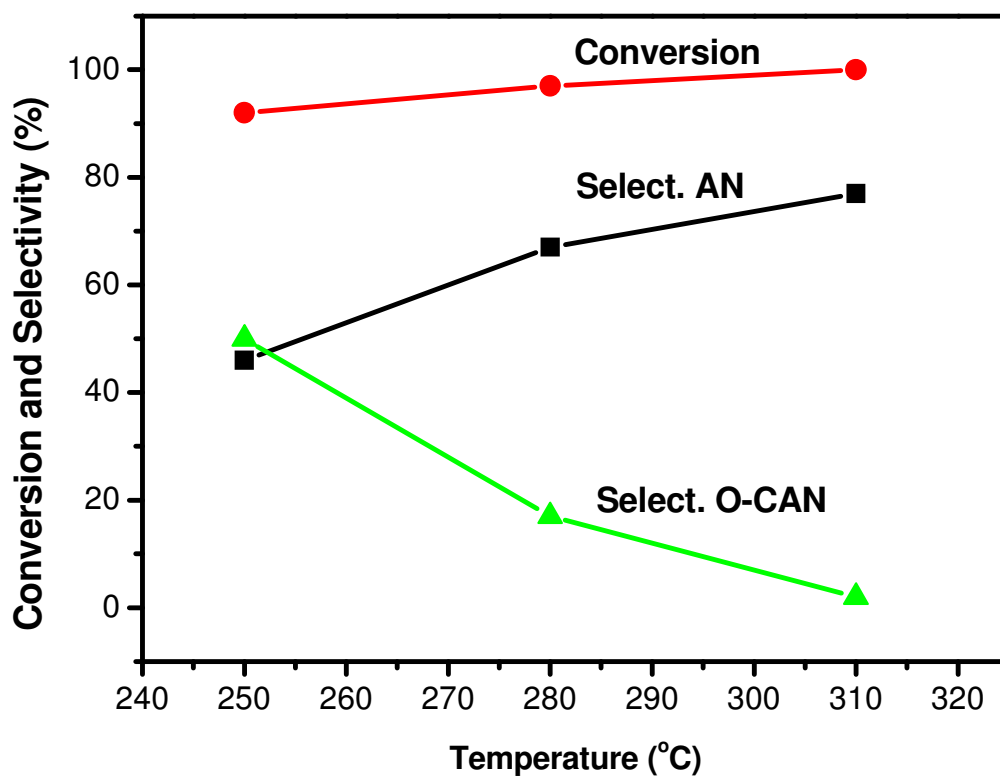


Figure 6.10: Effect of temperature on conversion and selectivity. Feed rate of O-CNB = 4.5 ml/h; $t = 1$ h; Wt cat. = 0.5g and $H_2/O-CNB = 5$.

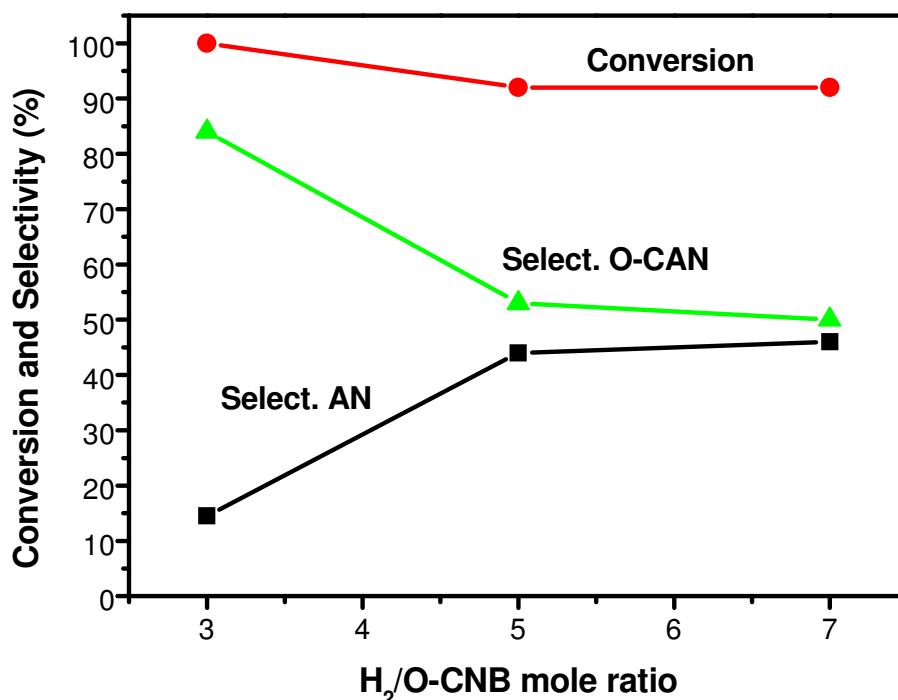


Figure 6.11: Effect of H₂/O-CNB mole ratio on conversion and selectivity. Feed rate of O-CNB = 4.5 ml/h; t = 1h; Wt cat. = 0.5g and T = 250 °C.

To examine the stability during the hydrogenation of O-CNB with reaction time, the Pd/TiO₂-M catalyst was studied for 5 h on stream (**Fig. 6.12**). A decline in conversion was observed. However, the selectivity for O-CAN and AN remained nearly stable with time on stream. The initial decrease in activity is attributed to poisoning due to the deposition of hydrocarbons or hydrochloride and carbonaceous species on the active sites (Pd coverage) of the TiO₂ support surface. The TGA profiles in **Fig. 6.13 (a and b)** attest to this finding. The TGA results of fresh TiO₂-M in **Fig. 6.13(a)** showed a total weight loss 6 % (RT to 160 °C) which is ascribed to the loss of moisture. The TGA profile of a spent catalyst in **Fig. 6.13(b)** revealed a

total weight loss of 20 %. The initial weight loss of 4 % at RT to 250 °C is ascribed to moisture followed by a 6 % loss (250 to 400 °C) which is ascribed to the removal of the deposited hydrocarbons on the surface of the catalyst during the reaction. The remaining 10 % weight loss (780 to 940 °C) is attributed to the removal of carbonaceous materials. Based on TGA data it is clear that the major deactivation agent is carbonaceous species followed by hydrocarbons adsorbed on the catalyst surface.

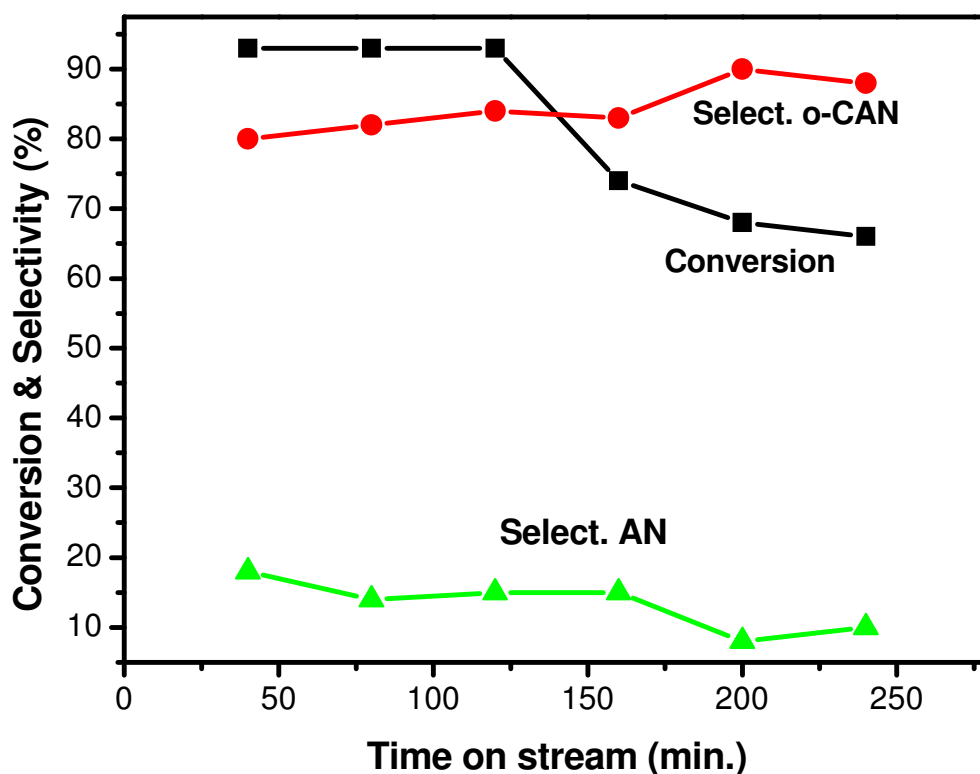


Figure 6.12: Effect of time on stream (TOS) on conversion and selectivity. Feed rate of O-CNB = 4.5 ml/h; $t = 1$ h; Wt cat. = 0.5g; $T = 250$ °C and $H_2/O\text{-CNB}$ ratio = 5.

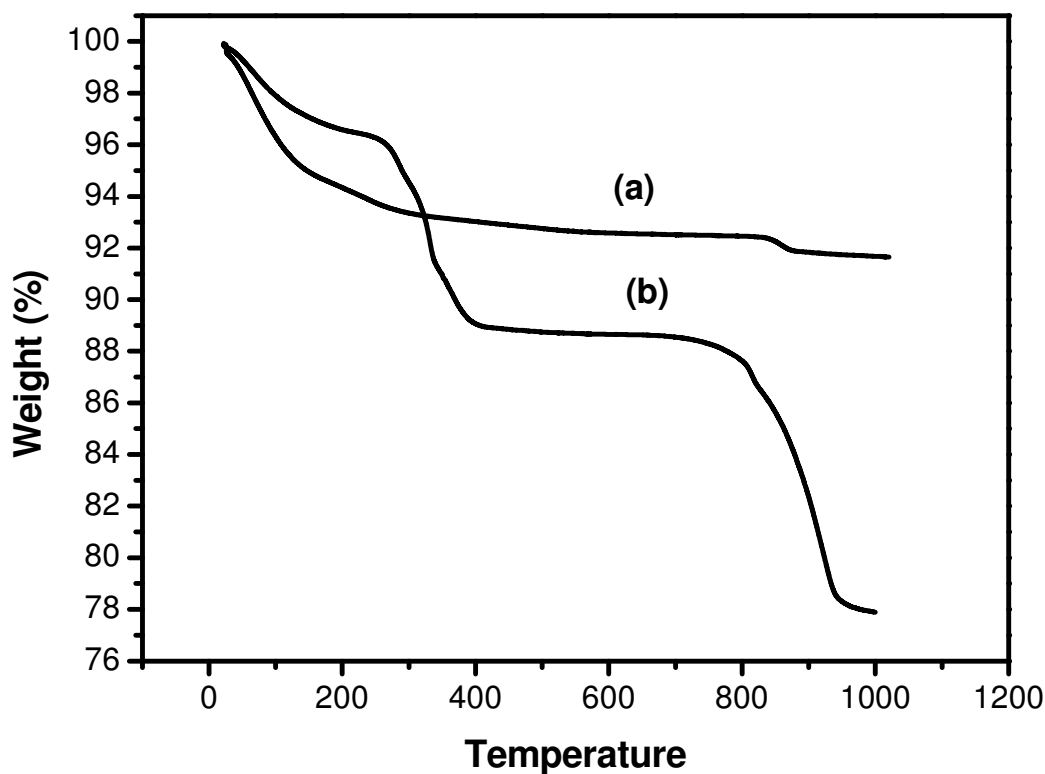


Figure 6.13: TGA profiles of fresh TiO₂-M (a) and spent TiO₂-M (b) catalysts

6.4. Conclusions

1. Both the morphological and surface properties of the material showed some promotional effect as TiO₂ derived nanotubes supported Pd catalyst delivered a maximum conversion of O-CNB (100 %) and high yields of O-CAN.
2. The TPR analysis of Pd/TiO₂-M revealed the absence of any reduction peaks due to palladium. HRTEM of higher Pd content sample revealed the presence of Pd

nanoparticle suggesting that Pd may have been pre-reduced on contact with the support and existed in a particle size too small to be detected.

3. The catalyst showed good conversion and stability with time on stream. Selectivity to O-CAN remained constant throughout the reaction.

6.5. References

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7

Potassium titanate: a new support for gold catalyzed carbon monoxide oxidation

7.1. Introduction

Most catalysts are used in supported form. The major advantage is that the catalyst, typically a metal, should generate a maximum surface area to produce maximum activity per unit of catalyst mass. Supports typically used include SiO_2 , Al_2O_3 , C and TiO_2 . The recent upsurge in the synthesis in materials at the nanoscale and the ability to characterize these materials by techniques such as electron microscopy had led to the synthesis of a new generation of shaped supports. For example, mesoporous silicas [1] and carbon nanotubes and carbon fibres [2] allow metals to interact with the supports in novel ways and this can lead to differences in catalytic activity when the shaped supports are compared to their amorphous counterparts.

Recently, simple procedures have become available to synthesize tubular TiO_x material [3,4]. There is still controversy as the precise nature of these materials and their formation with their properties being dependent on the synthetic route used [3, 5-13] While these materials hold promise in the areas of photovoltaics

and nanoelectronics [14,15], a few reports have recently appeared where they have been exploited as catalyst supports [3,5,16].

The tubular TiO_x materials has increased surface area relative to the standard Degussa P25 support and the morphology should lead to good interaction between the support and the metal catalyst, that could, for example, limit sintering. This in turn, may have benefits for the durability of supported gold catalysts, an aspect which has been often neglected in much research work reported to date [17]. Au supported on titania has been widely used in CO oxidation reactions [18-20], and numerous factors have been shown to enhance the activity of the Au/TiO_2 catalyst [17,21] including Au particle size [23,24]. Haruta et al. have demonstrated that the existence of strong interactions between Au particles and the support is imperative for high activity in CO oxidation [22]. Moreover, moisture is also known to positively enhance the activity at controlled concentrations [24]. Although the Au/TiO_2 catalyst is known to be very active for CO oxidation a major setback is that the catalyst is active over a short period of time due to deactivation at low temperatures. It is clear that the majority of studies on gold/titania by far have involved the use of commercial Degussa P25 titania, essentially a mixture of anatase and rutile, though some work with titania from other sources has been reported [15,25-31]. Systematic investigations of titania polymorphs are much rarer and the role of support morphology has been the subject of few studies. In the current study, we have used a titanate obtained from KOH/TiO_2 as a support for the Au catalyzed CO oxidation reaction. We also report on the effect of morphological and structural modification of titania on the activity and stability of Au supported catalysts for CO oxidation. The effect of the tubular structures on Au particle size is addressed and compared with that of P25. Very recently Zhu and co-workers also reported the use of Au supported on titania nanotubes as a catalyst for CO oxidation and we also compare our data with their results [16].

7.2. Experimental

7.2.1. Synthesis of titanate $\text{KTiO}_2(\text{OH})$ tubes

The synthesis procedure used to generate the titanate has been described elsewhere in the literature [12]. Commercial TiO_2 (P25) powder (25 g) was added to a 200 ml solution of 18 M KOH in a 1 L stainless steel autoclave. The mixture was heated for 24 hours at 120 °C (stirring at 500 rpm). The resulting material was cooled, then allowed to age for 2 days in the base solution. It was then repeatedly centrifuged and washed with deionised water until the conductivity was below $100 \mu\text{S cm}^{-1}$. The material was finally dried in air at 120 °C for at least 12 hrs. From here onwards the resultant material shall be referred to simply as the titanate, $\text{KTiO}_2(\text{OH})$.

7.2.2. Preparation of gold-supported catalysts

Deposition-precipitation was the method used to load gold onto the TiO_2 (P25) and $\text{KTiO}_2(\text{OH})$ [31]. In each case the support was slurried in distilled water (600 ml) and stirred vigorously. Required amounts of diluted HAuCl_4 solution (10^{-2} were added slowly to the supports with continuous stirring. The pH was maintained at 8.5 by adding 15% NH_4OH drop wise in the case of TiO_2 (P25) while in the case of $\text{KTiO}_2(\text{OH})$ the pH was already at ~9; so the addition of NH_4OH was not necessary. The precipitated solutions were aged for 2 hours. A solution of NaBH_4 was prepared in ice water and added in the required amount to ensure the (complete) reduction of Au (III) to Au (0). The resulting catalyst powders of Au- TiO_2 (P25) and Au- $\text{KTiO}_2(\text{OH})$ were dark purple and light pink and contained a maximum of 1.1 wt% and 0.8 wt% Au loading respectively.

7.2.3. Sample characterization

The X-ray diffraction patterns were obtained on a Philips PW 1820 diffractometer with Cu K α (1.54178 Å) radiation. High-resolution TEM images were obtained using a JEOL 2010 electron microscope with a LaB₆-cathode operated at a voltage of 200 kV. Raman measurements were made using the micro-Raman attachment of a Jobin-Yvon T64000 Raman spectrometer, configured in triple subtractive mode.

FTIR spectra were recorded using a Bruker Tensor 27 IR-spectrometer equipped with KBr detector and CaF₂ windows at a spectrum resolution of 4 cm⁻¹. The sample powder was pressed (~10 MPa) into a self-supporting disc that was placed in a sample holder fitted with an internal heating coil.

Nitrogen adsorption-desorption isotherms were measured on a Micromeritics TRISTAR 3000 analyzer. The samples were degassed under vacuum for several hours before nitrogen adsorption measurements. The specific surface area was determined by the Brunauer-Emmet- Teller (BET) method.

7.2.4. Catalytic activity measurement

All catalyst samples were calcined at 300 °C in either 20% O₂ (balance He) or 5% H₂ (balance He) for 2 hours prior to testing. The two catalysts were tested for CO oxidation activity in a continuous flow fixed-bed glass reactor (6 mm i.d). Between 50 mg and 100 mg of solid catalyst (powder particle size about 150 μm) samples were loaded into the reactor. The gas mixtures consisted of 1% CO and 5% O₂ balanced in He and the total flow was generally 47 sccm. The course of the reaction was monitored quantitatively by GC analysis, using a Carbosieve SII packed column (2 m x 2 mm). All measurements were carried out at room temperature (although always slightly higher due to the exothermic nature of the reaction) and atmospheric pressure.

7.3. Results and discussion

7.3.1. Textural characterization of the samples

In **Table 7.1** the textural data for the samples are summarized. The specific surface area of the titanate material $\text{KTiO}_2(\text{OH})$ was three times more than that of the commercial TiO_2 (P25). The deposition of gold on both materials did not significantly alter the features of the support.

Table 7.1: Physical properties of the studied samples

Catalyst	Gold loading (wt%)	S_{BET} m^2g^{-1}	Pore volume cm^3g^{-1}	Particle Size of Au (nm)*
TiO_2 (P25)	-	49.4	0.16	-
$\text{KTiO}_2(\text{OH})$	-	182	0.49	-
Au-TiO_2 (25)	1.1	49.1	0.30	5.1
$\text{Au-KTiO}_2(\text{OH})$	0.8	162	0.43	4.7

*Determined by HRTEM

7.3.2. Structural properties

7.3.2.1. Raman spectroscopy

The structural differences between TiO_2 (P25) and the titanate $\text{KTiO}_2(\text{OH})$ is revealed by the Raman results (**Fig. 7.1**). The TiO_2 (P25) profile showed more intense and sharper peaks than those of $\text{KTiO}_2(\text{OH})$ and this can be attributed to the fact that the former is more crystalline than the latter. Some of the peaks might have shifted due to a particle size effect [32]. New peaks were observed for the $\text{KTiO}_2(\text{OH})$ and are mainly due to the structural changes in the TiO_2 , e.g. from three-

dimensional crystallites to two-dimensional sheets. Gold did not have any influence on the characteristic Raman profiles of the two supports.

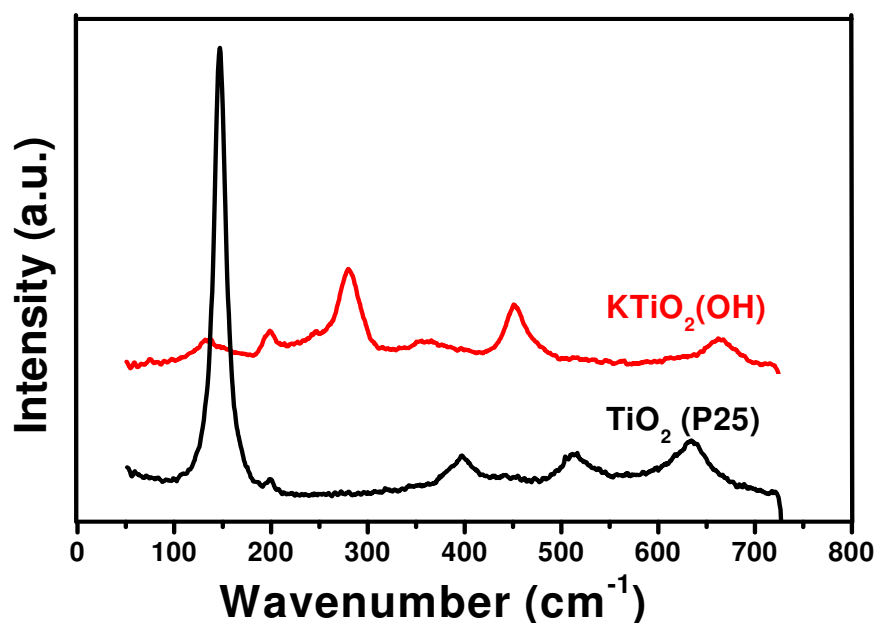


Figure 7.1: Raman spectra of as prepared titanate $\text{KTiO}_2(\text{OH})$ and commercial TiO_2 (P25).

7.3.2.2. X-ray diffraction analysis

Figure 7.2 shows the typical experimental powder XRD profiles taken from the titanate samples. The diffraction peaks are much broader for the $\text{KTiO}_2(\text{OH})$ sample than those obtained from TiO_2 (P25) (**Fig. 7.2**, inset) crystals, and a thorough literature search shows that the profile cannot be attributed to any of the known crystal structures of TiO_2 [33]. Gold was not readily detected on Au-TiO_2 (P25).

E.g., the Au (111) diffraction line at $2\theta = 38.4^\circ$ overlaps with that of the TiO_2 support.

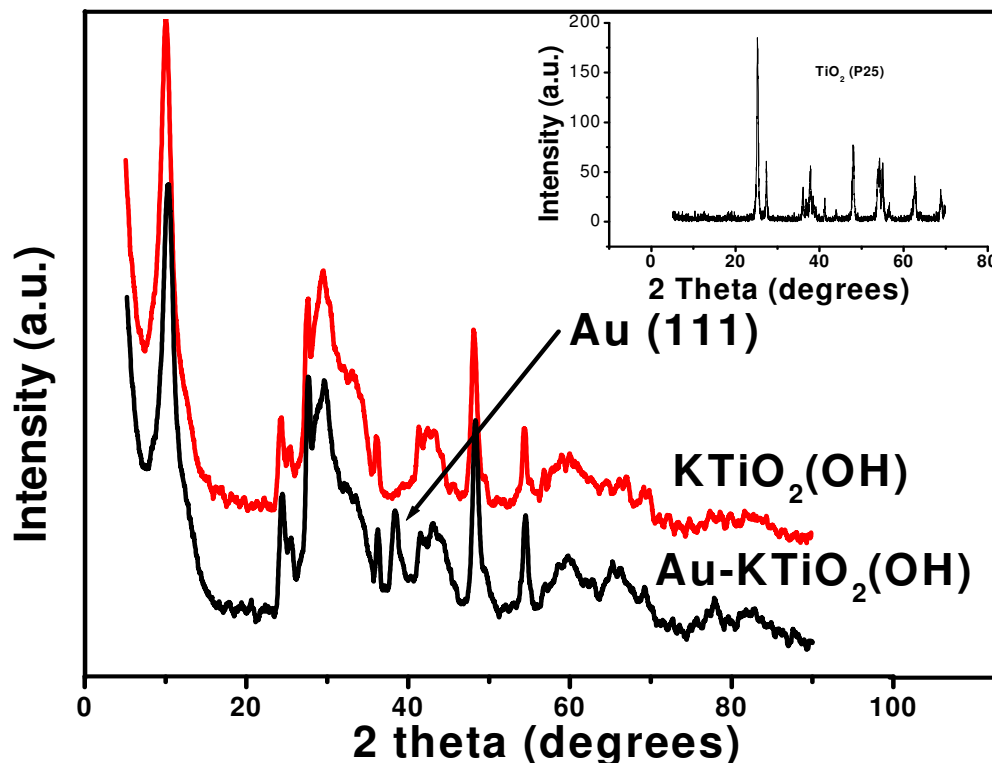


Figure 7.2: X-ray diffraction patterns of as prepared $\text{KTiO}_2(\text{OH})$ and $\text{Au-KTiO}_2(\text{OH})$ samples.

7.3.2.3. Electron microscopy

The morphology of the titanate $\text{KTiO}_2(\text{OH})$ was studied by the use of HRTEM and the image is shown in **Fig. 7.3**. Careful analysis suggested that the titanate was in the form of very thin sheets which could roll up into layered sheets of titanium oxide [33]. **Fig. 7.4** shows the high resolution TEM images of the as prepared $\text{Au-KTiO}_2(\text{OH})$ and $\text{Au-TiO}_2(\text{P25})$ catalysts. The Au average particle sizes were estimated to be 4.7 and 5.1 nm respectively for the $\text{Au-KTiO}_2(\text{OH})$ and Au-TiO_2

(P25) samples. The particle size distribution is shown in **Fig. 7.5**. The chemical composition of the Au- $\text{KTiO}_2(\text{OH})$ and $\text{KTiO}_2(\text{OH})$ samples was examined by EDS and the presence of potassium was confirmed in both samples.

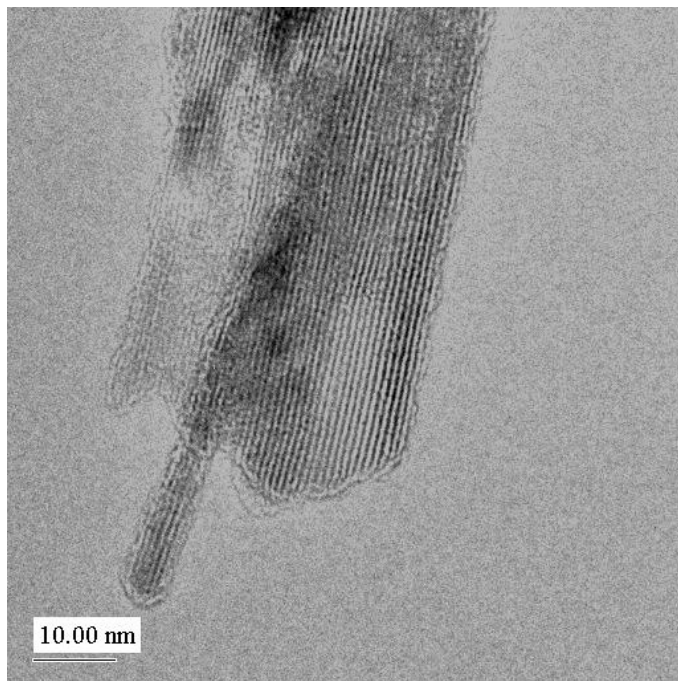


Figure 7.3: HRTEM image of as prepared titanate $\text{KTiO}_2(\text{OH})$ sheets.

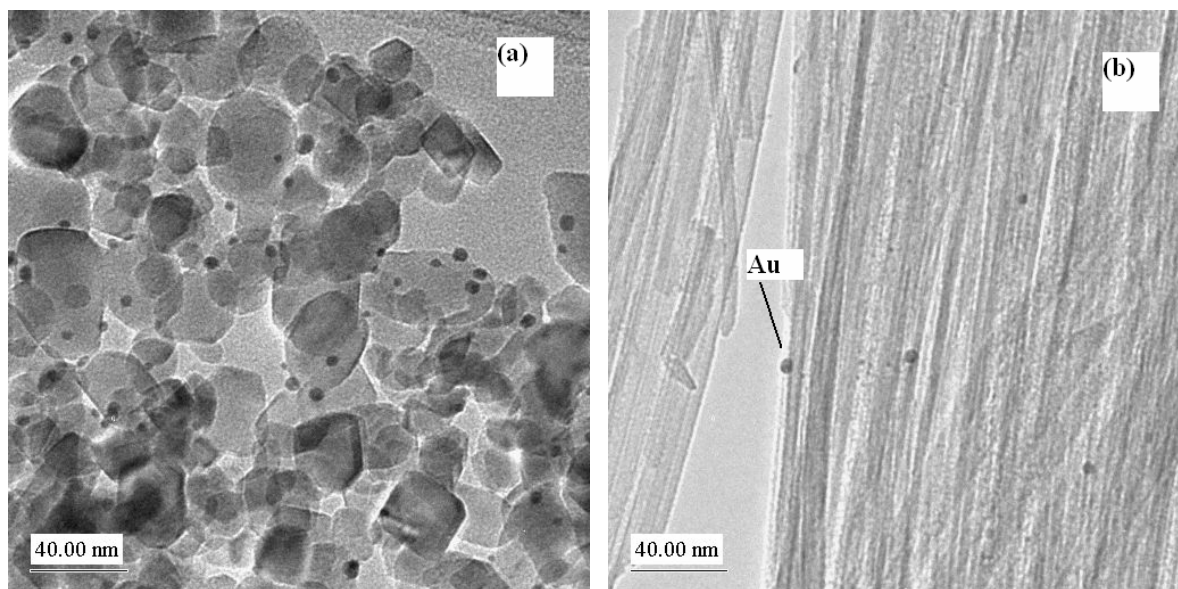


Figure 7.4: HRTEM images of as prepared (a) Au-TiO₂ (P25) and (b) Au- KTiO₂(OH).

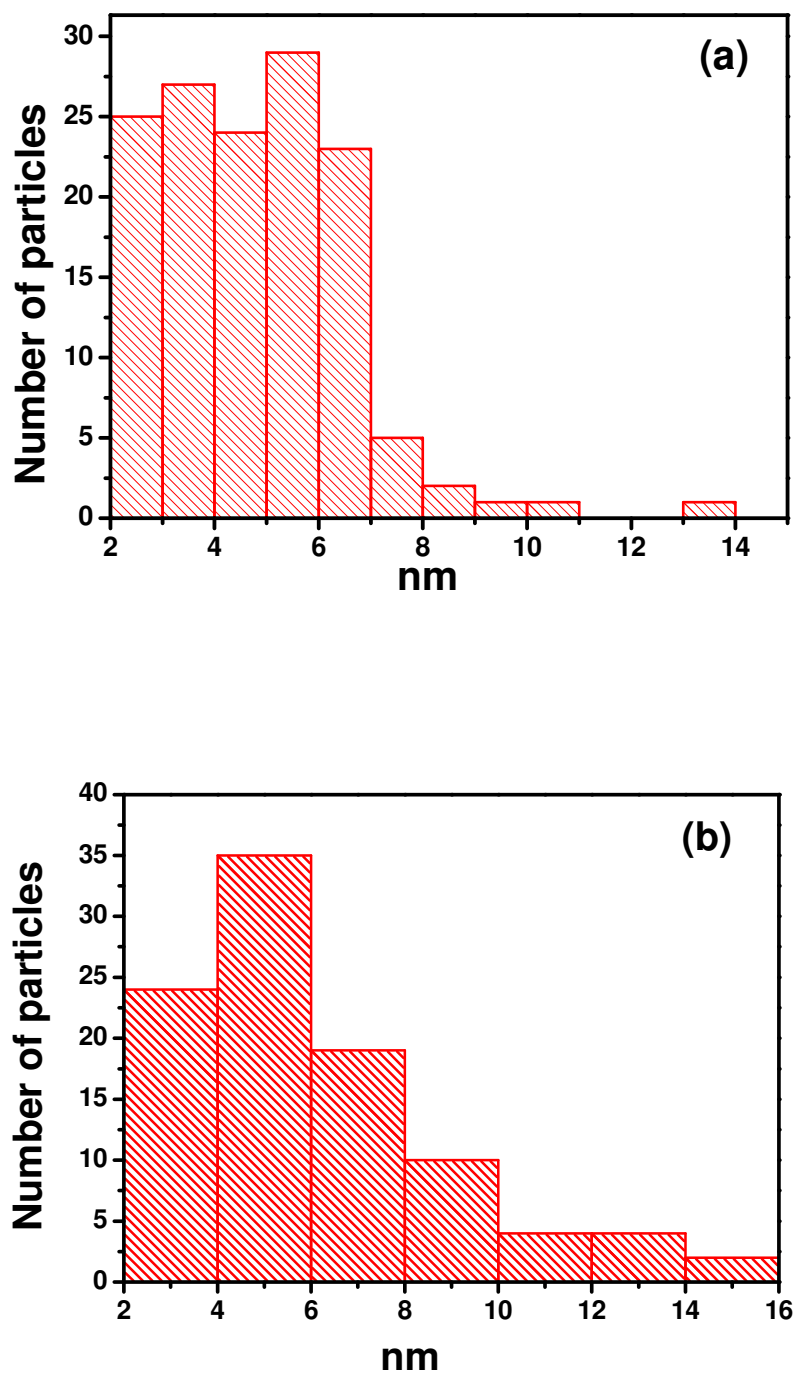


Figure 7.5: Size distributions of Au metallic particles in as prepared (a) Au-TiO₂ (P25) and (b) Au-KTiO₂(OH) as revealed by TEM.

7.3.2.4. Infrared spectroscopy and thermal analysis

FTIR was used to characterize the titanate $\text{KTiO}_2(\text{OH})$ sheet material and the IR data demonstrated the existence of large amounts of water and hydroxyl groups in the spectrum (H_2O at 1624 cm^{-1} and a strong O-H stretching vibration between 3600 and 2500 cm^{-1} ; **Fig. 7.6**) [34]. Two OH stretch vibrations at around 3645 cm^{-1} and 3707 cm^{-1} were still visible even after the sample had been heated up to 220°C where the dehydration of the sample was complete (as evidenced by DSC studies, which shows an endothermic peak of the dehydration of the sample at 173°C , **Fig. 7.7**). This suggested that the absorption bands could be considered to be contained in the crystal structure. The fact that there are two OH stretch vibrations suggests the presence of different chemical environments (bridging modes) of the hydroxyl groups in the titanate structure.

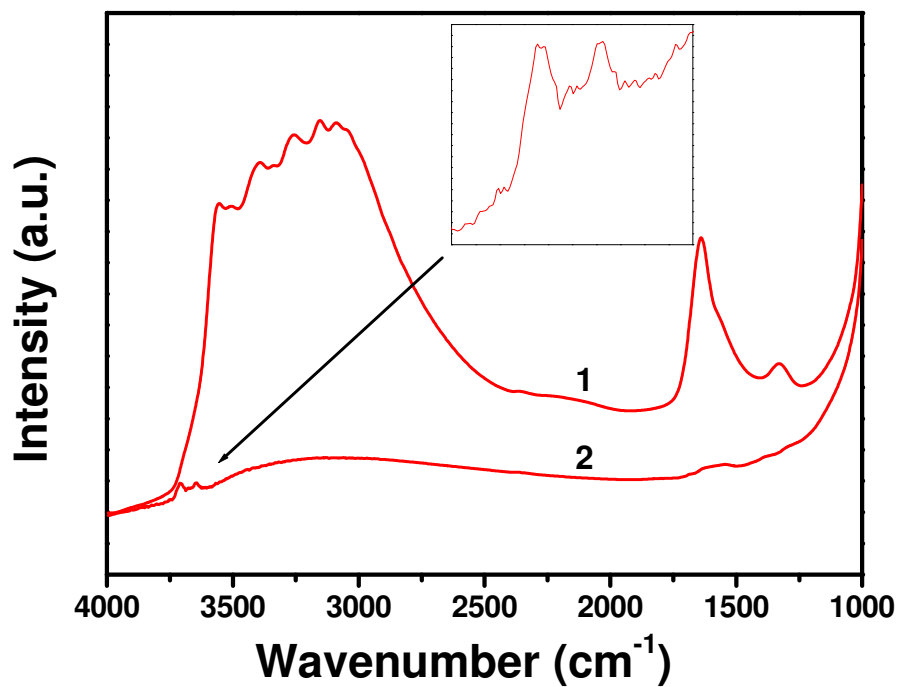


Figure 7.6: IR spectrum of $\text{KTiO}_2(\text{OH})$: (1) spectrum recorded at room temperature before heating the sample; (2) spectrum recorded at 220 °C after heating at 300 °C for 1 h.

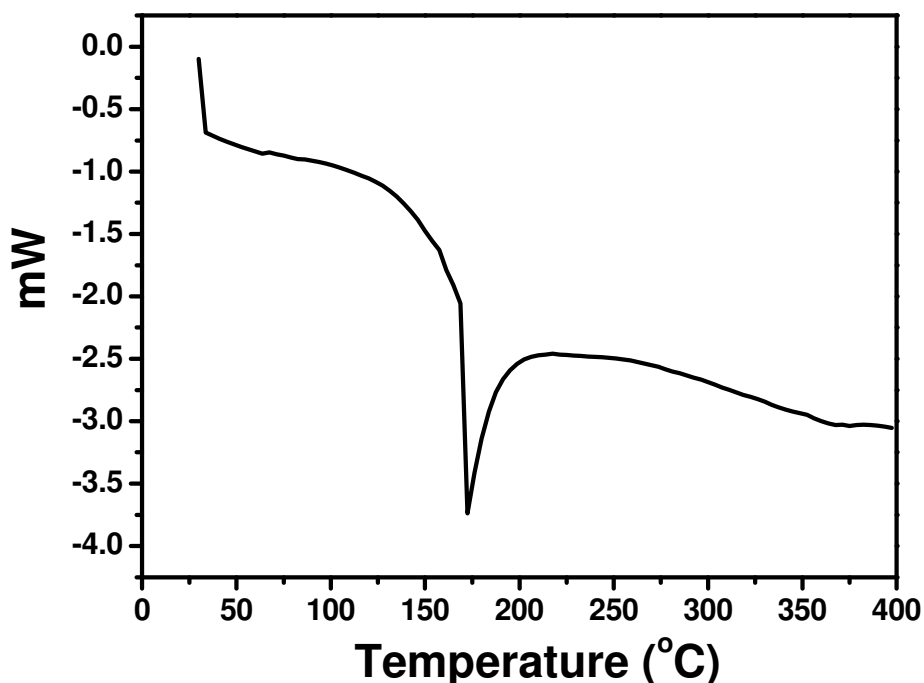


Figure 7.7: DSC plot of the titanate KTiO₂(OH) which was oven dried at 120 °C.

7.3.3. CO oxidation

The catalytic activities of differently conditioned catalysts for CO oxidation are plotted in **Figs. 7.8** and **7.9**. Treating the two catalysts Au-TiO₂ (P25) and Au-KTiO₂(OH) under an oxidizing atmosphere, generally results in the former being much more active than the latter at the lower temperatures. However above 120 °C the Au-KTiO₂(OH) catalyst showed superior activity. The reductively conditioned Au-KTiO₂(OH) catalyst showed a higher activity than the Au-TiO₂ (P25) catalyst treated under the same reductive conditions. The treatment conditions applied ultimately affect the composition of any catalyst and in this case the contribution of ionic Au species may have played a significant role. The increased activity of the Au-KTiO₂(OH) catalyst that was treated in reducing atmosphere may be due to the

reduction of ionic Au species and similar results have been reported for Au-TiO₂ [30]. XPS and HRTEM work needs to be done to establish whether enhancement in activity of reduced samples is due to a particle size effect or chemical effects. However, in view of the similar particle size distributions obtained for both Au-TiO₂ and Au-KTiO₂(OH) it seems likely that chemical effects may well be largely responsible for the observed differences in activity. In general terms, it may be assumed that the KTiO₂(OH) is a more basic support than TiO₂ and this factor also has to be considered. Basic oxides such as magnesia have been shown to be particularly active for supported gold [35-37], and more acidic oxides such as zeolites, for example, are in general less active [38]. Very little systematic work has however been reported to date and so the precise role of support acidity-basicity is not yet clear. The addition of Group 1 metal ions to TiO₂ has been observed to **increase or decrease** the activity of Au-TiO₂ catalysts subsequently prepared from the treated support, depending on the concentration level to which the Group 1 metal ions are added [39], an effect which appears to be related to the electronic environment of the gold in the solids [39]. A further factor may well be the detailed structure of the support at the nanoscale. Nanosized ceria, for example appears to lead to higher activity when used to support gold [40], than other forms of ceria. Nevertheless, the current work adequately demonstrates that titanate materials may well be useful in offering improved performance over titania in gold mediated catalysis, even if the precise reasons for the higher activity remain obscure. Further work will demonstrate whether the effect is a general one for gold-based catalysis.

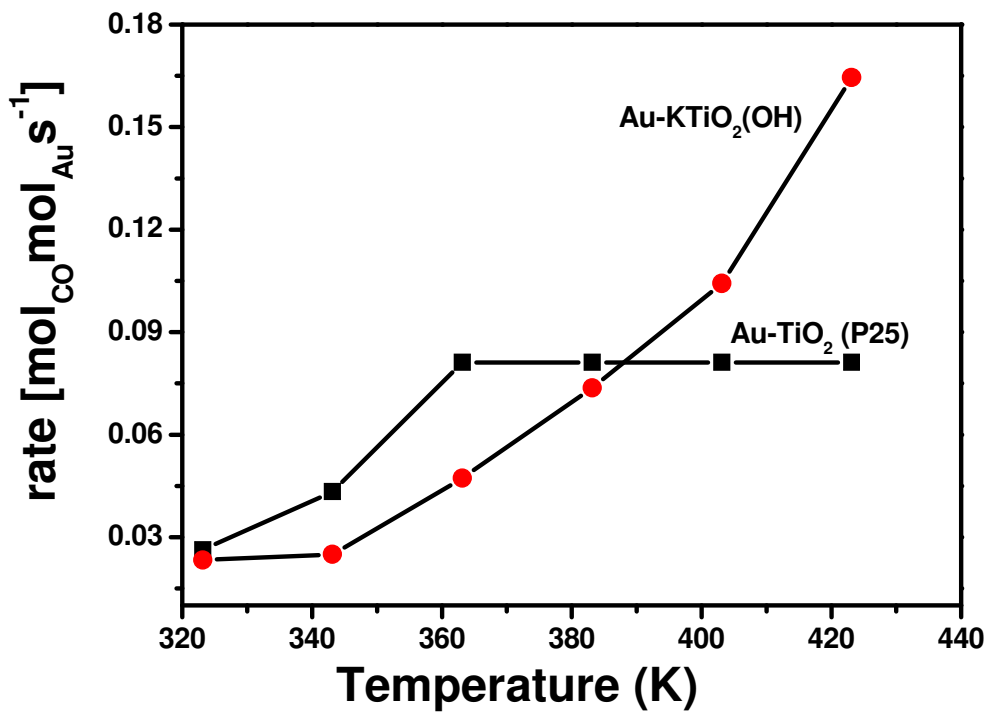


Figure 7.8: CO conversion over Au-TiO₂ (P25) and Au-KTiO₂(OH) catalysts that were calcined in 20 % O₂ (balance He) for 2 h prior to testing.

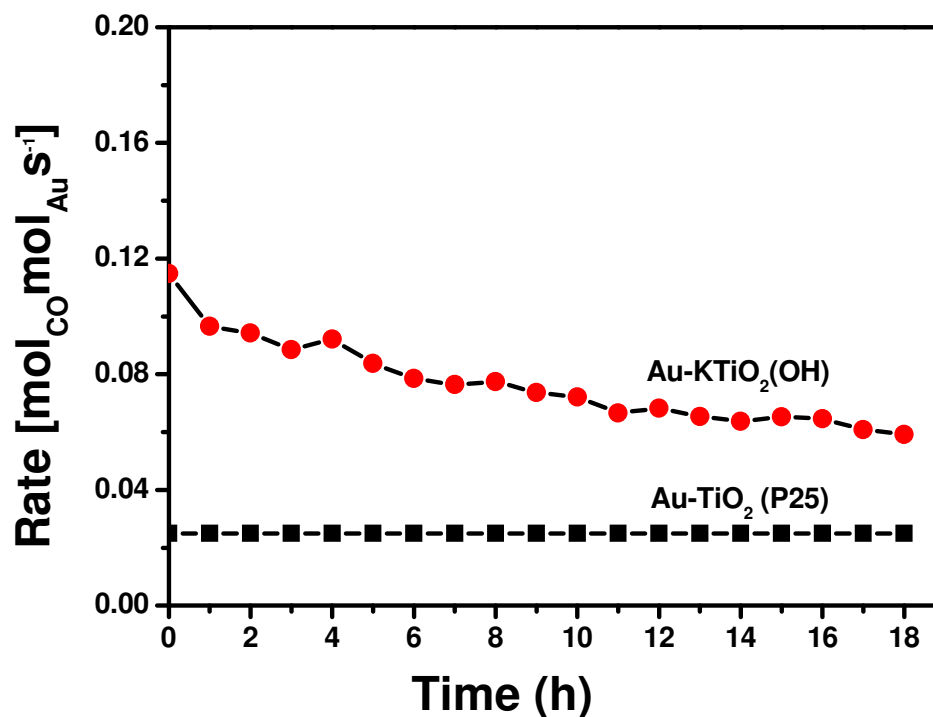


Figure 7.9: CO conversion over Au-TiO₂ (P25) and Au-KTiO₂(OH) catalysts that were pretreated in 5 % H₂ (balance He) for 2 h prior to testing. Reaction ran at 82 °C.

7.4. Conclusions

1. Au nanoparticles could be well dispersed on TiO₂ derived nanotubular support.
2. Au particle size and a possible existence of strong interactions between Au particles and the tubular support could be responsible for the high activity and stability for CO oxidation.

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8

A study of the anatase-rutile phase transition: the effect of Li ions

8.1. Introduction

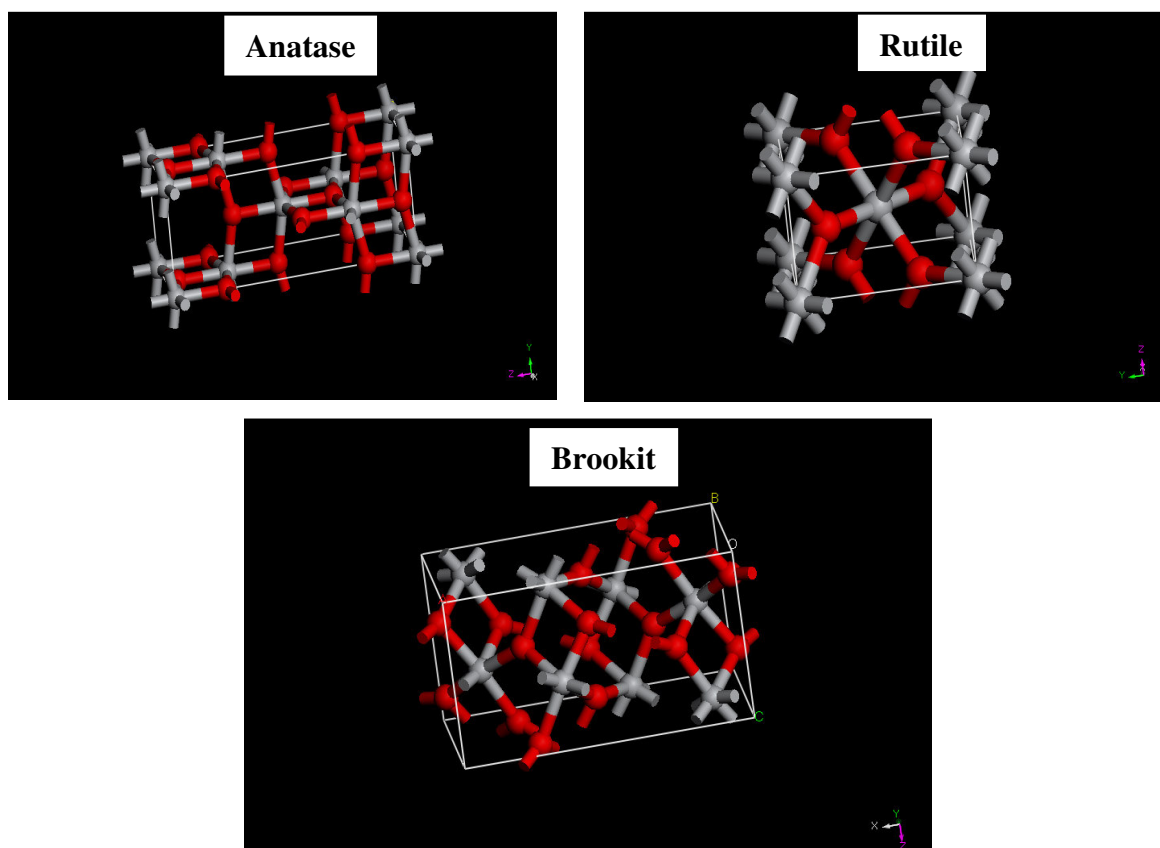
Titania is a very useful material which provides for a diversity of applications especially in photocatalysis and as a catalyst support [1]. In recent times the use of titania has been extended to medical applications such as use in an artificial heart valve and in dental implants [2,3].

A growing interest in the development of well-structured, porous, high surface area and complex forms of titania based materials has also led to these uses of TiO_2 in novel applications [4]. Semi conducting oxide catalysts in their powder form have shown great potential for the detoxification of both air and water in heterogeneous photocatalytic processes and as such they have received much attention [5].

Titania is generally known to exist in three naturally occurring polymorphs, namely: rutile, anatase and brookite. Rutile is deemed the most stable form of TiO_2 at ambient conditions [6]. The polymorphs or the nanocrystalline materials have different properties and applications. The nanocrystalline materials, like regular titania, have potential application in the areas of photocatalysis [7].

8.1.1. Phase transformation

When the anatase phase of TiO_2 is heated to high temperatures it normally becomes coarse and subsequently transforms into the rutile phase [8]. Zhang and Banfield have demonstrated that the phase transformation is reconstructive and that the only requirement for this to occur is the repositioning of Ti cations and a change in the oxygen arrangement. Both anatase and rutile are constructed from octahedrally coordinated Ti atoms (**Fig. 8.1**) [8].



Keys: Red = Oxygen; Grey = Titanium

Figure 8.1: Structural representations of anatase, rutile and brookite phases in a unit cell

Gouma and others demonstrated that upon heating anatase undergoes a phase transition to rutile with grain growth at temperatures between 400 and 1200 °C [9,10]. This is rather a gradual process that only reaches its completion at high temperatures.

Studies have also revealed that there are various factors affecting the transformation of anatase to rutile. These include temperature, pressure, particle size, additive/dopant, and the hydrothermal conditions employed [11]. Some of these studies were prompted by the desire to extend the photoresponse of TiO₂ and to improve its photoactivity by modifying its surface properties, composition, etc. [12,13].

In 2001 Zhang and co-workers reported for the first time on the structural phase transformations and temperature dependent changes of the particle sizes of iron-doped TiO₂ [14]. The conversion of pure TiO₂ from the amorphous state to anatase occurred at a lower temperature than for iron doped TiO₂. It was also shown that for titanium isopropoxide the transition from anatase to rutile takes place at lower temperatures (500 °C) than that of iron-doped TiO₂ (600 °C).

Talavera and co-workers demonstrated that the anatase-rutile phase transition depends strongly on the kind of cation (La, Zn, Al, K, Na, Ca, Ba, and Co) used to dope the titania material prepared by the sol-gel method. When different metal ions were used the anatase-to rutile phase transition occurred at different temperatures. Essentially the dopants create an oxygen deficiency in the crystal structure of titania which then resulted in some extra space being made available which assisted the promotion of the transition from anatase to rutile. The cations and the anions in titania are both reported to need some room to move to commence the phase transition [15]. The structure becomes contracted at the end of this process producing the rutile phase. In this regard the oxygen deficiency is reported to facilitate the anatase-rutile phase transition [16,17].

The literature shows that a dopant ion can be introduced into a matrix interstitially or substitutionally. The process depends on the ionic radius of the dopant compared with the size of the elements that form the network. The substitutionally doped ions in the network produce an oxygen deficiency in the crystal [18].

In their work, Talavera and co-workers investigated the correlation between the anatase-rutile phase transition temperature and the radius of the cations and their electric charge.

Fundamentally important is the charge of the ions and their role in the modification of the transition temperatures. This is so because it creates a deformation of the structure due to the electric forces between the dopants and the ions in the surroundings. In essence the charge exhibits a similar role to that of the ion size [18].

Europium ions were also used as dopants in a nanocrystalline titania material prepared by a special sol-gel method. The addition of europium as a dopant dramatically increased the anatase-rutile phase transition temperature. The increase is, however, not proportional to the amount of Eu ions, in that the highest increase was observed for 1 at % Eu doped samples. These samples retained the anatase phase (100 %) after calcination at 900 °C for 1 h [19].

Moreover, investigations have been carried out in an attempt to show that the titania materials that are synthesised by the sol-gel method are always amorphous in nature. The heat treatment of these amorphous materials converts them to a crystalline anatase structure [20]. The introduction of dimethylformamide (dmf) or dimethylsuloxide (dmso) solutions in the sol-gel process results in the production of crystalline material (anatase phase) regardless of heat treatment or any further hydrothermal treatment [21,22]. de Farias demonstrated that titania material synthesized in water is amorphous whereas the material synthesised in dmf or dmso is crystalline [23,24].

Ohno and his co-workers explored a different avenue for the transformation of anatase phase to rutile phase. They achieved the isolation of rutile phase by treating the P25 powder with 10 % HF solutions for 24 hours in ambient temperature. The disappearance of anatase particles as a result of acid treatment (HF solution) does not only indicate the phase transformation but shows that the rutile phase does not exist as an overlayer on the surface of anatase particles. It rather implies that both anatase and rutile phases exist separately in the P25 Degussa powder [25].

In 1993 Depero and co-workers studied the influence of laser-induced synthesis and the addition of a dopant to the anatase-rutile transformation. Pure samples of anatase were synthesized using laser-induced pyrolysis of titanium alkoxides. Using conventional wet impregnation methods, vanadium was loaded into the material. This resulted in the phase transition temperature for the anatase-rutile transformation occurring between 500 and 550 °C. The XRD patterns revealed that the rutile peaks are sharper than anatase peaks. It was evident that the presence of the dopant (vanadium ion) enhanced the phase transition temperature allowing crystallite growth of rutile phase at the expense of smaller and distorted anatase crystallites [26].

In this project we report on the addition of lithium ions to TiO_2 to influence the anatase-rutile phase transition temperature. The lithium metal ion was chosen because of its small ionic radius and to allow comparison of the effect of this small radius dopant (Li^+) with bigger radius dopants of the same group. The correlation between the dopant size and the anatase-rutile phase transition and the use of Li/TiO_2 as a catalyst will also be described.

8.1.2. Nanocrystalline titania

Among the three polymorphs of titania (anatase, rutile and brookite phases), anatase is known to have a higher photoactivity than both rutile and brookite [27,28]. It is

therefore advantageous to produce the anatase powder with a high degree of crystallinity and high surface area (or small grain size) to enhance the photocatalytic activity [29]. There are various methods available for the production of small TiO_2 particles but the sol-gel method has been widely used since it is deemed relatively inexpensive. Unfortunately, the sol-gel derived material is amorphous in nature and often requires a further treatment to induce crystallisation [30,31]. High calcination temperatures (higher than 350°C) are often necessary to expedite the transition from the amorphous material to the crystalline anatase phase but such high temperatures result in increased size of the nanoparticles and subsequently a decrease in the surface area [31-33].

8.2. Experimental procedures

8.2.1. Preparation of high surface area (HSA) TiO_2 [34-36]

P25 Degussa titania powder (~10 g) was placed in a 1L Teflon container together with 200 grams of sodium hydroxide pellets. Water (200 ml) was added to the mixture ($[\text{NaOH}] = 25 \text{ M}$). The mixture was heated for 20 hours at 120°C in an autoclave with constant stirring at the rate of 10 000 rpm. Unlike in the previous chapters (Chapters 4 and 7) the material was not aged. The solution was allowed to cool and then washed with deionised water. Subsequently the solid product was separated from the mixture by centrifugation. The washing was repeated until the conductivity of the solution was less than $100 \mu\text{S/cm}$. The solid was then suspended in 0.1M HNO_3 and stirred for 2 hours. The solution was washed with deionised water and then the solid was separated from the mixture by centrifugation. This procedure was repeated until the conductivity of the solution was less than $10 \mu\text{S/cm}$. The solid was dried in an oven at 120°C for 12 hours. The solid was sieved to a diameter of $1180 - 1700 \mu\text{m}$. It must be noted that the variation in the concentration of NaOH, using 25 M solution instead of 10 M solution reported in the literature [34-

36], in this study, resulted in the synthesis of nanosized TiO_2 that did not have a tubular structure.

The material was then characterised by powder XRD, BET analysis and Raman spectroscopy.

8.2.2. Preparation of low surface area (LSA) and the 'as prepared' TiO_2

P25 Degussa TiO_2 containing 80% of anatase and 20% of rutile was heated at 800 °C for 5 hours. This led to a 100 % yield of rutile phase. Although the P25 Degussa TiO_2 material used as a precursor to prepare low surface area TiO_2 was brittle the LSA TiO_2 was found to be hard due to grain growth and showed a higher crushing strength.

The 'as prepared TiO_2 was prepared by mixing TiO_2 (P25 Degussa) powder with water and then the mixture was compressed into a moist paste. This material was then dried in an oven at 120°C for 48 hours and after cooling it was crushed to give lumps of the material of desired size (1180 – 1700 μm in diameter).

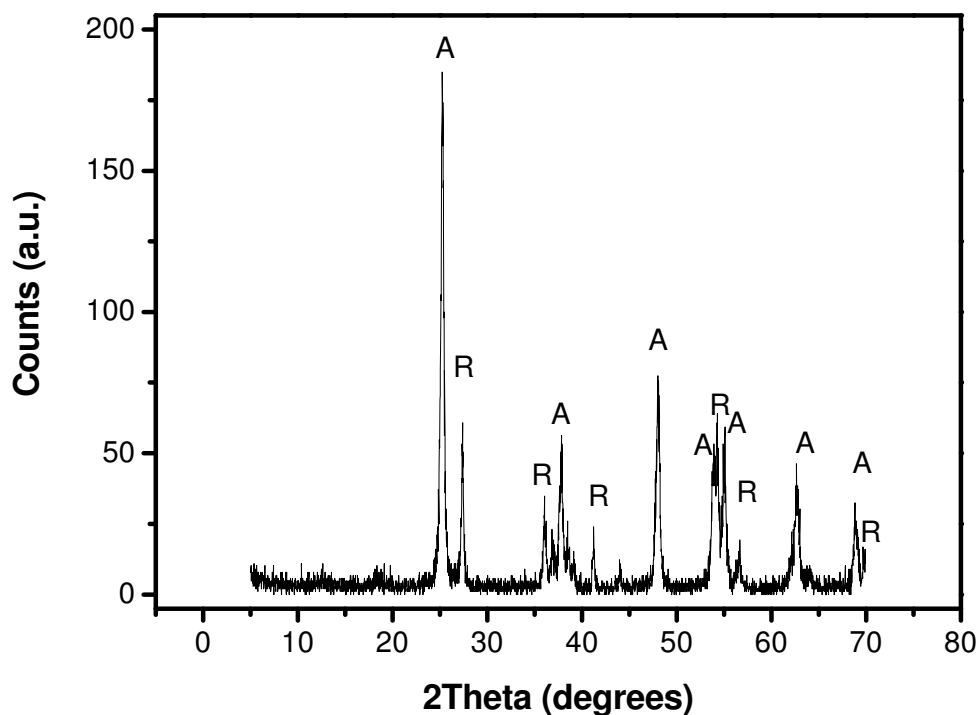
8.2.3. The addition of alkali metals (Li, Na, K, Cs) to TiO_2 based materials

The addition of alkali metals was achieved by an impregnation method where an appropriate amount of metal salt (nitrate source) was dissolved in 200 ml of water and then the solution was added to the TiO_2 support. The mixture was then dried at room temperature for 5 hours and then placed in an oven at 120°C for 5 hours. The catalyst was then calcined at 500 °C for 5 hours unless specified otherwise. The nitrate precursor was used for all catalysts to ensure a feasible comparison. The alkali metal content and the calcination temperature for various catalysts was the same. The metal ion to TiO_2 molar ratio of 1:15 was employed for all the catalysts unless specified otherwise.

8.3. Results and discussion

8.3.1. The P25 Degussa TiO₂ material

The XRD pattern of P25 Degussa TiO₂ is shown in **Fig. 8.2** and it clearly shows the presence of both anatase and rutile phases. Sharp peaks were observed for both anatase and rutile implying that the material (TiO₂) has a high crystallinity. The phase identification for anatase with XRD was based on (1001) (004) (200) (105) (211) (204) and (116) peaks at 25.34, 37.81, 48.10, 53.92, 55.14, 62.75 and 68.81 2-theta degrees respectively [37] whereas the rutile phase identification was based on (110) (101) (111) (211) (220) and (301) peaks at 27.45, 36.09, 41.23, 54.32, 56.64, and 69.01 2-theta degrees respectively [38]. It must be noted that the ratio of the two phases (anatase and rutile) gradually changes upon heating (from ~500 °C) until the material is completely converted into rutile at ~800 °C. This is in agreement with the data in the literature [39]. The presence of the brookite phase was not observed in this study and for this reason it is not considered in this analysis.



A = Anatase

R = Rutile

Figure 8.2: The powder XRD pattern of TiO₂ sintered at 500 °C.

8.3.2. The effect of sintering temperature on anatase-rutile transformation

Fig. 8.3a is an XRD pattern of TiO₂ material sintered at 800 °C for 5 hours. The figure illustrates the effect of sintering on the reaction at 800 °C. The anatase to rutile transition of TiO₂ in the absence of dopants or impurities only reaches its completion at ~800 °C (shown later).

Fig. 8.3b illustrates a dramatic increase in rutile peak height (rutile/anatase ratio) with an increase in sintering temperature calculated from the XRD pattern on addition of Li of Li/TiO₂ (1:1 mol/mol). The increase is accompanied by a slight

sharpening of the peaks. It is interesting to note that after sintering at 500 °C both anatase and rutile peaks became narrower and sharper, which suggests crystal growth of both phases. It has been shown before that the anatase to rutile transition largely depends on the anatase grain size [40,41]. This arises because material with smaller grains tends to have a higher structural energy due to the increase of surface free energy which reduces the energy required to reach the activated state. Banfield and co-workers have reported that in order for anatase to transform into rutile it must first attain a critical size in the range of 10 to 20 nm [11]. It was found that the anatase to rutile transformation is an irreversible process and that in the presence of Li the starting temperature of the anatase to rutile transformation is about 400 °C.

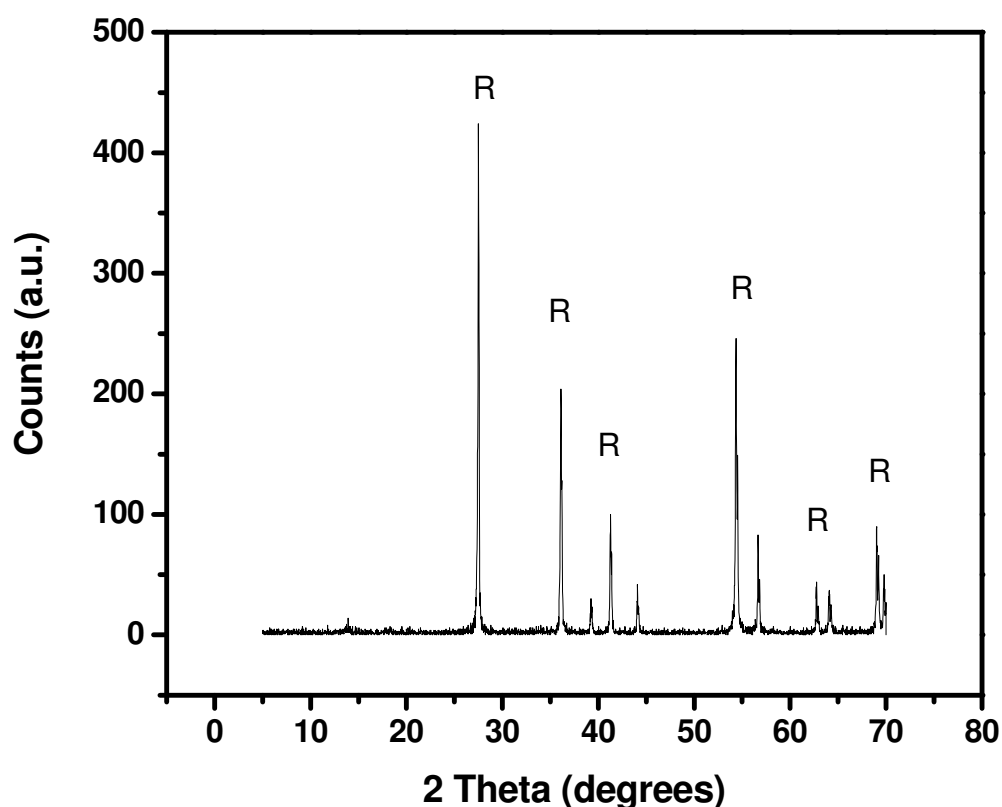


Figure 8.3a: The XRD pattern of TiO₂ sintered at 800 °C for 5h.

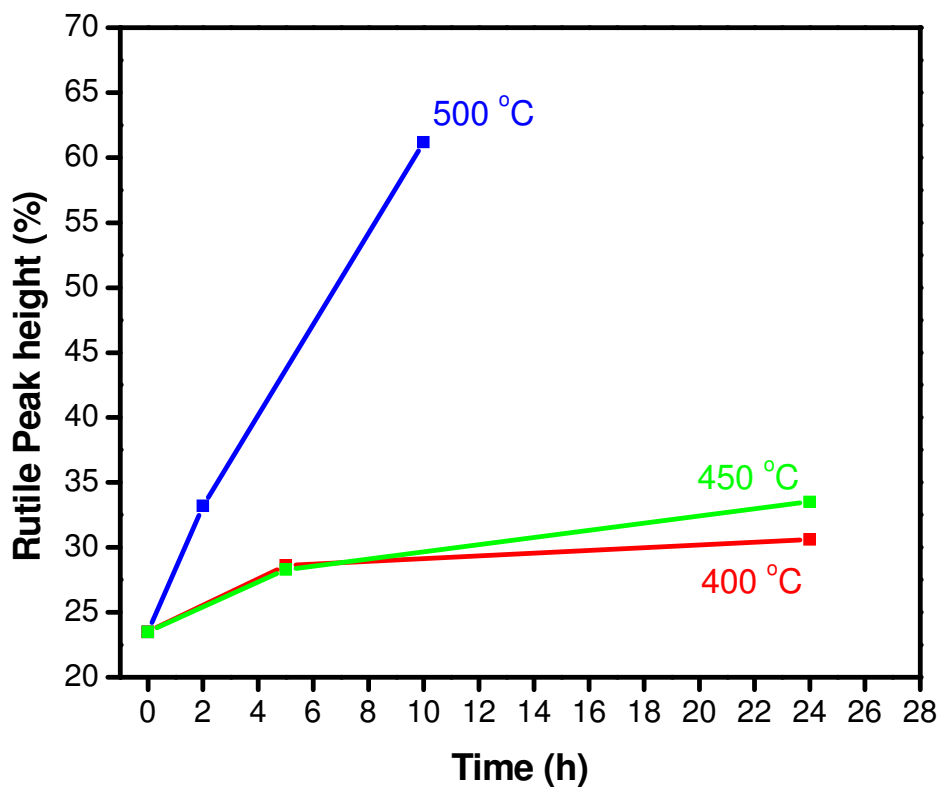


Figure 8.3b: The influence of sintering temperature on the enhancement of the rutile phase in Li/TiO₂ (1:1 mol/mol). The y-axis indicates the rutile/anatase phase ratio.

8.3.3. The effect of lithium addition to TiO₂

The XRD patterns of TiO₂ and Li/TiO₂ (1:15 mol/mol) are shown in **Fig. 8.4**. The XRD pattern of TiO₂ reveals that the amount of rutile phase is in excess of ~20 %. Moreover, the XRD pattern of Li/TiO₂ clearly shows an increase in the amount of rutile phase (~50 %). This suggests that the addition of lithium to TiO₂ catalyses the anatase to rutile phase transformation. Both TiO₂ and Li/TiO₂ materials in **Fig. 8.4**

were sintered at 500 °C. This effect is believed to be due to the substitution of titanium ions by lithium ions within the structural framework [42].

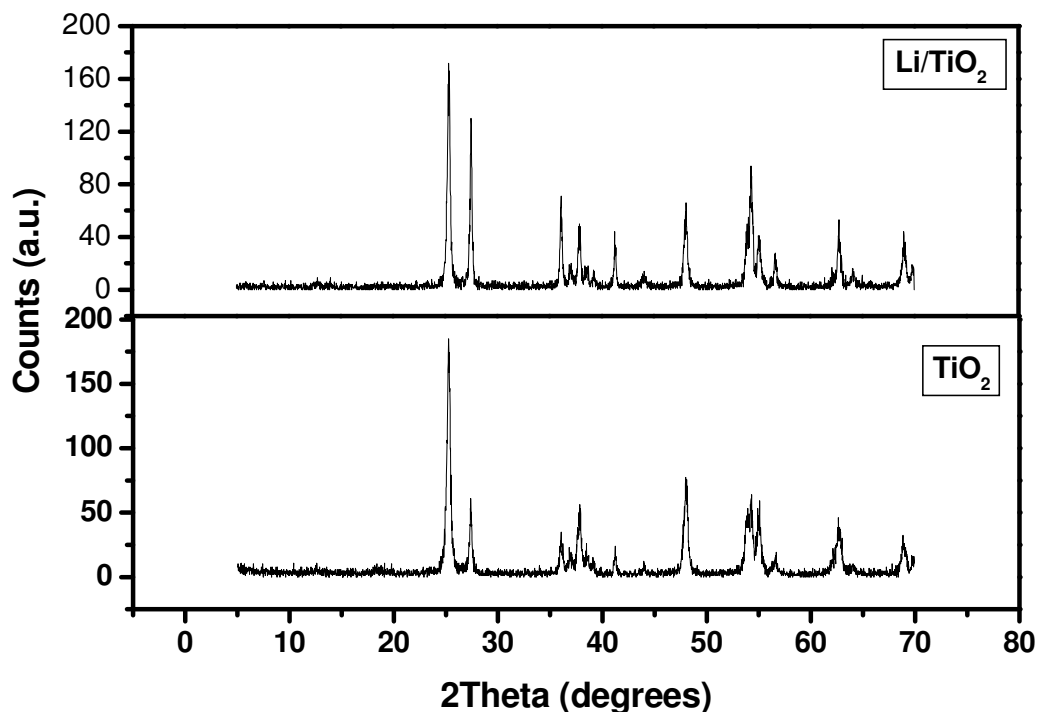


Figure 8.4: The powder XRD patterns of TiO_2 and Li/TiO_2 (1:15 mol/mol) sintered at 500 °C/5h.

8.3.4. The effect of various alkali metal ions

The influence of various alkali metal ions as dopants on the anatase to rutile transformation is illustrated in **Fig. 8.5**. It can be seen that when Na, K and Cs metal ions are added to TiO_2 (1:15 mol/mol, metal ion/ TiO_2) the major phase present is still anatase. Unlike the Na, K and Cs metal ions the Li metal ion, as a dopant in the TiO_2 system, has a more profound effect on both the structure of anatase and on the anatase-rutile transformation as shown in **Fig. 8.5**. The addition of Li to TiO_2 followed by sintering at 500 °C led to the rutile percentage yield of ~50 %.

Compared to the rest of alkali metal ions Li metal ion promotes the anatase to rutile transformation more completely at 1:15 mol/mol (metal ion:TiO₂). It is noteworthy that the XRD pattern of Cs/TiO₂ revealed the presence of an additional peak at the 2 theta value of ~28 ° which could not be ascribed to either the anatase or rutile phase. The peak was found to correspond to that of a cesium titanate structure, Cs₂Ti₆O₁₃ using the Expert High Score 2002 software.

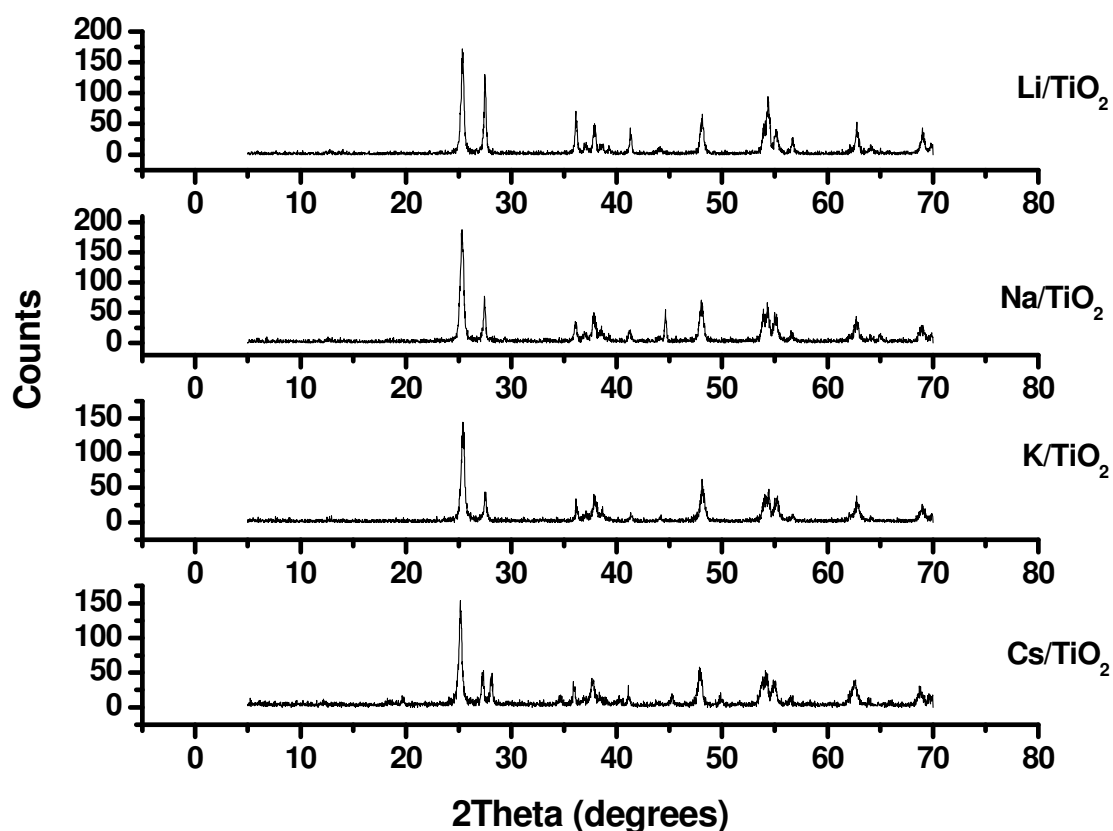


Figure 8.5: The XRD patterns showing various alkali metal ions on TiO₂ sintered at 500 °C /5h.

8.3.5. Raman spectroscopy

8.3.5.1. The influence of various alkali metal ions

The three most commonly known polymorphic forms of TiO_2 (viz. anatase, rutile and brookite) have been extensively studied using Raman analysis by numerous authors [43]. Investigations have been directed towards the assignment and analysis of Raman modes of individual polymorphs in TiO_2 . Other researchers have investigated the changes such as the positions, intensity, and width of peaks in the vibrational spectra as a function of thermal sintering of TiO_2 powders. These changes have been found to depend largely on the microstructure of the nanomaterials [44].

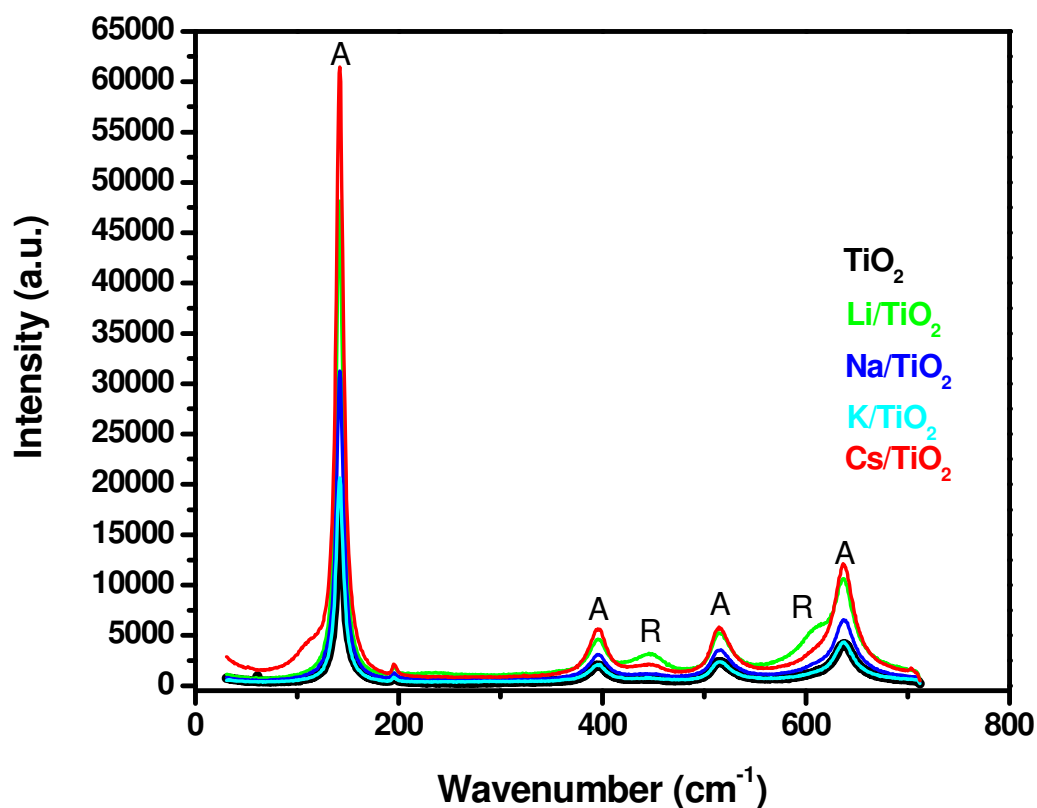
The details of the Raman band assignment for both anatase and rutile were obtained by comparing our data with corresponding Raman spectra in the literature. The typical bands for anatase were observed at 641, 518, 397 and 146 cm^{-1} while for rutile, typical Raman bands appear at 611, 447 and 248 cm^{-1} [45].

Fig. 8.6 illustrates the profile of Raman spectra for TiO_2 and alkali metals supported on TiO_2 (1:15 mol/mol) all sintered at 500°C . The TiO_2 and alkali metals supported on TiO_2 materials showed peaks characteristic of both anatase and rutile. It was observed that the peak intensity increased for Li/TiO_2 , Cs/TiO_2 and K/TiO_2 . The increase in peak intensity is indicative of improved crystallinity of the materials. Furthermore, both Li/TiO_2 and Cs/TiO_2 showed peak broadening and merging at around 641 cm^{-1} . The broadening was more pronounced for Li/TiO_2 . The broadening was a result of an increased amount of rutile phase. For instance, the weak band characteristic of rutile at $\sim 611\text{ cm}^{-1}$ essentially merged with the anatase band at 641. This effect is associated with grain growth.

Another band characteristic of rutile is observed at 447 cm^{-1} for Li/TiO_2 and Cs/TiO_2 . In both instances, the intensity of rutile peak is higher for Li/TiO_2 . This

clearly suggests that peaks characteristic of rutile structure arise as the lattice begins to transform from anatase to rutile.

The Raman data suggests that both Li and Cs metal ions have an accelerating effect on the anatase to rutile transformation. This effect was not detected by XRD analysis for Cs/TiO₂. Nevertheless, the effect is more pronounced for Li/TiO₂. It is clear that the anatase to rutile transformation is influenced by type and nature of the dopant.



Key: A = Anatase; R = Rutile

Figure 8.6: Raman spectra of various alkali metal ions on TiO₂ (1:15 mol/mol) sintered at 500 °C/5h.

8.3.5.2. The influence of sintering temperature monitored by Raman spectroscopy

Fig. 8.7 illustrates the changes in the profile of the Raman spectra at various sintering temperatures for Li/TiO₂ (1:15 mol/mol). The spectra revealed that the peak intensity characteristic of rutile increased while the peak position shifted as the sintering temperature was systematically increased from 200 to 600 °C. The spectra varied in a systematic fashion with grain size indicating peak broadening and merging with temperature. The peak shifts to longer wavelengths in the nanophase are ascribed to intergrain defects due to oxygen deficiency resulting from an average nonstoichiometry [46]. It is interesting to notice that the anatase rutile transition is completed by 600 °C with almost no anatase peaks visible as shown in **Fig. 8.7**. This clearly shows that the presence of Li has accelerated the anatase to rutile transition.

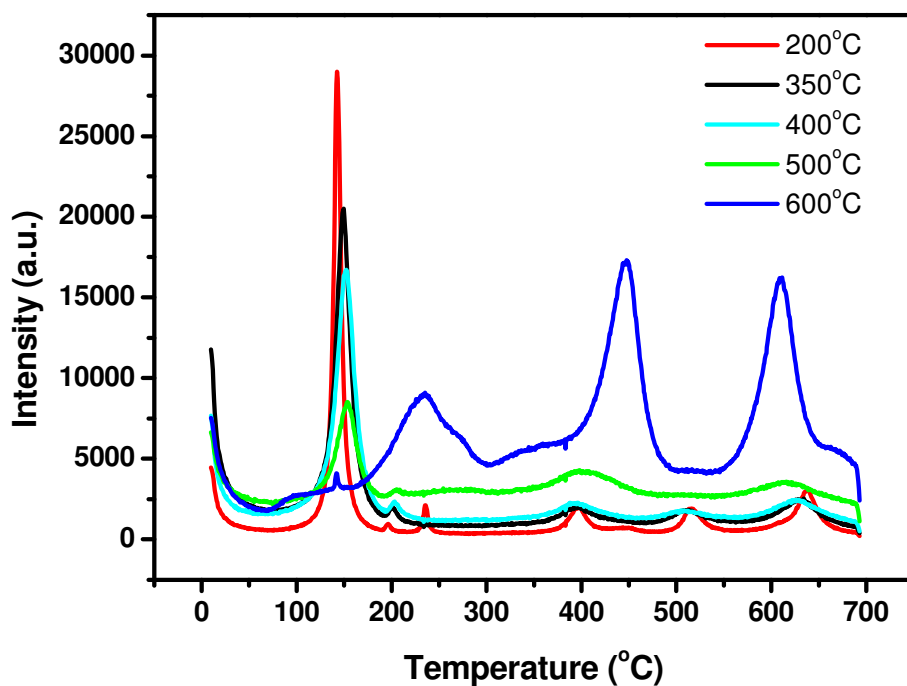


Figure 8.7: Raman spectra of Li/TiO₂ (1:15 mol/mol) sintered at various temperatures.

8.3.6. The influence of Li concentration

Fig. 8.8 shows the XRD patterns at various Li concentrations in the Li/TiO_2 system. It can be seen that the anatase to rutile phase transformation is influenced by the concentration of the dopant (Li). The XRD pattern of Li/TiO_2 (1:15 mol/mol) suggests that the equilibrium of the phase transformation may be controlled by the concentration of the dopant. The crystallographic data clearly indicate that the amount of rutile increases monotonically with the concentration of a dopant following sintering of material at 500 °C. The amount of rutile increased from 20 to ~50 % for Li/TiO_2 (1:15 mol/mol). A further increase in Li concentration, in Li/TiO_2 (1:1 mol/mol), resulted in an increased yield of rutile to ~70 % and this is accompanied by the formation of a new phase as shown by the XRD pattern (at 2-theta values of ~18, 38, etc.). When more moles of Li were added to TiO_2 , in Li/TiO_2 (8:1 mol/mol), both the anatase and rutile peaks had almost disappeared completely as the peaks of the new phase increased. The new phase was indexed to a hexagonal LiTiO_2 phase (JCPDS-40-1053). The hexagonal LiTiO_2 phase has been observed by XRD and calculated by first principle procedures [47]. With an increase in Li content the LiTiO_2 phase became more obvious as illustrated by the peak intensity of Li(8:1)TiO_2 in **Fig. 8.8**. The peaks of LiTiO_2 phase are marked as **a**.

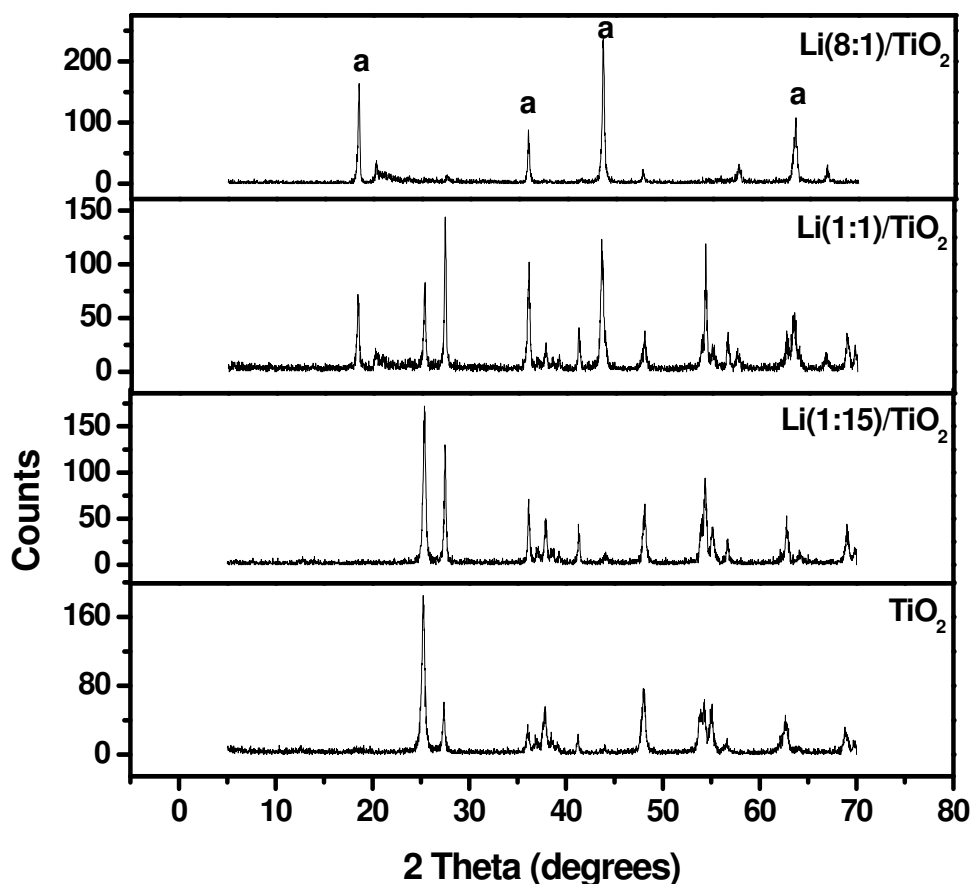


Figure 8.8: XRD patterns of various Li concentration (in mol/mol ratio) in Li/TiO_2 sintered at $500^\circ\text{C}/5\text{h}$ ($a = \text{LiTiO}_2$).

8.3.7. The surface analysis

It can be observed that the addition of the alkali metal supported on TiO_2 material resulted in a decrease in surface area which became more pronounced with increasing counter ion size (**Table 8.1**). A slight decrease in pore diameter following a decrease in surface area was observed. The decrease in pore diameter arises from a non-filling pore blockage upon the addition of counter ions to TiO_2 and this

phenomenon is common when the incipient wetness procedure is employed. Although the surface area decreased with the addition of counter ions the decrease was more pronounced in Li/TiO₂ while that of Cs/TiO₂ was also unexpectedly small. This effect is attributed to particle growth expedited by the anatase to rutile transformation.

Table 8.1: Physical properties of TiO₂ and alkali metals supported on TiO₂.

Catalyst	BET Surface Area (m ² /g)	Pore size (nm)
TiO ₂	49.5	6.0
Li(1:15mol)/TiO ₂	16.7	4.2
Na(1:15mol)/TiO ₂	32.6	4.5
K(1:15mol)/TiO ₂	38.0	5.1
Cs(1:15mol)/TiO ₂	33.1	4.5
TiO ₂ (rutile)	1.5	7.3

8.3.8. Nanocrystalline TiO₂

8.3.8.1. The effect of washing in the preparation of nanocrystalline TiO₂ (HSA TiO₂)

Fig. 8.9 shows the conductivity of the supernatant in the synthesis of nanosized TiO₂ (HSA TiO₂) as a function of time. Details of the procedure are described in the experimental section. It was observed that once TiO₂ has been treated with a concentrated solution of NaOH in an autoclave the removal of base (NaOH) can be a mammoth task and lengthy process which could last from several days to months. Throughout the washing process the material's conductivity was monitored. It was found that excess NaOH is lost rapidly during the first 150 minutes. This is followed

by a gradual loss of Na ions up to the 500th minute. It must be noted that the time spent idling between days serves to age the material and results in Na ions binding strongly to the TiO₂ material. Further removal of Na ions was achieved by treatment of TiO₂ material with 0.1 M HNO₃ solution followed by further treatment with deionised water. It was found that treatment with HNO₃ resulted in an increase in conductivity to 18 mS/cm due to the ionisation of an acid at the 526th minute. The washing was continued until the conductivity of the supernatant could not be reduced further. The conductivity was found to be constant at 0.7 mS/cm after the 800th minute. The EDX confirmed that the Na ions could not be completely removed from the material suggesting that Na ions may have been incorporated into the lattice of TiO₂.

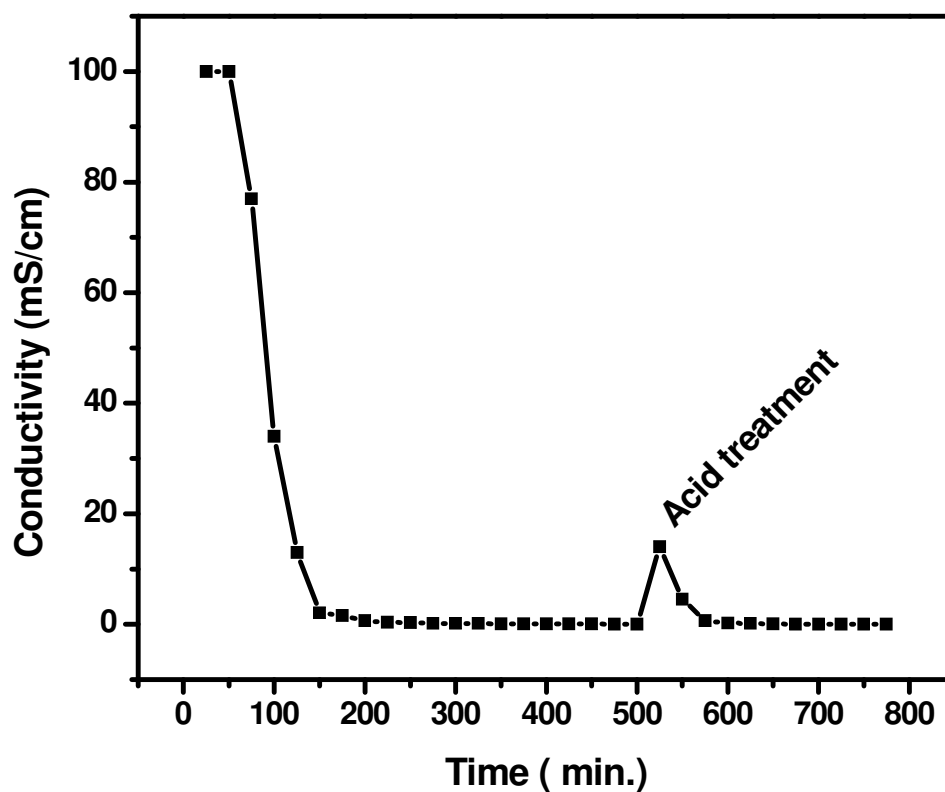


Figure 8.9: The conductivity measurement of the supernatant in the synthesis of nanosized TiO_2 as a function of time.

8.3.8.2. The XRD analysis of nanocrystalline TiO_2 (HSA TiO_2)

Fig. 8.10 shows the XRD patterns of HSA TiO_2 sintered at various temperatures. The XRD pattern of the non-sintered material shows that the material contains neither anatase nor rutile phase. The presence of ill-defined peaks is characteristic of amorphous material. After sintering at higher temperature broad anatase peaks appeared. As the sintering temperature increased the intensity of the anatase peaks became stronger and well resolved, indicating that larger size particles are formed.

At the high temperature of 400 °C only anatase peaks appeared clearly with relatively high intensity, showing that the amorphous to anatase transformation was almost complete. There have been a number of reports in the literature suggesting that the synthesis of nanosized TiO₂ results in the formation of anatase and/or brookite, which on coarsening, undergoes transformation to rutile after a certain particle size is reached [48]. It was observed that the anatase was composed of very fine particles with a white colour. Upon sintering the particles became hard and showed a yellow colour possibly due to an oxygen deficiency. The colour was restored during the cooling in air. It must be noted that rutile is the thermodynamically stable phase of TiO₂ and that once it is formed it cannot be easily transformed to another polymorphic form.

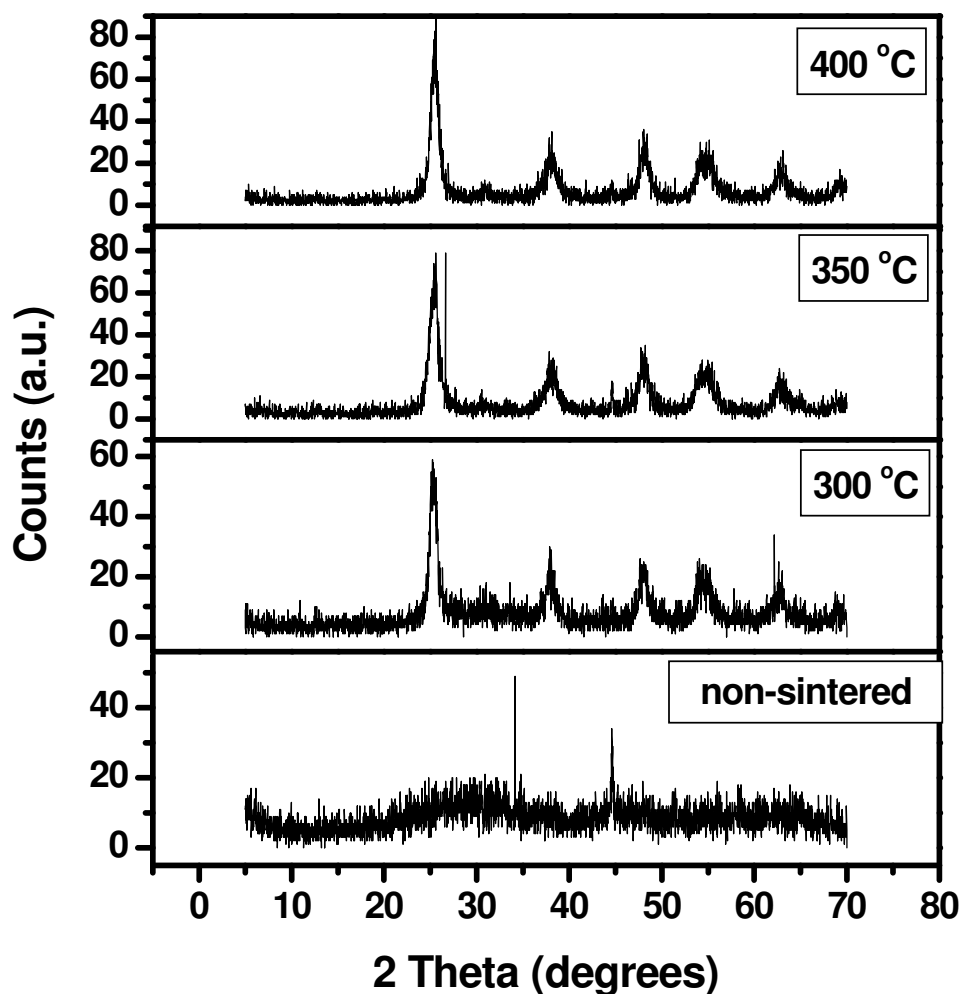


Figure 8.10: XRD patterns of nonsintered HSA TiO₂ and HSA TiO₂ sintered at various temperatures for 5 hours.

Fig. 8.11 shows that after sintering at 800 °C for 5 hours HSA TiO₂ still contained anatase phase. This is because at this temperature the transformation from anatase to rutile was not as complete as that of TiO₂ (P25 Degussa). The amount of rutile formed was ~80 %. This clearly shows that the nature of the nanosized TiO₂ material produces a significant effect on the stability of the anatase. Finally when the

sintering temperature was increased to ~ 1000 °C the anatase peaks disappeared, indicating the end of phase transformation from anatase to rutile in the nanophase of TiO_2 (**Fig. 8.11**, inset). The occurrence of the anatase to rutile transformation at a higher temperature than that of the bulk value (~ 800 °C) is ascribed to the suppression of crystal growth due to surface diffusion. The EDX showed that a small amount of Na ions left in the material after washing and it might have influenced the stability of the material. It must be noted that the presence of Na ions in Na/ TiO_2 did not yield the same results. This is because the Na ions in HSA TiO_2 may be part of the framework. Rodríguez-Talavera and co-workers made similar observation on the effect of Na ions on the stability of the anatase by way of suppressing the anatase to rutile transformation [49]. Considering that nanocrystalline material containing Na ions significantly increased the phase transformation temperature it should be reasonable to infer that the presence of Na ions suppresses the nucleation process.

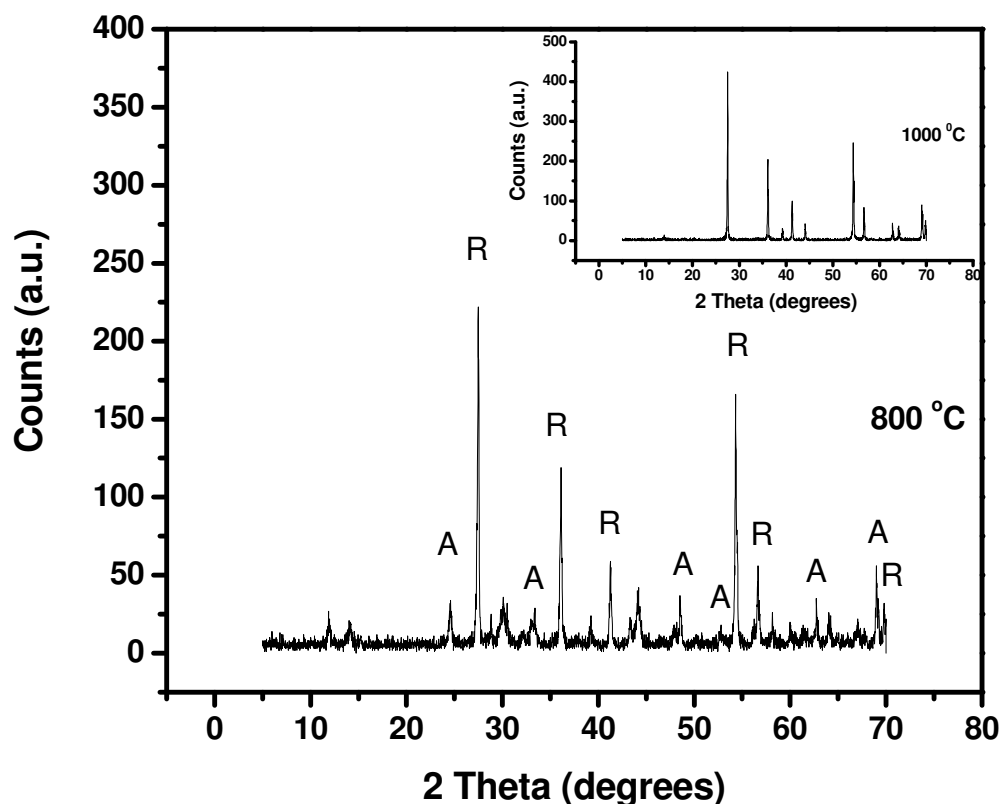


Figure 8.11: The XRD patterns of HSA TiO₂ sintered at 800 and 1000 °C (inset) for 5 h.

8.3.8.3. The physical properties of the nanocrystalline TiO₂ (HSA TiO₂)

Table 8.2 shows the surface properties of TiO₂ and HSA TiO₂.

The thermal hydrolysis synthesized nanocrystalline material (HSA TiO₂) has a larger specific surface area (417 m²/g) as compared to that of TiO₂ (50 m²/g). The large surface area of the material is due to the treatment with NaOH in an autoclave which resulted in the formation of nanosized crystals. The large surface area of HSA TiO₂ material is a result of the small crystal sizes. This is also confirmed by the broad XRD peaks of the nonsintered HSA TiO₂ material in **Fig. 8.10**. The material displays

a lack of stability as shown by a sharp decrease in surface area with an increase in sintering temperature. A dramatic decrease in surface area from 417 to 7 m²/g as the temperature was systematically increased to 800 °C is indicative of crystal growth with sintering temperature. It can be observed that the grain size increases with an increase in sintering temperature mainly because the crystals coalesce and grow. It must be noted that anatase generally has a much higher surface area than rutile although a high surface area rutile can be synthesized according to the literature [50,51].

Table 8.2: The physical properties of the nanocrystalline materials

Catalyst	BET Surface Area (m ² /g)	Pore size (nm)
TiO ₂	49.5	6.0
HSA TiO ₂ nonsintered	417	2.6
HSA TiO ₂ sintered at 350°C	116	3.9
HSA TiO ₂ sintered at 800°C	7.1	3.8

8.3.9. Mechanism: anatase to rutile transformation

The anatase to rutile transformation described in this chapter is referred to as kinetic differentiation. In this mechanism the formation of individual polymorphs (i.e. anatase, rutile or brookite) is underpinned by the kinetic and thermodynamic factors that control the process. The mechanism is based on the fact that the difference in kinetics and thermodynamics is adequate to explain the formation of anatase and rutile under different conditions [52].

Many parameters are believed to influence the kinetics of both the transformation and growth processes. The parameters include particle size, nature and type of dopant, and synthetic route used. The thermodynamic stability of individual phases of TiO_2 plays a fundamental role in defining the kinetics of transformation [53,54].

It has been proposed elsewhere that anatase is typically the first product to form (i.e. kinetically favoured product). It is believed that anatase nanoparticles remain stable up to a certain size. Below this size limit, particle sizes increase via a process called Ostwald ripening [55]. In this process the new material is efficiently deposited around the entire particle in a typical solid state process. Nevertheless, when the critical size limit is reached, the anatase to rutile transformation begins and continues to propagate slowly with time.

8.4. Conclusions

From the investigation carried out and the results obtained numerous conclusions were drawn:

1. The addition of Li metal ion to the TiO_2 (P25 Degussa) resulted in the incorporation of Li into the TiO_2 lattice.
2. The addition of Li metal ion showed an accelerating effect on the anatase to rutile transformation. The addition of Li led to a significant decrease in the anatase to rutile transformation temperature.
3. The anatase to rutile transformation also showed a high degree of dependency on the concentration of Li metal ion. The extent of the transformation was found to be dependent on the concentration of Li while the transformation temperature decreased with an increase in the concentration of Li.
4. The increase in Li content resulted in the formation of a LiTiO_2 phase.

5. The anatase to rutile transformation depends largely on impurities, grain size and the synthesis of TiO_2 . It was also established that the nature of interaction between the impurity and TiO_2 material is crucial.
6. The synthesis of nanosized TiO_2 (HSA TiO_2) resulted in the formation of amorphous material, due to the small particle size, which then transformed to anatase and subsequently to rutile upon sintering. This led to an increase in transformation temperature due to a suppression in particle growth.
7. It was observed that the anatase material was rather fine whereas the rutile was made up of hard and crystalline particles.
8. The mechanism of the anatase to rutile transformation is temperature dependent.

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9

The esterification of aromatic compounds: the reaction of benzoic acid with propanol

9.1. Introduction

Esterification of acids is a widely used organic process in which an organic acid and an alcohol mix in the presence of an acid catalyst to give an ester and water. Conventionally, esterification reactions are industrially carried out in a homogeneous liquid phase. Moreover, a major setback is that the esterification processes are equilibrium limited. Hence, constant removal of products from the reactor system is a crucial step. In order to avoid low conversion that is limited by the reaction equilibrium, a catalytic reaction that involves the use of solid base catalysts can be employed [1]. The use of a fixed bed flow reactor is also advantageous.

Although various methods for the synthesis of aromatic esters have been developed there is still a need to develop environmentally friendly and economically viable routes. The use of solid catalysts is desirable from the environmental view of point especially in terms of corrosion and transportation. Furthermore, when solid catalysts are used catalyst reusability becomes practical [2].

Although solid acids such as zeolites, oxides, aluminophosphates, and sulphated oxides have been extensively studied as an alternative replacement for Lewis/Bronsted acid catalysts [3-8], solid base catalysts have shown better activity [9]. The advantages of using solid base catalysts, instead of solid acid catalysts, include higher yields at moderate temperatures and short reaction times [10].

Godye and co-workers have reported on the high yields obtained from the esterification of benzoic acid with various alcohols heated in the presence of microwaves [11,12]. Recently, Pipus reported on the use of microwaves in the presence of a homogeneous mineral acid catalyst (sulphuric acid) for the esterification of benzoic acid. The use of microwave heating in the esterification of benzoic acid is geared towards increasing reaction rate and obtaining higher conversions. The limitation with the use of microwave heating is the depth of penetration of microwaves in absorbing materials [13].

The most commonly used esterifying agents are alcohols. However, the major setback with the use of alcohols is the production of water as a by-product. Water is detrimental as it deactivates the catalysts. In order to obtain higher yields of the ester the removal of water during the reaction becomes imperative. In order to overcome this problem alternate esterifying agents such as dimethyl carbonate (DMC) have been used as replacement for alcohols [14]. DMC is a non-toxic building block which can be used as a substitute for toxic and corrosive reagents [15].

In this chapter the esterification of benzoic acid with propanol in the presence of solid base catalysts is investigated. Temperature-programmed desorption of CO₂ was used to characterise the basic strength distribution of the catalysts and to establish the relationship between the catalytic activity and basicity of the catalysts.

9.2. Experimental

9.2.1. Catalyst preparation and characterisation

In this chapter three different supports were prepared using P25 Degussa TiO_2 as a precursor, namely the 'as prepared' TiO_2 , TiO_2 (rutile) and high surface area (HSA) TiO_2 . The 'as prepared' TiO_2 support, containing both rutile and anatase, was prepared using the method described in Chapter 4. However, the variation in the concentration of NaOH in this study resulted in the synthesis of nanosized TiO_2 that did not have a tubular structure.

The rutile only support was prepared by calcining the precursor (P5 Degussa TiO_2) for 4 hours in air at 800 °C. At this temperature all the anatase was completely converted to a very crystalline rutile phase.

The high surface area (HSA) TiO_2 support was prepared by a hydrothermal treatment of TiO_2 with NaOH using a procedure similar to that described in Chapter 8 and previously reported by Kasuga and co-workers [16,17]. TiO_2 (10g, P25 Degussa) was mixed with 200 ml of 25 M NaOH aqueous solution in a 1 L Teflon lined vessel. The mixture was then placed in a stainless steel vessel and maintained at 120 °C for 20 hours. After the hydrothermal treatment step the precipitate was separated by centrifugation and washed with deionised water until the conductivity of the supernatant was below 100 $\mu\text{S}/\text{cm}$ and then washed with a 0.1 M HNO_3 . The precipitate was subsequently washed with more deionised water to remove the acid until the conductivity of the supernatant was below 10 $\mu\text{S}/\text{cm}$. The product was further dried in an oven at 120 for 12 hours and then calcined at 500 °C for 5 hours.

The group 1 (alkali metals) metal ion loading was achieved by a simple impregnation procedure using an appropriate amount of aqueous metal ion salt (nitrate) solutions as precursor. The loading of catalysts was kept at 1:15 mol/mol for all catalysts

unless otherwise specified. The experimental details were previously described in Chapter 4.

Catalyst characterisation was carried out using various techniques described in Chapter 4. The techniques include BET analysis, XRD, TGA, TPD and Raman.

9.2.2. The esterification of benzoic acid

The esterification of benzoic acid to give alkyl benzoate as ester product was used to test the different catalysts and their catalytic performance in terms of their bulk and surface properties. The reactions were carried out in the vapour phase in a fixed bed flow reactor in the presence of nitrogen gas. Prior to the reaction, catalysts were pretreated in a glass tube reactor at high temperature (500 °C) so as to activate the material. The solid catalysts were cooled to the reaction temperature. A reactant mixture (benzoic acid in propanol) with a specified molar ratio was fed, from the top, into the reactor at a fixed total flow rate by means of a Sage syringe pump, using a nitrogen flow. The effluent was collected into a collector and was periodically extracted and analysed by means of an FID-GC with a packed capillary column. A Teknokrona 30 m long x 0.53 mm capillary column was used in the temperature range of 40-220 °C (8 °C/min ramp). The reaction products were further identified and confirmed by GC-MS.

9.3. Results and discussion

9.3.1. BET analysis

Table 9.1 lists the BET surface area and average pore diameter of various TiO₂ materials and TiO₂ based catalysts used. It can be seen that the rutile only TiO₂ has a very small surface area due to particle agglomeration caused by high temperature heat treatment of the material. The hydrothermally treated TiO₂ material showed a

relatively large surface area ($417 \text{ m}^2/\text{g}$) which decreased by more than half the initial surface area after the addition of Cs and Li metal ions and calcination. This shows that the hydrothermally treated material is thermally unstable. This effect was observed in materials synthesized by a similar procedure in Chapter 5. The surface area of the 'as prepared' TiO_2 ($\text{TiO}_2\text{-D}$) material was found to be $50 \text{ m}^2/\text{g}$. Although the surface areas of alkali metal ions supported on $\text{TiO}_2\text{-D}$ were found to be smaller than that of $\text{TiO}_2\text{-D}$ the surface area increased with the increase in metal ion size (ionic radius). It is interesting to note that the surface area of Li/TiO_2 is significantly smaller than the rest and that Cs/TiO_2 has a slightly smaller surface area than expected. This is attributed to the fact that both Li and Cs metal ions were found to have an accelerating effect on the anatase to rutile transition as shown in **Fig. 8.6** in Chapter 8. However, Li metal ion has shown greater transition temperature depression strength when compared with Cs metal ion and hence a relatively smaller surface area. This means that the decrease in surface areas in both cases is not only because of pore filling but also because of increased agglomeration of TiO_2 particles due to both Li and Cs metal ions. The pore diameter are comparable except in the case of HSA TiO_2 where a small particle diameter of 2.6 nm was obtained and it increased to 3.9 and 4.2 nm after the addition of Cs and Li metal ions, respectively, followed by calcination.

Table 9.1: The properties of various forms of TiO₂ and group 1 metal ions supported on TiO₂ and TiO₂ derived supports

Catalyst	Designation	BET surface Area (m ² /g)	Pore diameter (nm)
TiO ₂ (Rutile)	TiO ₂ -R	1.47	7.3
TiO ₂ (P25 Degussa)	TiO ₂ -D	49.5	6.0
Li/TiO ₂	Li/TiO ₂	16.7	4.2
Na/TiO ₂	Na/TiO ₂	32.6	4.5
K/TiO ₂	K/TiO ₂	38.0	5.1
Cs/TiO ₂	Cs/TiO ₂	30.6	4.5
HSA TiO ₂	HSA TiO ₂	417.3	2.6
Cs/HSA TiO ₂	Cs/HSA TiO ₂	117.0	3.9
Li/HSA TiO ₂	Li/HSA TiO ₂	115.2	4.2

9.3.2. XRD and Raman analysis

The XRD results revealed that the presence of Li metal ion in TiO₂, as a dopant, has a more profound effect on the structure of TiO₂ and on the anatase to rutile transformation as illustrated in **Fig. 8.5** in Chapter 8. The presence of rutile was detected to be in higher concentration than that of anatase when Li was added to TiO₂ followed by sintering at 500 °C. The anatase to rutile transformation was almost complete at this temperature. The XRD pattern of Cs/TiO₂-D also showed some structural changes as a result of the addition of Cs metal ion. This is shown by the presence of an extra peak at 2 θ angle of 28 °. The peak is ascribed to Cs₂O.

The Raman analysis results showing the effect of the alkali metal ions on TiO₂ were shown in **Fig. 8.6** in Chapter 8. All samples have the same metal ion to TiO₂ mole

ratio of 1:15 and were all sintered at 500 °C. At this temperature the peaks for rutile were more pronounced in Li/TiO₂-D and Cs/TiO₂-D. The broad peaks are believed to be because of the mixed absorptions of intermediate structures as the anatase transforms to rutile as well as the formation of the LiTiO₂ phase and possibly the CsTiO₂ phase. The peaks for both Na/TiO₂-D and K/TiO₂-D are similar to those of the 'as prepared TiO₂ implying that the addition of Na metal ion has no structural and transformational effect on TiO₂. It must be noted that the addition of K metal ion to TiO₂ was found to increase the stability of the anatase phase thereby increasing the transformation temperature (Chapter 8).

9.3.3. TPD studies

The TPD profile of TiO₂ (without metal ions) did not show any desorption peak for CO₂. Na/TiO₂-D showed the presence of two overlapping peaks at 178 and 282 °C as illustrated by the CO₂-TPD in **Fig. 9.1**. The two peaks represent two sites of different basic strength. Both instances are ascribed to desorption of weakly bound CO₂. The TPD profile of K/TiO₂-D (**Fig. 9.1**) is similar to that of Na/TiO₂-D but revealed the presence of 3 adsorption peaks that also overlap (223, 311, and 412 °C). The two low temperature peaks are ascribed to desorption of weakly bound CO₂ whereas the peak at 412 shows desorption of moderately bound CO₂. This is indicative of the existence of both weak and moderate basic sites.

Figure 9.2 shows the TPD profiles of Li/TiO₂-D and Cs/TiO₂-D. The two catalysts primarily consist of strong basic sites. Li/TiO₂-D shows two small peaks at 182 and 400 °C which are attributed to weak and moderate basic sites. The high temperature peak at 589 °C is attributed to the strong basic sites. Cs/TiO₂-D showed the presence of a single peak at 671 °C rendering the strongest adsorption of CO₂. The TPD data suggest that the addition of alkali metals to TiO₂ generate basic sites with different strength. The data suggest that the base strength of the catalysts increases with the increase in atomic number except in the case of Li (i.e. Na<K<Li<Cs) probably because of its influence on the anatase-rutile transformation.

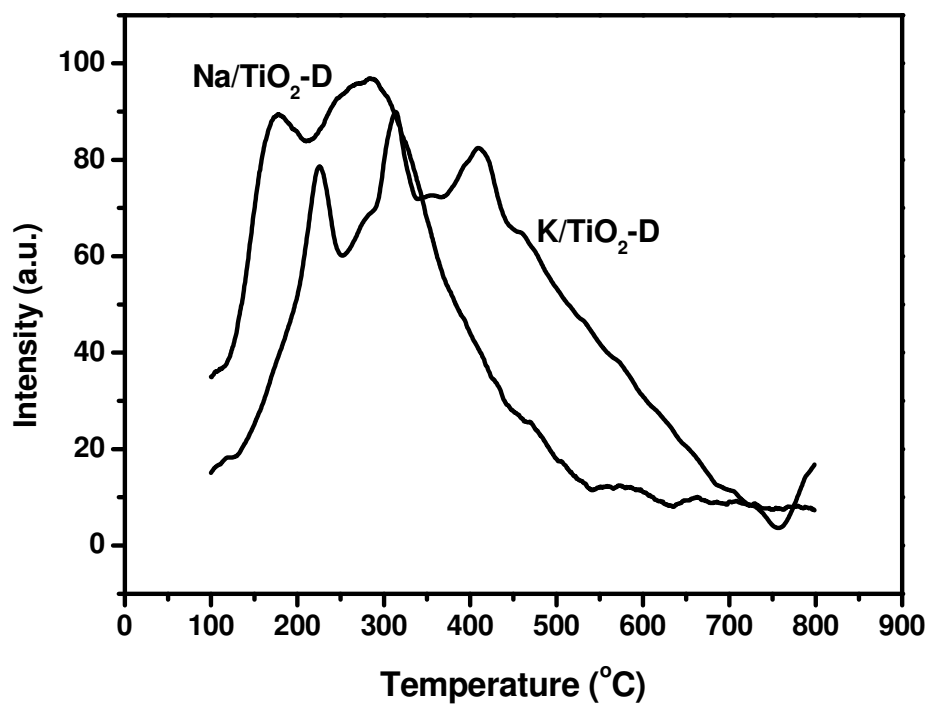


Figure 9.1: TPD profiles of Na/TiO₂-D and K/TiO₂-D

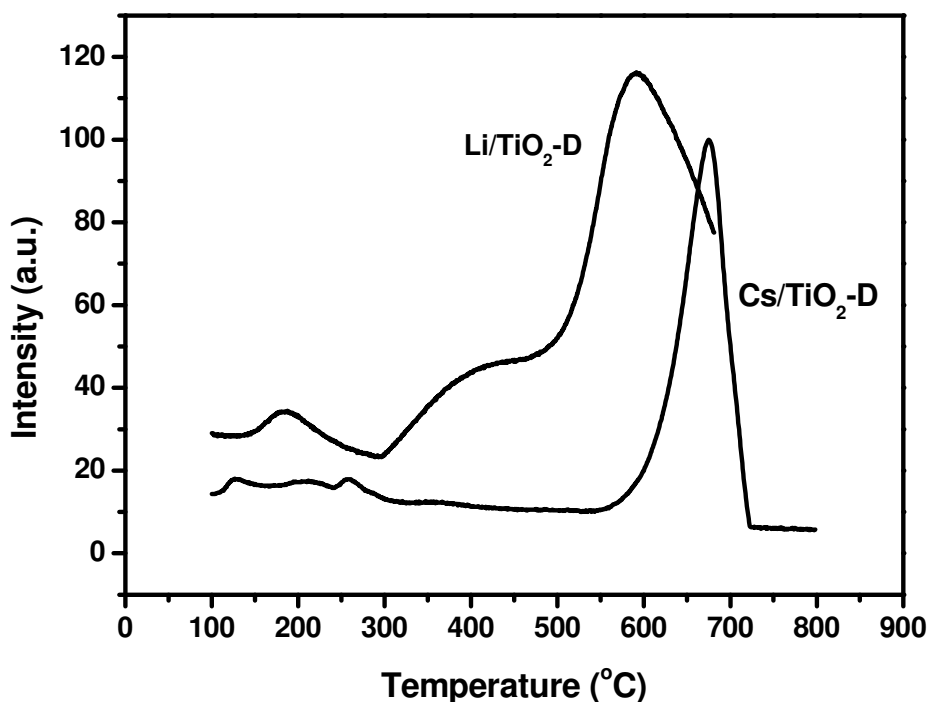
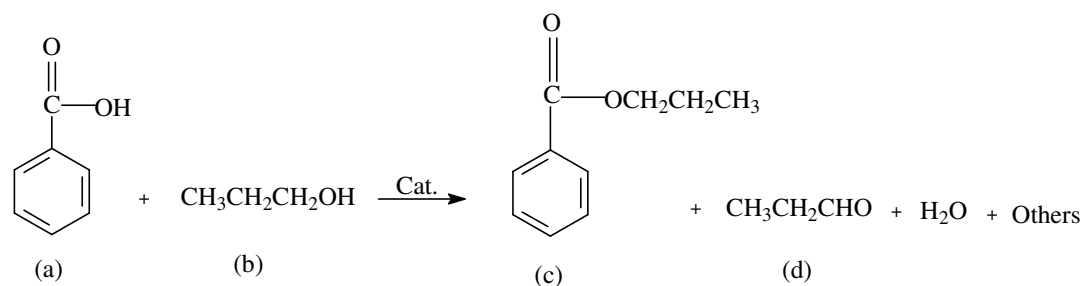


Figure 9.2: TPD profiles of Li/TiO₂-D and Cs/TiO₂-D

9.3.4. Esterification of benzoic acid

Esterification of benzoic acid (a) in propanol (b) may be a tedious process and tends to yield numerous by-products at the same time as shown in **Scheme 9.1**. The purpose of this study was to achieve a high yield of propylbenzoate (c) without producing significant amount of by-products such as propionaldehyde (d) and 2-methylpentanol. The aromatic ring in benzoic acid does not take part in the resonance stabilization of the carboxylate ion. Therefore, substituents on the ring influence the acidity via the inductive effect. The yield of an ester is dependent on the nature of the substituent on the ring as well as the nature of the catalyst used.



Scheme 9.1: The esterification reaction pathway of benzoic acid

Three supports were tested for the esterification of phenol and the results are shown in **Fig. 9.3**. The sintered support ($\text{TiO}_2\text{-R}$) showed a low conversion of 1 % with high selectivity to propylbenzoate (~92 %). $\text{TiO}_2\text{-D}$ gave a conversion of 37 % with the selectivity of 74 % while HSA TiO_2 gave a much better conversion of 45 % with the selectivity of 86 %. This shows that the supports ($\text{TiO}_2\text{-R}$, TiO_2 , and HSA TiO_2) can be used as catalysts, in the absence of added alkali ions, with different catalytic activity and catalytic strength. Furthermore, it is clear that the conversion of benzoic acid is influenced by the nature of the support material as well as the physical state of the support.

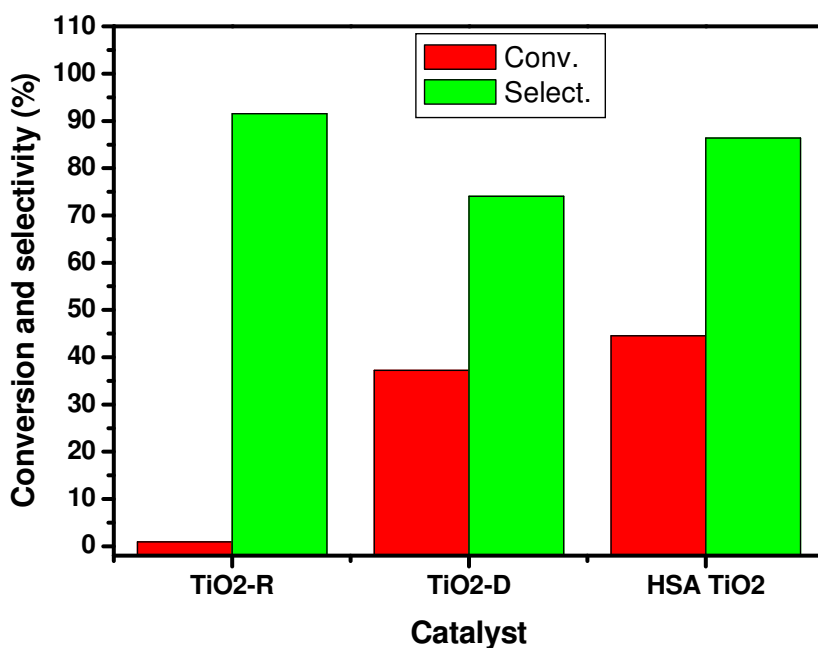


Figure 9.3: The reactivity of various TiO₂ supports

Table 9.2 shows the influence of alkali metal ions on the conversion of benzoic acid to give propylbenzoate. It can be observed that conversion increases with an increase in the alkali metal ion size up to K⁺. Cs/TiO₂ gave a reasonably high conversion of 66 % better than that of Li/TiO₂. The deviation in the trend with Cs/TiO₂ is consistent with the surface area of the catalyst and it is attributed to the suppression of anatase-rutile transition with both Li and Cs metal ion supported on TiO₂. When Cs was added to HSA TiO₂ support a conversion of 81 % was attained with a selectivity of 97 %. This suggests that a large surface area is imperative for the esterification of benzoic acid. The addition of alkali metal ions to TiO₂ showed a favourable effect on the selectivity to propylbenzoate. The addition of Li and Cs to HSA TiO₂ led to an improved conversion. This suggests that the conversion is greatly influenced by the surface and the structural properties and composition of the support. The highest conversion obtained with Li/HSA TiO₂ is attributed to strong

interaction between Li and nanocrystalline TiO_2 (HSA TiO_2). It is known that anatase exhibits stronger metal-support interaction than rutile [18]. HSA TiO_2 revealed the anatase phase after calcination at 300 °C.

Table 9.2: The effect of the addition of alkali metal ions to TiO_2 on conversion and selectivity (metal ion: TiO_2 = 1:15 mol/mol)

Catalyst	Conv. (%)	Selectivity (%)			
		PB	PD	MP	Others
HSA TiO_2	45.0	86.0	8.5	4.3	1.2
Li/ TiO_2	43.4	96.5	1.7	0.8	1
Na/ TiO_2	75.6	96.4	1.3	1.9	0.4
K/ TiO_2	92.3	96.9	1.5	0.6	1
Cs/ TiO_2	66.3	98.3	1.1	0	0.6
Cs/ TiO_2 (HSA)	81.4	96.7	1.1	1.9	0.3
Li/ TiO_2 (HSA)	99.0	93.0	2.3	2.2	2.5

Key: PB = Propylbenzoate; PD = propionaldehyde; MP = 2-methylpentanol.

(T = 350 °C; Feed rate = 5.1 ml/h; Wt. cat. = 2g; t = 1h).

Figure 9.4 illustrates the difference in conversion at different feed rates for different alkali metal ion based catalysts. As expected it can be seen that the conversion decreases with increasing feed rate in all systems as this reduces the contact time of the reactant with the catalyst. The decrease is more rapid when Li/ TiO_2 -D and Cs/ TiO_2 -D are used. In order for a catalyst to produce maximum activity the catalyst must generate a maximum surface area.

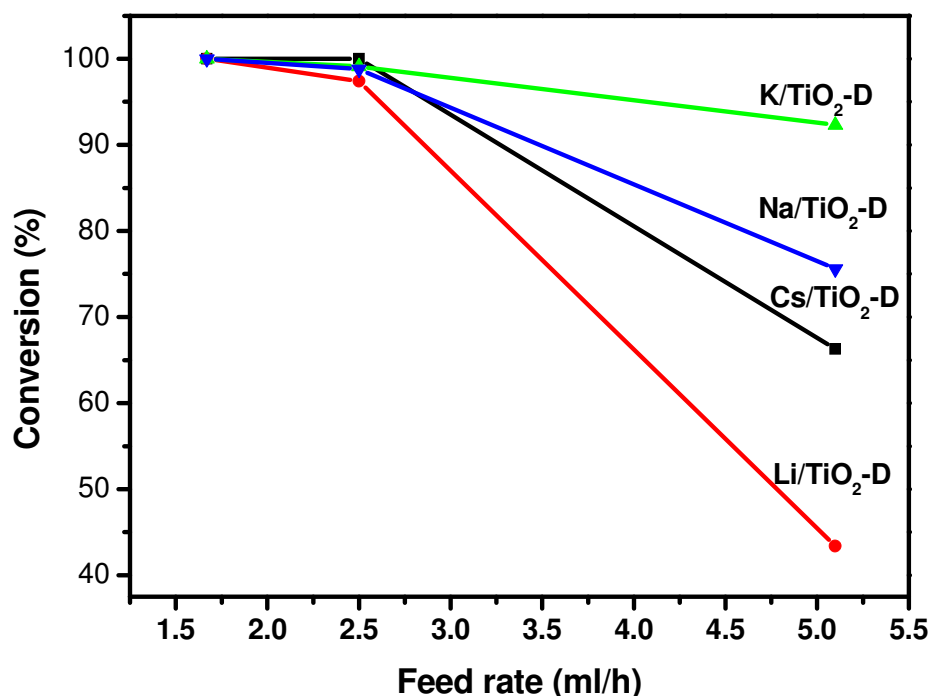


Figure 9.4: The effect of reactant (benzoic acid/propanol mixture) feed rate on conversion of benzoic acid. $T = 350\text{ }^{\circ}\text{C}$; Wt. cat. = 2g; $t = 1\text{ h}$.

The effect of feed rate on the selectivity over alkali metals based catalysts is graphically illustrated in **Fig. 9.5**. The selectivity to propylbenzoate was not significantly affected by the increase in feed rate for all the catalysts except Cs/TiO₂-D. The selectivity remained high and almost constant at around 96 % with Li/TiO₂-D, Na/TiO₂-D, and K/TiO₂-D. Furthermore, the selectivity obtained with Cs/TiO₂-D increased from 40 to 98 %. The reason for the initial lower selectivity obtained with Cs/TiO₂-D is believed to be because of the large ionic radius of Cs which may lead to poor dispersion over the support (TiO₂-D) leading to poor/weak metal support interaction which may result in low selectivity. The comparison of the selectivity obtained with Cs/TiO₂-D and Li/TiO₂-D suggests that the ionic size effect overrides

the anatase to rutile transformational effect. The observed increase in selectivity with an increase in feed rate is attributed to the decrease in conversion.

The longer residence time of reactant in the reactor promotes the formation of by-products such as propanaldehyde and 2-methylpentanol. This suggests that propanol reacts with the active sites on the surface to form propanaldehyde (oxidation reaction) which will further undergo a self condensation reaction with another propanaldehyde molecule to yield 2-methylpentanol.

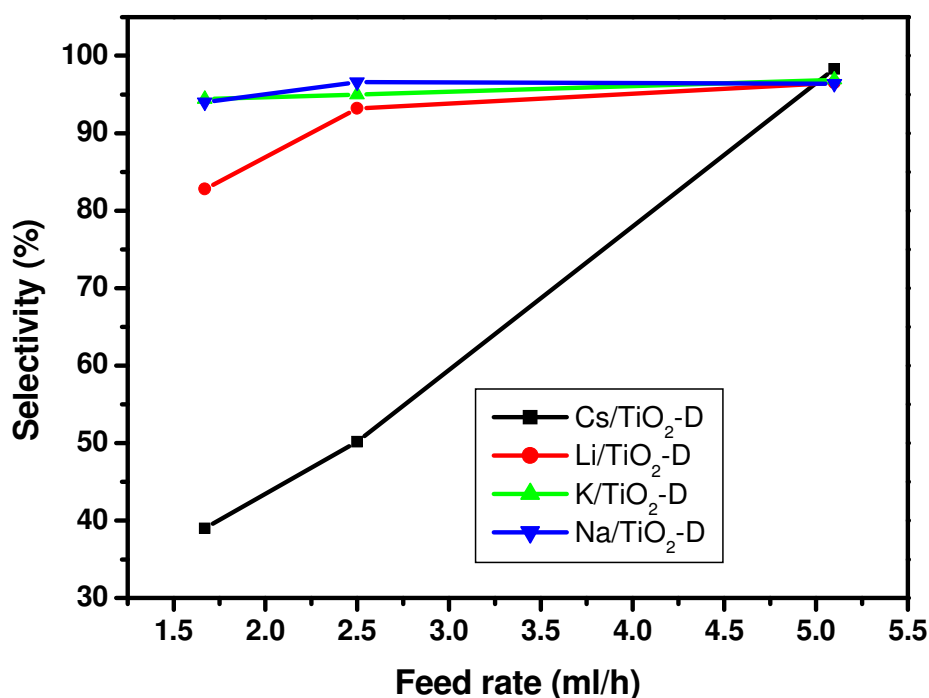


Figure 9.5: The effect of reactant (benzoic acid/propanol mixture) feed rate on selectivity to propylbenzoate. $T = 350\text{ }^{\circ}\text{C}$; Wt. cat. = 2g; $t = 1\text{ h}$.

Figure 9.6 represents the temperature dependence of the conversion of alkali metals based catalysts (Li/TiO₂-D, Na/TiO₂-D, K/TiO₂-D, and Cs/TiO₂-D). As it can be seen similar tendencies are detected. It is clear that the reaction temperatures significantly influence the catalytic performance of the alkali metals based catalysts

for the esterification of benzoic acid. The conversion increased with the increase in temperature reaching the maximum at 400 °C for each catalyst. The Li/TiO₂-D catalyst exhibits the lowest conversion within the reaction temperature range. The initial conversion of only 5 % was obtained at 270 °C. When the temperature was systematically increased the conversion increased reaching the maximum of 90 % at 400 °C. When the reaction temperature was increased for the rest of the catalysts the conversion also increased and full conversion was obtained at 400 °C. Although K/TiO₂-D gave the best conversion within the reaction temperature range Na/TiO₂-D also gave higher conversions than both Li/TiO₂-D and Cs/TiO₂-D. From the TPD data it is clear that catalyst basicity is a controlling factor. K/TiO₂-D showed stronger basic sites than Na/TiO₂ up to 500 °C (calcination temperature) and hence better conversion. The two high temperature peaks observed with Li/TiO₂-D and Cs/TiO₂-D are not available for the reaction when the catalysts are calcined at 500 °C. So the two catalysts virtually show little CO₂ adsorption within the calcination temperature range. This explains why Li/TiO₂-D and Cs/TiO₂-D are not as active as K/TiO₂-D and Na/TiO₂-D. K/TiO₂-D and Na/TiO₂-D show activities which are in accord to their basic strengths. At higher temperature (400 °C) the activity of both Li/TiO₂-D and Cs/TiO₂-D appear to be levelling off and this is primarily because strong basic sites are gradually becoming activated and also possibly because the conversion is approaching 100 %.

The difference in catalytic activity of these catalysts is also attributed to different crystallographic phases and surface properties of the catalysts. It must be noted that the XRD patterns of both Na/TiO₂-D and K/TiO₂-D are similar although their surface areas are different. The catalysts also change phase or crystallinity on heating. Therefore, the surface and mechanical properties of the catalysts are decisive in the process.

Figure 9.7 shows the effect of temperature on selectivity to propylbenzoate of TiO₂-D based catalysts. The selectivity remained almost constant as the temperature was systematically varied. It is clear that the selectivity to propylbenzoate over alkali

metals supported on TiO_2 catalysts is nearly independent of the reaction temperature. The selectivity of about 96 % was attained in all cases. This clearly shows that all alkali metals based catalysts are selective towards propylbenzoate.

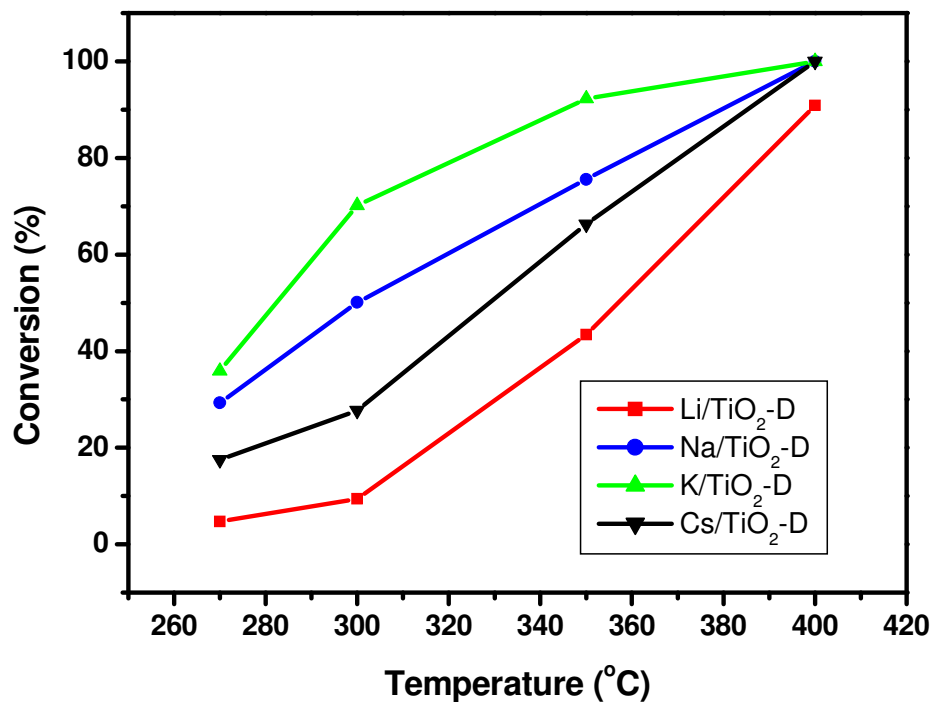


Figure 9.6: The effect of temperature on the conversion of benzoic acid.

FR = 5.1 ml/h; Wt. cat. = 2g; t = 1h.

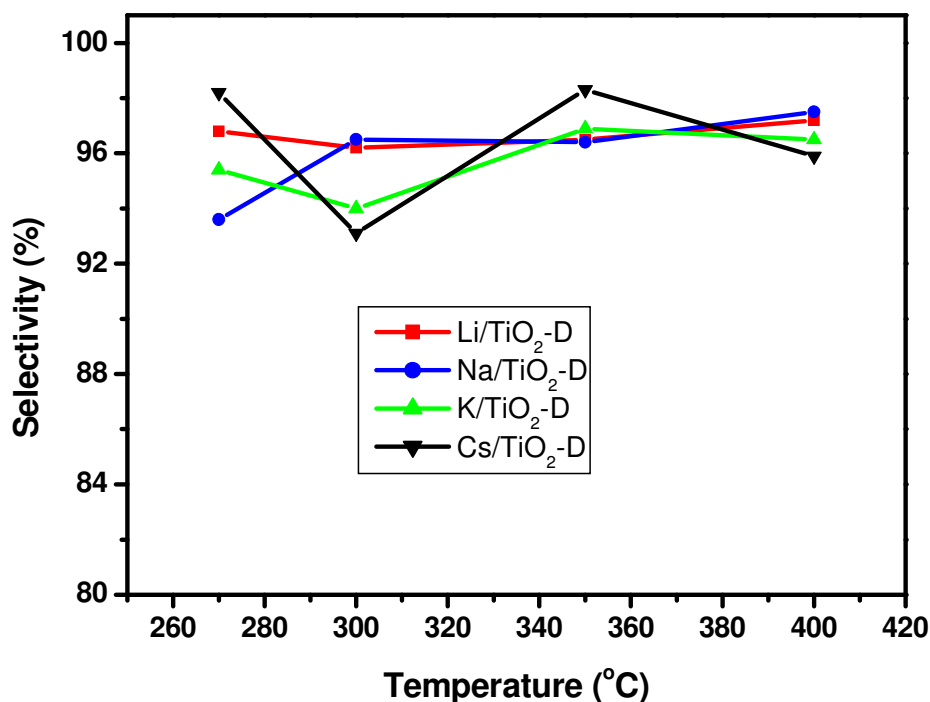


Figure 9.7: The effect of temperature on selectivity to propylbenzoate.

FR = 5.1 ml/h; Wt. cat. = 2g; t = 1h.

The effect of metal loading on both the selectivity and conversion of K/TiO₂-D is illustrated in **Fig. 9.8**. When the potassium loading was increased the selectivity remained high and constant (~100 %) irrespective of the K content. The conversion increased from 64 to 95 % as the K content was increased from 5 to 40 %. The increase becomes smaller at high K content clearly suggesting that the reaction was dependent on surface K (not bulk K). The increase in conversion with potassium loading is believed to be due to the proportional increase in the number of active sites.

Based on all the results it can be inferred that catalytic properties of titanium dioxide (TiO₂) can be enhanced by addition of small amounts of alkali metals ions and that

high temperature treatment transforms titanium dioxide, the support, from anatase to rutile ($\sim 800^\circ\text{C}$). The addition of Li and Cs metal ions showed the same transformational effect at lower temperature thereby making the catalysts lose their catalyst properties as a result of changes at crystal level. It must be noted that the surface area is crucial for the catalysts and that the phase transformation results in the loss of the surface area. As already mentioned, both in nature and in materials applications that involve heating, anatase coarsens and transforms to rutile [19]. The transformation is accelerated by heat treatment and occurs at various temperatures depending on various factors. It depends on the nature, the structure, the impurity and the preparation conditions of the precursor phase. It is assumed that the phase transformation can be reconstructive through the repositioning of both Ti cations and a change in the oxygen arrangement.

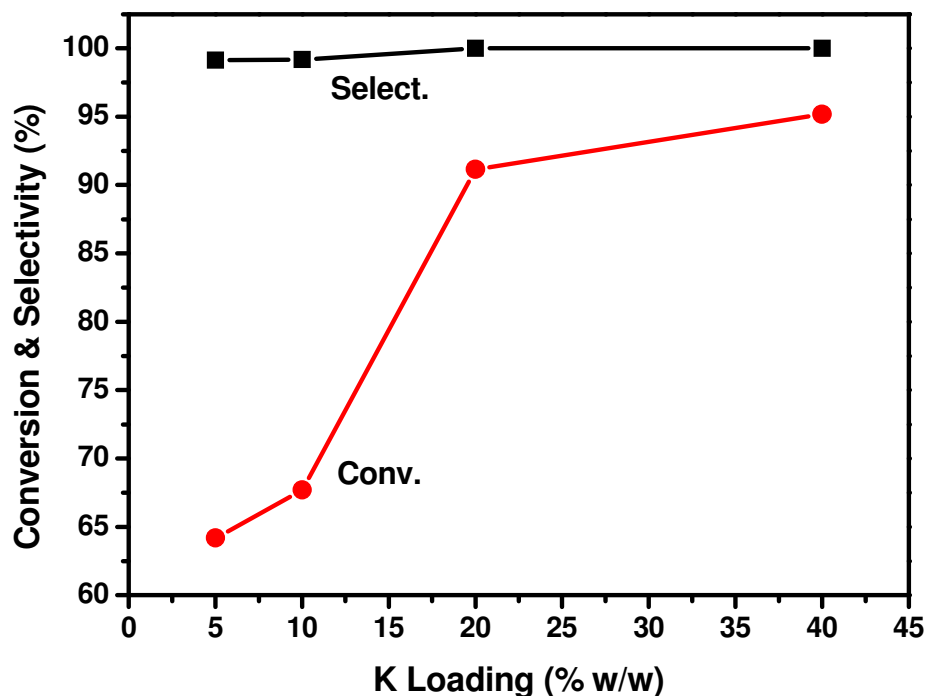


Figure 9.8: The influence of K loading on conversion and selectivity over K/TiO₂-D system. T = 350 °C; FR = 5.1 ml/h; Wt. cat. = 2g; t = 1h.

9.3.5. Deactivation studies

A comparison of conversion and product distribution over Li and Cs dispersed on high surface area TiO₂ derived support is presented as a function of time on stream in **Fig. 9.9**. No substantial decrease in conversion was observed for Li/HSA TiO₂ with time on stream study (~2h). A conversion of 100 % was attained with Li/HSA TiO₂ and it remained almost constant. A slight decrease in conversion was observed when Cs/HSA TiO₂ was used. It is interesting to note that Li is a better catalyst when supported on HSA TiO₂ support than Cs. It was found that HSA TiO₂ undergoes a phase transition from amorphous to a crystalline anatase phase and subsequently to rutile phase (Chapter 8). As a result the effect of Li on the anatase to rutile transformation appears to be much less pronounced. A marginal increase in selectivity was observed and it is associated with the slight decrease in conversion especially when Cs/HSA TiO₂ (Cs on high surface area material) was used.

9.3.5.1. The effect of H₂O and hydrocarbons

Cs/TiO₂-D (Cs on P25 Degussa material) showed poor selectivity to propylbenzoate at low flow rate of the reactant (**Fig. 9.5**). This low selectivity suggests that Cs/TiO₂-D promotes the adsorption of propanol (competitive adsorption) at low flow rate. The adsorption of propanol will subsequently lead to the formation of carbonaceous material on the surface and hence catalyst deactivation. Low selectivity to propylbenzoate means the catalyst favours the production of propanaldehyde and subsequently the condensation reaction to produce 2-methylpentanol. Characteristic of condensation reactions is the release of water as a by-product. The amount of water released from the esterification process and that released from the condensation of propanaldehyde could easily deactivate the catalyst.

The TGA data obtained on spent catalysts (Li/TiO₂-D, Na/TiO₂-D, K/TiO₂-D, and Cs/TiO₂-D) at reaction temperature of 350 °C are shown in **Fig. 9.10**. After the

reaction was carried out at 350 °C over Na/TiO₂-D, Li/TiO₂-D, K/TiO₂-D, and Cs/TiO₂-D the total weight losses of about 3, 4, 6, and 8 %, respectively, were obtained. The losses are ascribed to the desorption of hydrocarbon and carbonaceous species. Despite the high conversion obtained with Cs/TiO₂-D, it displayed a gradual decline in conversion with time. Some changes in chemical composition and structure of the surface layer or the bulk of the catalyst were assumed to occur during esterification of benzoic acid. The changes may be due to phase transformation (i.e. anatase to rutile transition) which may have affected the active sites.

The total weight loss obtained with Cs/TiO₂-D is in accord with the gradual decline in the conversion with time. Interestingly more hydrocarbons and carbonaceous species are adsorbed on K/TiO₂-D surface than Li/TiO₂-D. Moreover, a comparison of TGA profiles of spent and fresh catalysts revealed that indeed there was a formation of hydrocarbons and carbonaceous species. Carbonaceous species deposition at high temperature contributes to the catalyst deactivation, which can lead to reduction of conversion of benzoic acid.

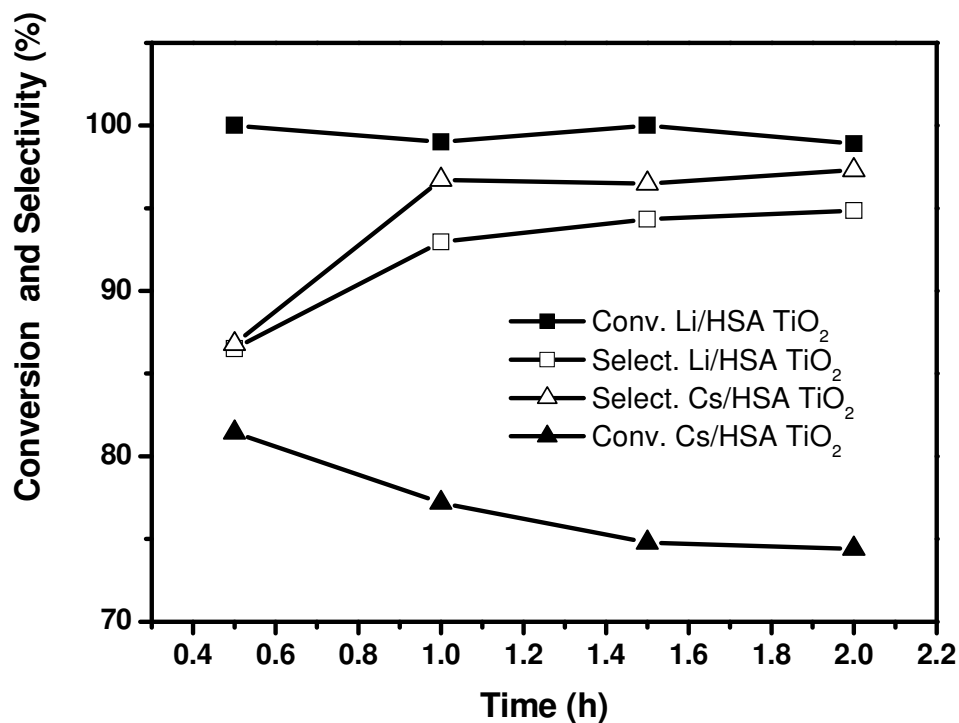


Figure 9.9: The effect of time on stream on esterification of benzoic acid over Li/HSA TiO₂-D and Cs/HSA TiO₂-D. T = 350 °C; FR = 5.1 ml/h; Wt. cat. = 2g; t = 1h.

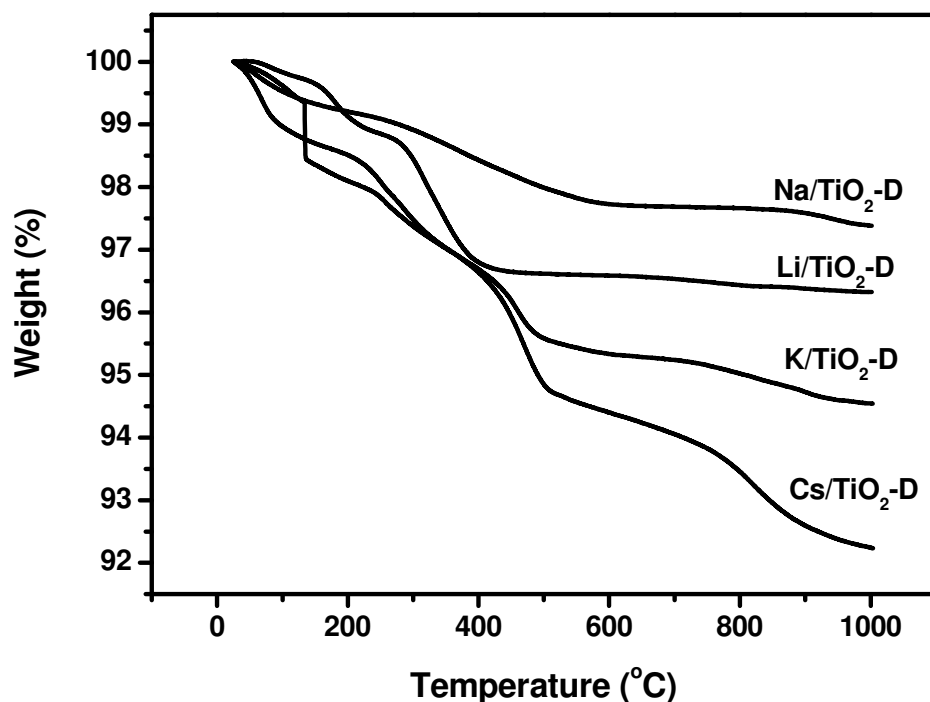


Figure 9.10: TGA plots for various alkali metals supported on spent TiO₂-D at 350 °C.

9.4. Conclusions

1. All the alkali metals showed promotional effects when added to TiO₂. Furthermore, other overriding effects such as the crystallographic phase of TiO₂ arising from the addition of these alkali metals were observed.
2. The addition of K metal ion did not show any influence on the anatase phase and resulted in K/TiO₂-D being the best catalyst for the esterification of benzoic acid. This implies that TiO₂ particles remain almost unchanged and small.
3. A larger BET surface area is beneficial and improves the activity and stability of alkali metal supported TiO₂-D catalysts.

4. The addition of alkali metal ions resulted in an improved selectivity to propylbenzoate relative to TiO_2 .
5. The strengths of the basic sites are crucial for the conversion of benzoic acid to propylbenzoate.

9.5. References

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10

The esterification of aliphatic systems: the reaction of butyric acid with propanol

10.1. Introduction

Very strict environmental legislation has generated a compelling need for cleaner methods of chemical production. For instance, technologies that reduce or, preferably, eliminate the generation of waste and avoid the use of toxic and/or hazardous reagents and solvents are preferred routes in chemical processes [1,2]. This trend towards green chemistry necessitates a shift from the traditional concept of process efficiency that focuses only on chemical yield to one that considers economic value in eliminating wastes.

The preparation of perfumery and flavour grade esters requires stringent specifications for the final product. The most widely employed and apparently cleaner production technique for such esters requires the reaction of the appropriate carboxylic acid with an alcohol in the presence of a mineral acid catalyst or a heterogeneous catalyst under reflux conditions, followed by separation of the ester by distillation [3]. The use of a solid acid or base catalyst can be effective from the

view of activity, selectivity, reusability and economy in the manufacture of perfumery esters [3].

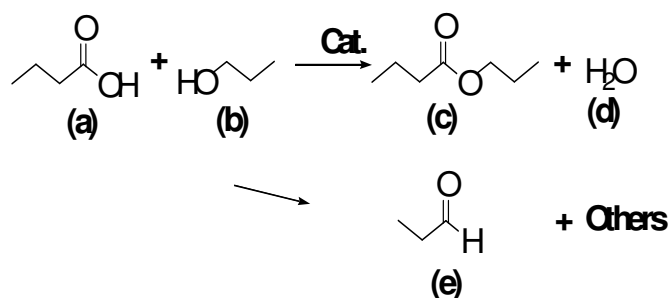
Low molecular weight carboxylic acids have been widely studied in an attempt to address principles of esterification because of their simplicity, availability and ease of reaction analysis. However, limited information is available on solid base catalysed esterification reactions. Correlations between chemical structures and chemical reactivity may provide insight into differences in chemical behaviour between low molecular weight carboxylic acids and their larger and bulkier counterparts.

Most studies have been devoted to homogeneous catalysis and the qualitative invention and quantitative correlations observed presents a rational basis for understanding possible structural effects of large carboxylic acids that can be transferred to the development of heterogeneous catalysts [4,5]. In this chapter butyric acid was used as a linear chain carboxylic acid to obtain information of the esterification of low molecular weight carboxylic acid and aromatic carboxylic acid (benzoic acid) using heterogeneous catalysts.

In the previous chapter (Chapter 9) a series of catalysts based on alkali metal ions (Li, Na, K and Cs) supported on titania have been successfully used as solid base catalysts for the esterification of benzoic acid with propanol, attaining conversions of up to 100% and high selectivity (> 90%) using appropriate reaction conditions. It was shown that the use of nanocrystalline TiO₂ material (high surface area TiO₂) both in the presence and absence of a promoter resulted in higher activity than that obtained with commercial TiO₂ based catalysts. It is anticipated that the nanocrystalline TiO₂ could also promote the esterification of butyric acid with propanol. This can be achieved through tailoring a catalyst particle size via nanoparticle synthesis and assembly in order to perform specific chemical conversions at high yield and do so with good selectivity.

In the literature TiO_2 materials have been prepared, using various methods, for use as catalyst or supports for a wide range of reactions [6]. The problem with the TiO_2 preparation methods reported in the literature is the lack of control of the conditions during the formation of the new anatase nuclei and their further crystal growth. It is important to note that the kinetics of the formation of precipitates is very important both for the reproducibility of the preparations and for the final physiochemical characteristics of the TiO_2 [7]. While pure anatase is prepared by hydrolysis of TiCl_4 in solution and in the gas phase [8] or by sol-gel methods [9-13] an alternative to these methods is the preparation of TiO_2 derived nanotubes. These were achieved by treatment of TiO_2 (either the anatase phase or the rutile phase or their mixture) with NaOH aqueous solution as reported by Kasuga and co-workers [14]. The variation in the concentration of NaOH in this study resulted in the synthesis of nanosized TiO_2 that did not have a tubular structure as detailed in Chapters 8 and 9.

The esterification of butyric acid (a) with propanol (b) was taken as the model reaction and the effect of various reaction parameters were evaluated to assess the conversion and selectivity in the reaction. The general reaction scheme is shown in **Scheme 10.1**. Esterification of butyric acid with propanol is an important reaction with considerable industrial interest due to the enormous practical importance of organic esters such as propylbutyrate [15,16]. Among other applications, propylbutyrate (c) is particularly of great interest for the production of flavours and aromas (e.g. imitation of banana) [3]. While the production of esters is generally trivial the production of water (d) as a by-product is inevitable. The preparation of catalyst with a hydrophobic surface of the catalyst is hence desirable. Other detectable by-products include propanaldehyde (e).



Scheme 10.1.

10.2. Experimental

Catalysts and supports used in this chapter are similar and/or prepared in a similar manner to those described in Chapter 9. The designation used here is hence similar to that used in Chapter 9. Catalysts used in this chapter, unless otherwise specified, were of metal ion to TiO_2 ratio of 1:15 mol/mol while the butyric acid to propanol mole ratio was kept at 1:10 w/w.

$\text{H}_2\text{SO}_4/\text{TiO}_2$ was prepared by an impregnation method where an appropriate amount of an acid (H_2SO_4) was added to the TiO_2 support. The preparation procedure used is similar to that described in Chapter 8.

10.3. Results and discussion

10.3.1. Characterisation of $\text{H}_2\text{SO}_4/\text{TiO}_2\text{-D}$ (1:15 mol/mol)

H_2SO_4 was added to TiO_2 to increase the acidic sites and to subsequently compare the effect of acidity and basicity on both conversion and selectivity. The powder XRD pattern of $\text{H}_2\text{SO}_4/\text{TiO}_2\text{-D}$ (1:15 mol/mol) calcined at 500 °C for 5 hours is shown in **Fig. 10.1**. It can be seen that both the anatase and rutile phases of titania are present in the sample.

Fig. 10.2 shows the basic nature and strength of $\text{H}_2\text{SO}_4/\text{TiO}_2\text{-D}$ (1:15 mol/mol) as determined by the CO_2 TPD. The profile reveals the presence of two peaks that are due to desorption of moderately- and strongly-bound CO_2 molecules (medium and strong basic sites) at 509 and 772 °C respectively. The high temperature peak is not active during the reaction since the calcination, pre-treatment and reaction temperatures are carried out at 500 °C (maximum). The low temperature peak shows that the desorption of CO_2 begins at about 300 °C and reaches the maximum at 509 °C. However, the peak intensity suggests that the amount of these basic sites is relatively small. The basicity was probably neutralised by H_2SO_4 .

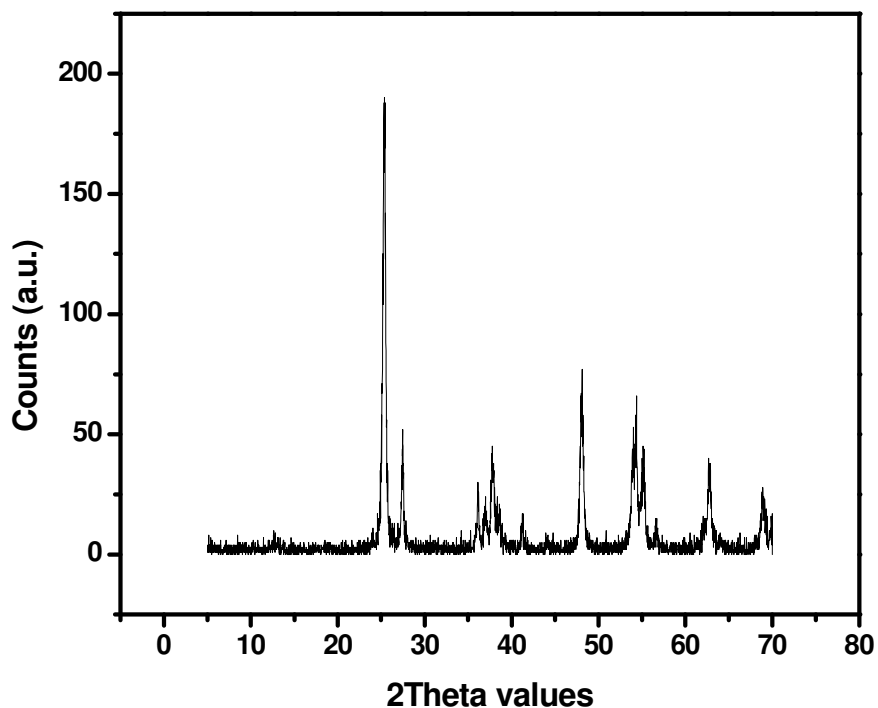


Figure 10.1: An XRD pattern of $\text{H}_2\text{SO}_4/\text{TiO}_2\text{-D}$

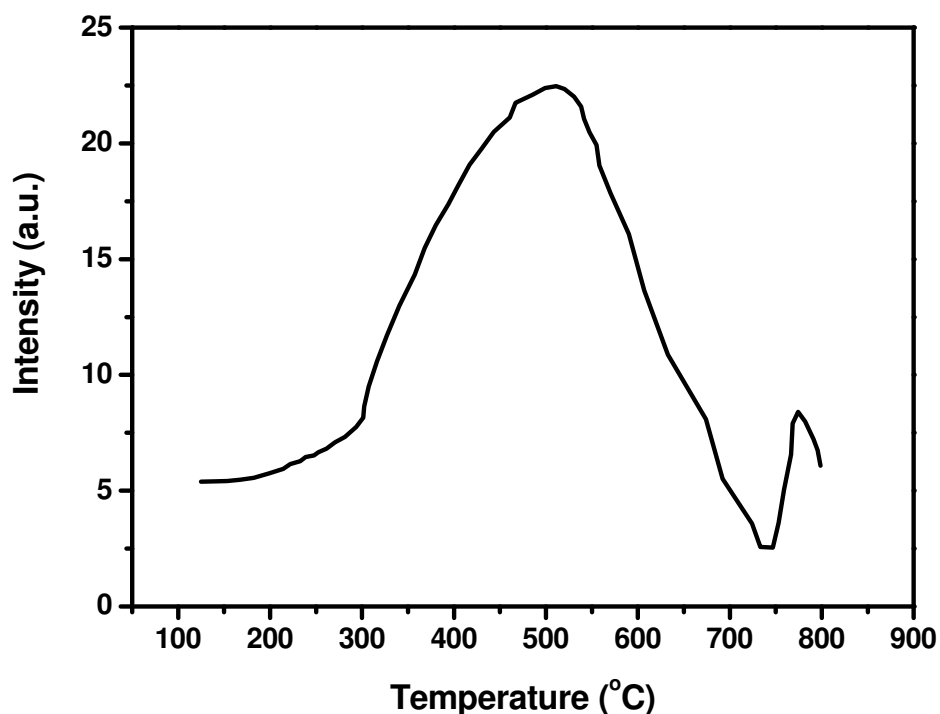


Figure 10.2: A TPD profile of $\text{H}_2\text{SO}_4/\text{TiO}_2$ (1:15 mol/mol)

10.3.2. Esterification of butyric acid

The initial studies were focussed on the investigation of the influence of various supports derived from P25 Degussa TiO_2 ($\text{TiO}_2\text{-D}$) on the esterification of butyric acid. Reactions were carried out to establish a comparison in terms of catalytic strength among the supports. **Figs. 10.3a** and **10.3b** represent conversion and selectivity of the esterification reaction over the three TiO_2 based supports ($\text{TiO}_2\text{-D}$, HSA TiO_2 and $\text{TiO}_2\text{-R}$). $\text{TiO}_2\text{-R}$ (TiO_2 rutile) gave poor conversion which gradually decreased from 37 to 22 % with time. $\text{TiO}_2\text{-D}$ showed a higher conversion of 89 % and remained almost constant with time on stream. HSA TiO_2 showed a better conversion than either the $\text{TiO}_2\text{-D}$ or $\text{TiO}_2\text{-R}$ support. The catalytic strength of the three supports is in accord with their particle size. The nanosized material (HSA

TiO₂) gave the best conversion whereas the sintered material gave the least conversion. The surface areas of the materials were also found to follow the same trend (Chapter 9).

Fig. 10.3b illustrates the influence of various supports on the selectivity towards propylbutyrate. The selectivity of the three supports did not change significantly with time on line. HSA TiO₂ showed the highest selectivity of up 93 % whereas TiO₂-D showed selectivity of up to 90 %. TiO₂-R showed the lowest selectivity with time (up to 70 %). This difference in the influence can be attributed to the surface area as shown in **Fig. 10.3c**. It can be observed that the amount of propylbutyrate correlates with the surface area of the material.

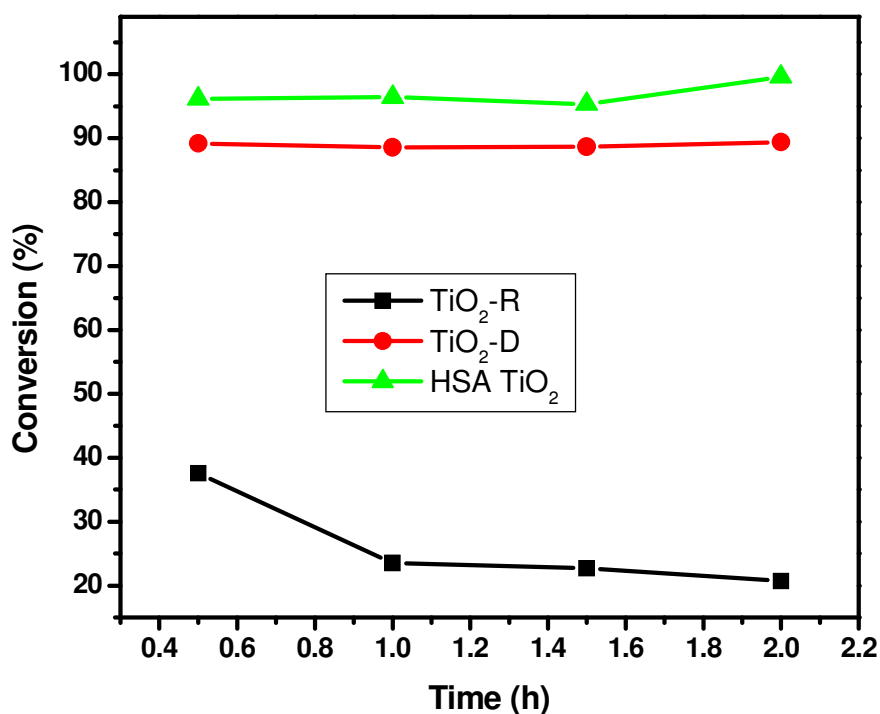


Figure 10.3a: Effect of different TiO₂ based supports on the conversion of butyric acid against conv. and select. (t = 1h). T = 350 °C; FR = 5.1 ml/h; Wt. cat. = 2g.

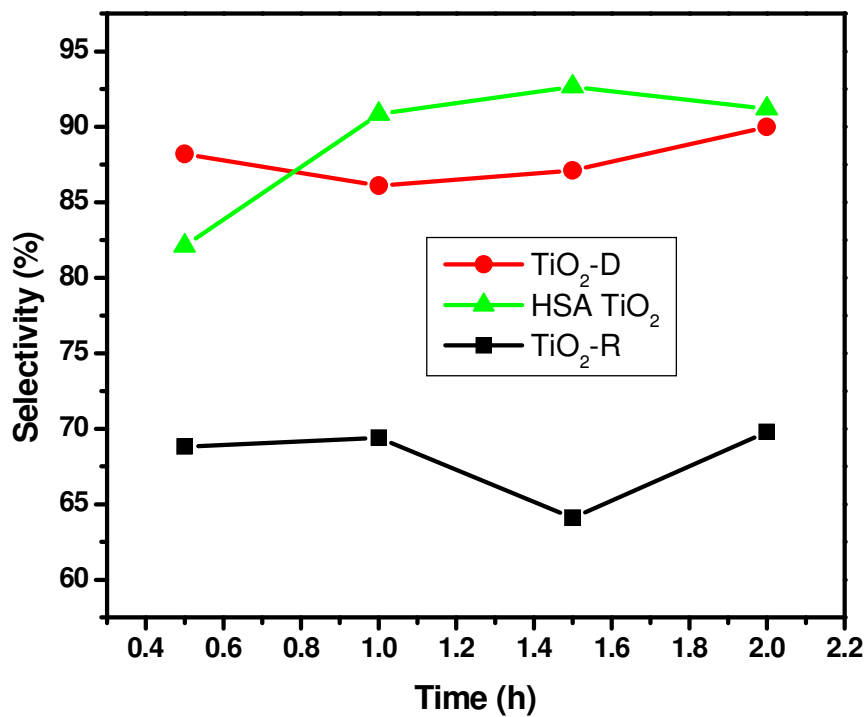


Figure 10.3b: Effect of different TiO₂ based supports on the selectivity to propylbutyrate against conv. and select. (t = 1h). T = 350 °C; FR = 5.1 ml/h; Wt. cat. = 2g.

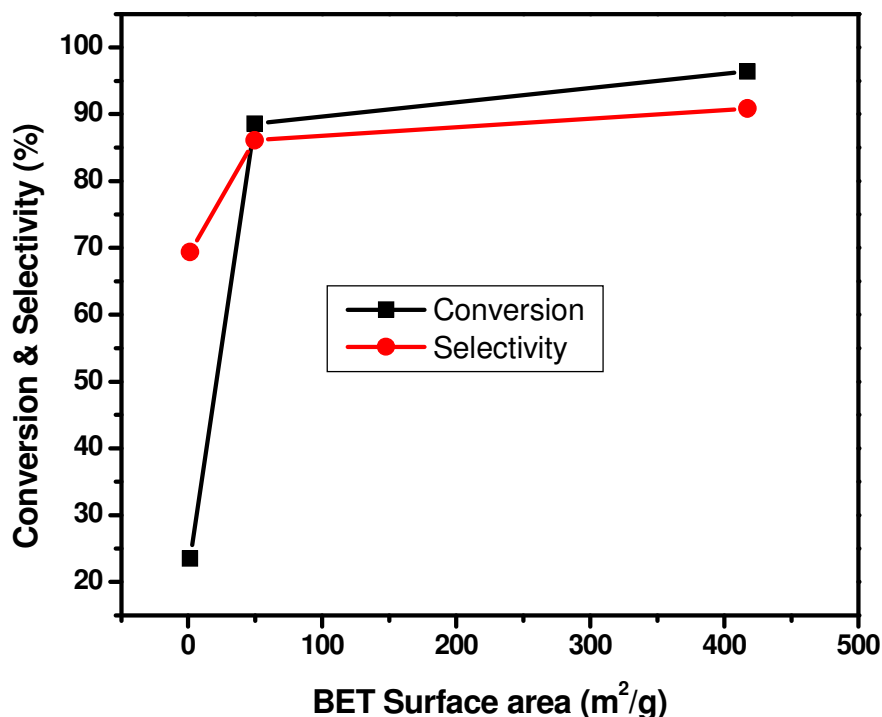


Figure 10.3c: Effect of different TiO₂ based supports on BET surface area against conv. and select. (t = 1h). T = 350 °C; FR = 5.1 ml/h; Wt. cat. = 2g.

10.3.3 Effect of various TiO₂-D supported catalysts

Different solid catalysts were used to evaluate the activity in this reaction. The catalysts used were H₂SO₄/TiO₂-D, Li/TiO₂-D, Na/TiO₂-D, K/TiO₂-D and Cs/TiO₂-D. **Fig. 10.4** shows the conversion of butyric acid and selectivity to propylbutyrate, for the various catalysts at T = 350 °C. Butyric acid conversion is independent of the nature of the alkali metal ion. A total conversion of 100 % was attained with each catalyst. The selectivity to propylbutyrate was ~99 % and was attained with all the alkali metal ions supported on TiO₂-D catalysts. The H₂SO₄/TiO₂-D showed a lower

selectivity of 75 %. This effect is attributed to the acid-base properties of the catalyst arising from the addition of the acidic precursor to the support. The TPD profile of $\text{H}_2\text{SO}_4/\text{TiO}_2\text{-D}$ showed the presence of a smaller amount of basic sites than that of alkali metal ions supported on TiO_2 . However, the basic sites were sufficient to generate high selectivity and activity.

It is clear that the activity of the catalyst for the esterification of butyric acid is independent of the acidic or basic nature of the catalyst. The reaction proceeds with very high conversion over acidic or basic surfaces.

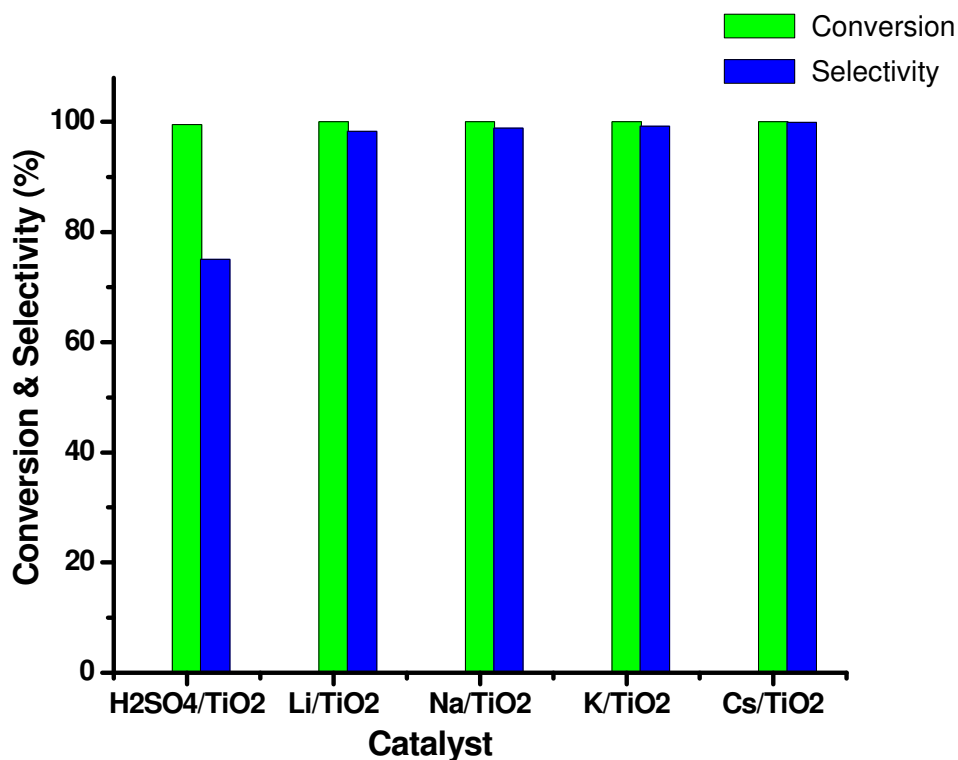


Figure 10.4: The effect of the type of alkali metal impregnated on $\text{TiO}_2\text{-D}$ on the esterification reaction of butyric acid with propanol (1 : 10 w/w) at 350 °C after 2 hours. FR = 5.1 ml/h; Wt. cat. = 2g; t = 1h.

10.3.4. Effect of reaction temperature

The effect of temperature on conversion and selectivity was studied in the temperature range of 300 to 400 °C as shown in **Fig. 10.5**. The conversion of butyric acid was found to be as low as 56 % and decreased to 35 % with time at 300 °C. However, total conversion (100 %) was attained at 350 and 400 °C and remained constant with time. This clearly suggests that the reaction is temperature dependent and that the activity of the catalysts is a function of temperature. The total conversion at high temperatures (350-400 °C) could also be due to the coverage with a material that needs thermal energy to be removed.

Fig. 10.5(b) illustrates the dependency of selectivity to propylbutyrate on the reaction temperature. Although the highest selectivity was initially ($t = 0.5\text{h}$) obtained at 350 °C it was observed that the selectivity decreased with temperature ($t = 1,5\text{-}2\text{ h}$) This is attributed to the decrease in the conversion with increasing temperature.

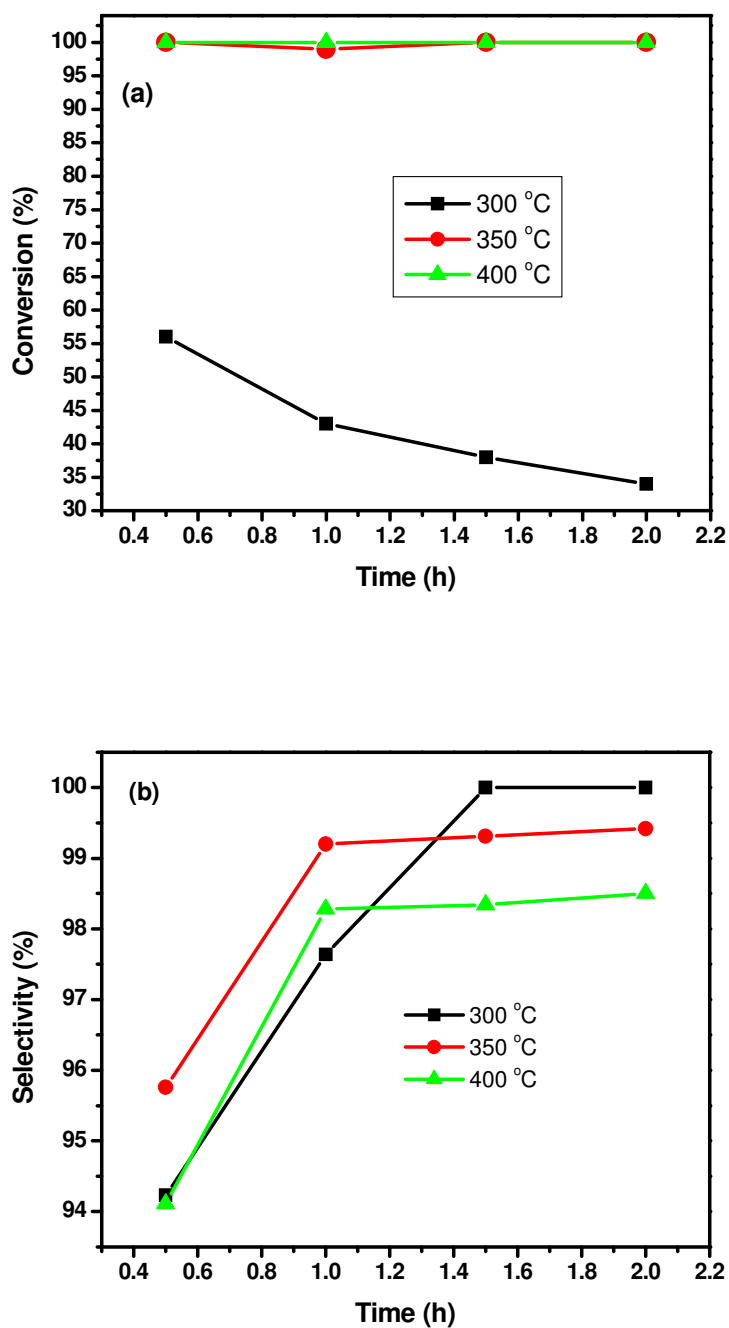


Figure 10.5: Effect of temperature on the (a) conversion of butyric acid and (b) selectivity to propylbutyrate over Cs/TiO₂-D (1:15 mol/mol). Butyric acid : propanol mole ratio = 1:10 w/w); FR = 5.1 ml/h.

10.3.5. The effect of feed composition

The effects of butyric acid concentration in the feed on both the conversion and selectivity as a function of reaction time are illustrated in **Fig. 10.6**. The conversion increased with increasing butyric acid concentration. Conversion increased from 24 to 98 % with variation in the concentration of butyric acid (1:10 to 1:2 w/w) at $t = 1\text{h}$, see **Fig. 10.6a**. This observed conversion trend shows that the conversion is dependent on the concentration of butyric acid. The observed decrease in conversion with time can be ascribed to catalyst poisoning by trace amounts of water formed during the reaction and a possible deposition of hydrocarbons on the surface (to be discussed later).

The selectivity was not greatly affected by the increase in concentration (**Fig. 10.6b**). A slight increase in selectivity with time could be due to a decrease in conversion.

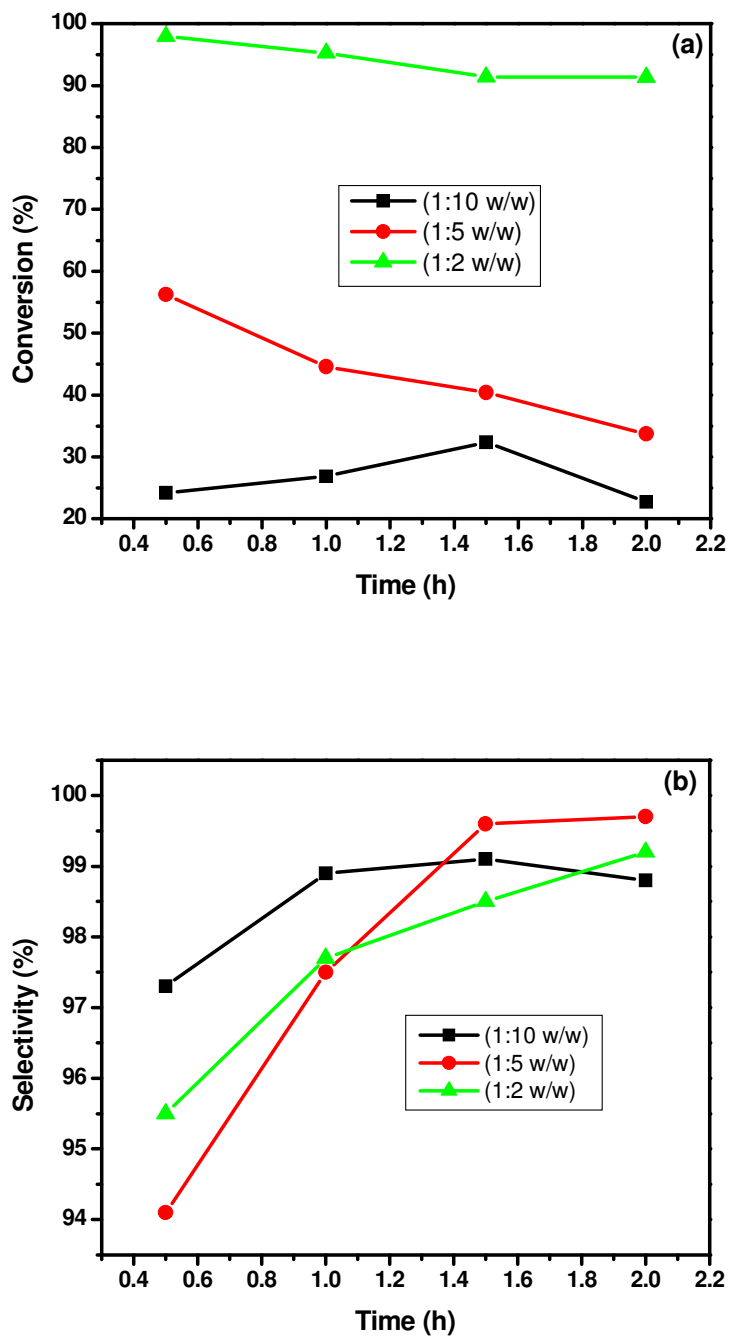


Figure 10.6: Effect of feed composition on the (a) conversion of butyric acid and (b) selectivity to propylbutyrate over Cs/TiO₂-D (1:15 mol/mol). T = 350 °C; FR = 5.1 ml/h; Wt. cat. = 2g.

10.3.6. Catalyst deactivation and regeneration

Solid catalysts are more advantageous than homogeneous catalysts especially in terms of reusability. In order to evaluate the reusability of Cs/TiO₂-D the esterification of butyric acid was carried out at 350 °C as already described. After 2 hours on stream the reaction was stopped and the catalyst was heated at 400 °C for 4 hours. After calcination a new reaction cycle was started with fresh reactants. The conversion for each cycle was plotted as a function of time as shown in **Fig. 10.7**. In the first cycle the conversion decreased from 56 to 33 % with time. After calcination of the used catalyst at 400 °C a conversion of 62 % was attained and had decreased to 48 % with time. The highest conversion of 62 % was attained in the third cycle followed by a decrease to 50 % with time. It is clear that the catalyst retains 100 % of its original activity after calcination suggesting that the catalyst can be reactivated. A constant drop in conversion was observed during each reaction cycle.

To investigate the cause of catalyst deactivation the spent catalyst was subjected to a TGA analysis and the profile is shown in **Fig. 10.8**. The total weight loss of 3 % was observed for Cs/TiO₂-D (1:15 mol/mol). A 1 % weight loss occurred between 38-250 °C and is ascribed to the loss of water. Water formed as a by-product in the esterification of butyric acid is suspected to have poisoned the catalyst. When the catalyst was used between the reaction cycles, the trace amounts of water chemically and physically bonded to the surface may have led to deactivation.

The 1 % weight loss observed between 250-500 °C is attributed to the removal of hydrocarbons whereas the third weight loss (1 %) observed at 500-800 °C is attributed to the removal of carbonaceous species. Both the hydrocarbons and carbonaceous species can give rise to the blockage of the surface micropores. The deposition of hydrocarbons and water on the surface can be reversed by calcination at 400 °C and leads to a reactivation of the catalyst. It must be noted that the combination of material deposition and thermal and chemical cycling may aggregate, poison, decompose the structure, or change the shape, composition or morphology of

the material. But the regeneration of spent catalyst could successfully restore the activity or performance of the original fresh catalyst for numerous cycles. After a few cycles a decrease in the restored conversion was observed (not shown) and was believed to be due to the amount of carbonaceous species becoming more significant.

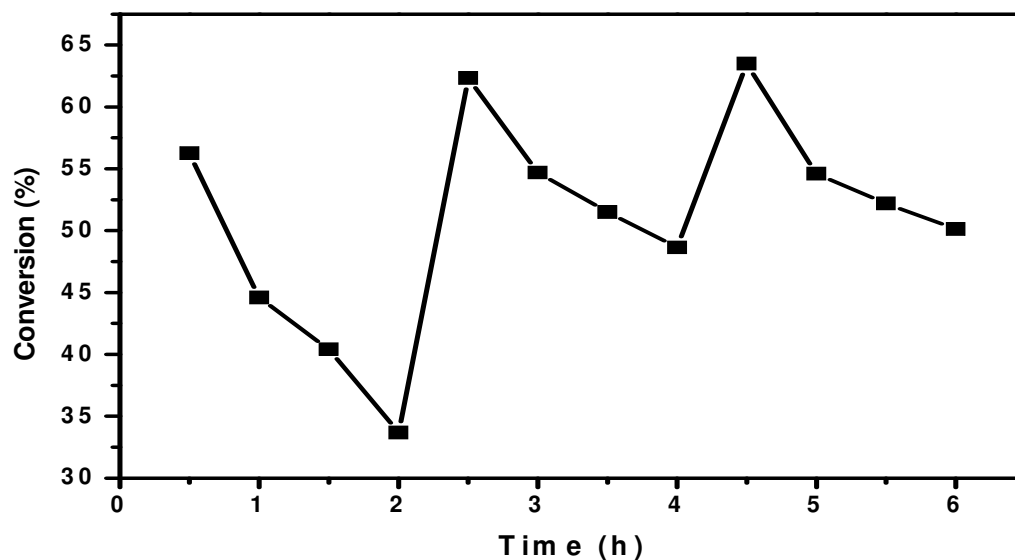


Figure 10.7: Effect of regenerative properties of Cs/TiO₂-D (1:15 mol/mol) on conversion of butyric acid with heat treatment at 400 °C (2 h cycles).
T = 350 °C; butyric acid : propanol ratio = 1:5 w/w; FR = 5.1 ml/h;
Wt. cat. = 2g.

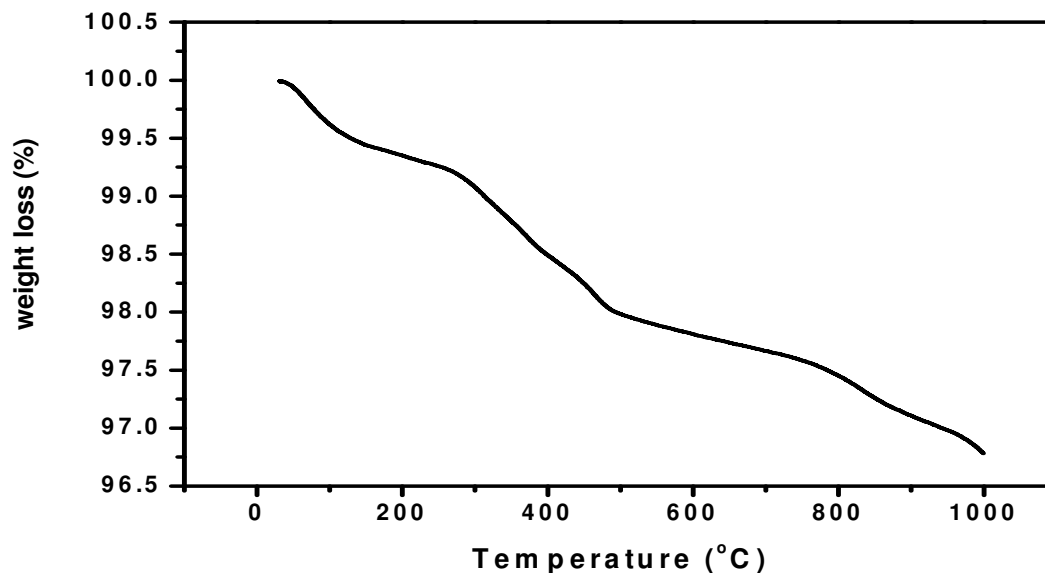


Figure 10.8: A TGA profile of spent Cs/TiO₂-D (1:15 mol/mol).

10.3.7. Comparison of reactivity between butyric acid (aliphatic) and benzoic acid (aromatic)

TiO₂-D, TiO₂-R and HSA TiO₂ supports were used as catalysts for the esterification of butyric acid and benzoic acid with propanol. The order of reactivity in both instances was as follows: HSA TiO₂>TiO₂-D>TiO₂-R. It was found that butyric acid reacted more easily with propanol in the presence of a catalyst than did benzoic acid. When used as a catalyst, HSA TiO₂ gave a conversion and selectivity that was very high. Thus addition of a promoter to enhance the esterification of butyric acid could not be monitored. However, the addition of a promoter was required to enhance the activity for the esterification of benzoic acid.

The addition of alkali metal ions to TiO₂-D showed a promotional effect on the conversion and selectivity for the esterification of benzoic and butyric acids.

The conversion of benzoic acid showed a higher dependency on reaction temperature whereas the conversion of butyric acid remained relatively high over a wide range of temperature.

The above correlations outline the difference in chemical reactivity of low molecular weight carboxylic acid (aliphatic) and their larger and bulkier (aromatic) counterparts. The reactivity of carboxylic acid using solid base catalysis is dependent on the structural effect of the carboxylic acids. Butyric acid (aliphatic) reacts more readily with propanol than benzoic acid (aromatic). The reactivity seems to decrease with an increase in the size of carboxylic acid. Data from reactions using homogeneous catalysis have bearing on the study [17]. There are two possible factors contributing to the decrease in reactivity, viz. an inductive effect and a steric effect [18]. The inductive effect arises from the increase in electron-donating ability of the bulkier carboxylic acid. Though the inductive effect promotes the protonation of the carbonyl oxygen, it also reduces the electrophilicity of the carbonyl carbon. This leads to a more energy-hindered rate limiting nucleophilic attack by propanol. Moreover, the steric effect involving the reactivity of the carboxylic acid is also a crucial factor for the esterification. The steric hindrance increases with molecular size causing electronic repulsion between the non-bonded atoms of reactant molecule. The repulsive hindrance reduces the electron density in the intermolecular region thereby disturbing the bonding interactions [18-20]. This means that as the steric effect increases with an increase in the size of carboxylic acid. It is noteworthy that the steric constraints are not solely controlled by the size of the molecule but also by their preferential conformations giving rise to a “conformational levelling” effect [21,22]. Consequently it is more difficult for propanol to reach the carboxylic group in benzoic acid due to a bulky aromatic ring blocking the access.

In the esterification of benzoic acid the aromatic ring does not take part in the resonance stabilization of the carboxylate ion. This implies that the acidity can be influenced by the substituents on the ring possibly by the inductive effect.

Other factors that could influence the reaction include the difference in both the pH and boiling points of the two acids. The pH of butyric acid was found to be ~3.17 and that of benzoic acid to be ~4.56. This clearly shows that butyric acid is more acidic than benzoic acid. The acidity of the starting material could be very crucial. The boiling point of butyric acid was found to be ~162 °C whereas that of benzoic acid was found to be ~249 °C. The reaction data were collected between 300 and 400 °C for the esterification of both butyric acid and benzoic acid. The difference in boiling points of the two acids suggests that the vapour phase esterification of butyric acid could be more favourable than that of benzoic acid within the reaction temperature range.

The catalyst deactivation was found to be more pronounced for the esterification of butyric acid than benzoic acid especially at low alkali metal ion loading. The different extents of deactivation for both systems (butyric and benzoic acids) could be due to the presence of water formed as a result of high conversion, among other factors. Butyric acid was found to react more readily with propanol than benzoic acid. Consequently, water is constantly formed as by-product in larger amounts for the esterification of butyric acid. Inevitably the formation of water leads to catalyst deactivation. Certainly, catalyst with a hydrophilic surface is desirable for the esterification of both benzoic acid and butyric acid since water formation is inevitable.

10.4. Conclusions

1. The use of TiO₂-D based catalysts for the esterification of butyric acid showed beneficial results. Conversions of up to 100 % were attained with various catalysts.

2. Contrary to the traditional beliefs, the acidity of the catalyst is not always a controlling factor. Alkali metal ions supported on TiO_2 -D catalysts showed better selectivity to propylbenzoate than $\text{H}_2\text{SO}_4/\text{TiO}_2$ -D.
3. The effect of anatase to rutile ratios showed no influence on the esterification of butyric acid.
4. Catalyst deactivation was due to the presence of water and the deposition of hydrocarbons and carbonaceous species thereby blocking the micropores of the catalysts.
5. It was possible to completely reactivate the catalyst by calcination at 400°C for 4 hours in air.

10.5. References

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11

General Conclusions

The common thread linking the chapters together was the use and synthesis of TiO_2 as a support or catalyst. The chapters in which new results were described can be summarized as follows:

- (1) The use of nanotubular titanate as a support for Pd in the phenol hydrogenation reaction (Chapter 4) and o-chloronitrobenzene hydrogenation reaction (Chapter 6).
- (2) The use of high surface area TiO_2 prepared from NaOH as support for Pd in the hydrogenation of phenol (Chapter 5).
- (3) The use of nanotubular titanate as a support for Au in the CO oxidation reaction (Chapter 7).
- (4) A study of the anatase to rutile phase transformation in commercial TiO_2 (P25 Degussa) and high surface area TiO_2 (Chapter 8).
- (5) The use of TiO_2 (Degussa) as support for alkali metal ions in the esterification of benzoic acid (Chapter 9) and butyric acid (Chapter 10).

The hydrothermal treatment of TiO_2 with either KOH or NaOH aqueous solution was used to synthesize TiO_2 derived materials (Chapters 4, 5, 6 and 7). It was found that the variation in synthesis conditions to produce TiO_2 derived material, such as

ageing time, resulted in production of materials with different properties and morphologies. The concentration of the base (NaOH, KOH) was also found to have a profound effect on the nature of the resulting material. The novel route employed in this work yielded both the tubular and non-tubular materials with relatively large specific surface area. The formation of both sheet-like structures and tubular structures was attained by varying the ageing time. It was established that the tubular materials have a titanate structure, viz. $\text{KTiO}_2(\text{OH})$ when made with KOH. The surface areas of these materials also varied with ageing. The materials were used as catalyst supports. Supported precious metals such as Pd and Au were used for the hydrogenation of phenol and the oxidation of CO respectively.

Pd catalysts supported on titania derived nanotubes showed better activity and selectivity for the hydrogenation of phenol than that found for commercial TiO_2 . The activity was found to be significantly enhanced by the presence of nanotubular structures. The high surface area support gave rise to the formation of very small Pd nanoparticles as determined by HRTEM. The presence of basic properties on the surface of the catalysts was detected by TPD. Increasing the reaction temperature resulted in the desorption of surface phenol accompanied by a decrease in conversion. Phenol hydrogenation is a characteristic stepwise reaction where cyclohexanone and cyclohexanol are the partially and fully hydrogenated products, respectively. Pd catalyst supported on material over-aged (61 days) gave a catalyst that generated a relatively lower conversion of phenol and favoured complete hydrogenation to cyclohexanol.

The deposition of hydrocarbons at high temperatures (300 °C) significantly suppressed the activity for Pd supported on TiO_2 derived nanotubular catalysts, which led to the retardation of the hydrogenation of phenol.

Nanosized TiO_2 materials made of spherical particles and with specific surface areas larger than that of TiO_2 (Degussa) were prepared by hydrothermal treatment of TiO_2 with NaOH solution (25 M). The surface area of the material was found to be

dependent on the amount of time spent in an autoclave. Pd supported on the larger surface area material gave higher conversion of phenol and better selectivity to cyclohexanone than the smaller surface area material. A correlation between the total basicity of the catalyst and conversion of phenol was observed.

The prepared Pd/TiO₂-M (TiO₂ derived nanotubes) displayed excellent catalytic properties for the hydrogenation of ortho-chloronitrobenzene (O-CNB) to the corresponding ortho-chloroaniline (O-CAN). The catalytic activity for this reaction over nanotubular based Pd catalyst was found to be higher than the most effective ruthenium and platinum catalysts previously reported. The hydrogenolysis of the C-Cl bond in O-CNB was hindered over the nanotubular catalyst Pd/TiO₂-M. The catalyst showed good stability with time on stream whereas the selectivity was found to be independent of time on stream.

TiO₂ derived nanotubes have been used as a support for the preparation of nano-sized gold based catalysts. It was observed that the nano-sized gold particles could be well dispersed on the surface of TiO₂ derived nanotubular material by deposition precipitation (DP). The study revealed that Au/KTiO₂(OH) is highly active for the oxidation of CO and that Au/KTiO₂(OH) presents a relatively higher activity than a Au/TiO₂ catalyst. The catalytic activity was enhanced by the large surface area of the KTiO₂(OH) support. It is expected that other chemical rather than particle size effects may also be responsible for the difference in activity. The catalytic behaviour of Au/KTiO₂(OH) correlates with the structural peculiarity and the nature of the material. Thus, KTiO₂(OH) can be assumed to be a more basic support than TiO₂.

The microstructure studies of the alkali metal ion doped TiO₂ have shown that the presence of lithium and caesium metal ions enhance the anatase to rutile phase transformation. In the presence of Li ions the anatase to rutile phase transformation occurs at reduced temperature when compared with the modified TiO₂. The transformation was found to be dependent on the concentration of Li ions. Lithium

metal ion was incorporated into the TiO_2 lattice structure as well as being deposited on the surface. The anatase to rutile transformation was found to be influenced by nature of the impurities (dopant), grain size, and the synthesis of the TiO_2 material. This suggests that the way the impurity interacts with TiO_2 material is important.

The hydrothermally prepared high surface area TiO_2 material exhibited a small particle size and the material did not show any long term periodicity. Upon sintering the material transformed to anatase and subsequently to rutile at temperatures higher than that of commercial material.

The esterification of benzoic acid to propylbenzoate was achieved in high yield and selectivity in the presence of alkali metal ions supported on TiO_2 catalysts. Furthermore, the addition of Li and Cs metal ions to TiO_2 followed by calcination at $500\text{ }^\circ\text{C}$ expedited the anatase to rutile transformation and this resulted in relatively low conversions. The addition of alkali metal ions showed a promotional effect. K/TiO_2 was found to be the best catalyst for the esterification of benzoic acid. The surface area was found to be crucial for the activity of the catalyst. The strength of the basic sites is crucial for the conversion of benzoic acid to propylbenzoate. The bulky aromatic ring in benzoic acid reduced the reactivity of the carboxylic acid relative to the aliphatic butyric acid. This behaviour was ascribed to steric and inductive effects.

The esterification of butyric acid with propanol progressed with ease in the presence of alkali metal ions supported on TiO_2 catalysts. Maximum conversions were obtained with all catalysts (at $350\text{ }^\circ\text{C}$). The conversion was independent of the anatase to rutile transformation. The addition of H_2SO_4 to TiO_2 gave rise to lower selectivity than that obtained with alkali metal ion based catalysts. This suggests that the acidity of the catalyst is not an important factor in the reaction. Butyric acid was found to be more reactive with propanol than was benzoic acid. This was attributed to acidity (lower pH) and the boiling point (lower boiling point) of the butyric acid.

Titania (TiO_2) is an important functional material with a wide range of applications across immensely different fields. Titania has become an attractive material due to its electronic properties. However, the electronic properties are largely dependent on the material's atom distribution and can be altered by doping with different impurities (elements). The presence of the dopants accompanied by sintering may accelerate or decelerate the anatase to rutile transformation. The isolation of individual polymorphs gives rise to a number of applications.

The mesoporous nanocrystalline and nanotubular materials derived from TiO_2 with different compositions, pore system and novel properties have been of particular interest because of their remarkably large surface areas and narrow pore size distributions, which make them ideal candidates for catalysts or supports. Different properties of the TiO_2 nanoparticles and/or TiO_2 derived nanoparticles were found to be dependent on the crystal sizes, morphologies, and crystallographic structures of the materials. Hence, a controlled preparation method for the synthesis of nanoparticles is imperative. Not only was TiO_2 used as catalyst or support but also as a precursor for the synthesis of TiO_2 derived nanotubes or non-tubular nanocrystalline materials.

Further examination of the role of the base concentration (i.e. 10–25 M) and the type of the base (i.e. NaOH, KOH, CsOH, etc.) on the synthesis of TiO_2 nanomaterials would be necessary, since by comparing the roles of concentration and type of the base, a better understanding of the nature of the base in the TiO_2 material could be obtained. It is also desirable that the future work should examine the chemisorptive properties of Au and Pd supported on TiO_2 derived nanotubes. This work would build up on the studies described on this thesis and provide a better understanding of the dispersion of metals on the nanotubular titanate materials.