SYNTHESIS AND CHARACTERIZATION OF ZIRCONIA COATED SILICA NANOPARTICLES FOR CATALYTIC REACTIONS

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By

Sunanda Giri

Under the Guidance of

Dr. G. Hota

DEPARTMENT OF CHEMISTRY

NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA

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6th May, 2008. **Sunanda Giri**

Guide Certificate

Dr. G. Hota
M.Sc., Ph.D
Department of Chemistry
National Institute of Technology,
Rourkela - 769008

Certificate

This is to satisfy that the thesis entitled "SYNTHESIS AND CHARACTERIZATION OF ZIRCONIA COATED SILICA NANOPARTICLES FOR CATALYTIC STUDY " being submitted by **Sunanda Giri** (Roll No. – 407CY113) for the partial fulfillment of the requirements for the award of M.Sc. degree in Chemistry at the National Institute of Technology, Rourkela, is an authentic work carried out by her under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other university or institute for the award of a degree or diploma.

Date:

Place: **Dr. Garudadhwaj Hota**

Abstract:

Silica nanoparticles and zirconia coated silica nanoparticles were prepared by Stober method.and various subsequent methods. The nanoparticles obtained were characterized by XRD, SEM, EDAX and IR analytical techniques. The XRD study of pure ZrO_2 shows well crystalline characteristics with the presence of 100% monoclinic phase. The coated nanoparticles are found to be amorphous in nature. SEM study indicate the particles to possess disorder morphology with the particle are attached to each other through grain boundary to form agglomerated structure. The zirconia coated silica nanoparticles were used as a efficient catalyst for the synthesis of Bis(indolyl) methane under solvent free condition.The Bis(indolyl) methane were obtained with high yield and purity.

Contents

CHAPTER-1

1.1 INTRODUCTION

Nanoparticles are essentially small clusters of atoms, which are about 1-100 nanometer in dimensions.The term nano derives from Greek word nanos, which means dwarf or extremely small. The prefix nano means one billionth (10^{-9}). Hence a nanometer is one billionth of a meter.

Nanoparticles are essentially larger than individual atoms or molecules but are smaller than bulk solid. Hence they are obeying neither absolute quantum chemistry nor laws of classical physics and have properties that differ markedly from those expected from the bulk materials. Because of their ultra fine size, high surface area and useful interfacial defects nanomaterials are used as the key component for many areas such as electronics and optical devices, pharmaceuticals, paints, coating, superconductors, semiconductors and catalysis.

Nanotechnology is the creation & utilization of materials, devices and system through the control matter at length scale less than 100 nm. It is recognized worldwide as key future technology that has the potential to unlock a new generation of materials & devices having revolutionary properties. It is a multidisciplinary area where principle of physics, chemistry and engineering are combined to create new useful knowledge.

1.2 Physical and Chemical Properties of nanoparticles

The main physical and chemical properties of nanomaterials include

1. High Density
2. Low thermal conductivity
3. Chemical inertness
4. Resistance to molten metals
5. Ionic electrical conduction
6. Wear resistance
7. High fracture toughness
8. High hardness
9. Use temperatures up to 2400°C

1.3 Different types of nanoparticles:

Extensive libraries of nanoparticles, composed of an assortment of different sizes, shapes, and materials, and with various chemical and surface properties, have already been constructed. The field of nanotechnology is under constant and rapid growth and new additions continue to supplement these libraries. The classes of nanoparticles listed below are all very general and multi-functional, however, some of their basic properties and current known uses in biotechnology, and particularly nanomedicine, are described here.

1.Fullerenes: Buckyballs and Carbon tubes

Both members of the fullerene structural class, buckyballs and carbon tubes are carbon based, lattice-like, potentially porous molecules. Buckyballs are spherical in shape while carbon tubes are cylindrical. The diameter of a carbon tube can be several nanometer but the length can be much greater, up to several micrometer, depending on its intended use. Carbon nanotubes have many applications in materials science due to their strength and unique electrical properties. However, they have also found use in the field of biomedicine as carriers for vaccines, drugs and other molecules. A single wall carbon tube is a one-atom-thick sheet of graphite, resembling chicken wire, rolled seamlessly into a tube. There are also multi-walled and other types of tubes depending on the shape, diameter, density (hollow versus solid) and other properties.

2.Liposomes

Liposomes are lipid-based nanoparticles used extensively in the pharmaceutical and cosmetic industries because of their capacity for breaking down inside cells, once their delivery function has been met. Liposomes were the first engineered nanoparticles used for drug delivery but problems such as their propensity to fuse together in aqueous environments and release their payload, have lead to replacement, or stabilization using newer alternative nanoparticles.

3.Nanoshells

Also referred to as core-shells, nanoshells are spherical cores of a particular compound surrounded by a shell or outer coating of another, which is a few nanometers thick. One application in biomedicine is to create nanoshells that absorb at biologically useful wavelengths, depending on the shell thickness. One common formula for the construction of nanoshells is to use silica for the core and another sticky compound to adhere gold particles to the outside surface, creating the shell. Nanoshells such as these have been used to kill cancer cells in mice. Once injected into a tumor, radiation is applied and the nanoshells heat up enough to kill the tumor cells.

4.Dendrimers

Dendrimers are highly branched structures gaining wide use in nanomedicine because of the multiple molecular "hooks" on their surfaces that can be used to attach cell-identification tags, fluorescent dyes, enzymes and other molecules. The first dendritic molecules were produced around 1980, but interest in them has blossomed more recently as biotechnological uses are discovered. Nanomedical applications for dendrimers are many and include nanoscale catalysts and reaction vessels, micelle mimics, imaging agents and chemical sensors, and agents for delivering drugs or genes into cells. There are two basic structural types. One is the globular structure with a central core from which branches radiate. The second type has no central core and consists simply of a series of highly branched polymers.

5.Quantum dots.

Also known as nanocrystals, quantum dots are nanosized semiconductors that, depending on their size, can emit light in all colours of the rainbow. These nanostructures confine conduction band electrons, valence band holes, or excitons in all three spatial directions. Examples of quantum dots are semiconductor nanocrystals and core-shell nanocrystals, where there is an interface between different semiconductor materials. They have been applied in biotechnology for cell labelling and imaging, particularly in cancer imaging studies.

6.Superparamagnetic nanoparticles

Superparamagnetic molecules are those that are attracted to a magnetic field but do not retain residual magnetism after the field is removed. Nanoparticles of iron oxide with diameters in the 5-100 nm range, have been used for selective magnetic bioseparations. Typical techniques involve coating the particles with antibodies to cell-specific antigens, for separation from the surrounding matrix. Used in membrane transport studies, superparamagenetic iron oxide nanoparticles (SPION) are applied for drug delivery and gene transfection. Targeted delivery of drugs, bioactive molecules or DNA vectors is dependent on the application of an external magnetic force that accelerates and directs their progress towards the target tissue. They are also useful as MRI contrast agents.

7. Nanorods

Typically 1-100 nm in length, nanorods are most often made from semiconducting materials and used in nanomedicine as imaging and contrast agents. Nanorods can be made by generating small cylinders of silicon, gold or inorganic phosphate, among other materials. Current concerns over the safety of nanoparticles have lead to the development of many new facets of research. As a result, our collection of knowledge about nanoparticle interactions within cells is still rapidly growing.

1.4.CORE SHELL/COMPOSITE NANOPARTICLES

The synthesis of nanoparticles, their surface modification via core-shell and composite formation is attracting increasing attention arising out of its growing awareness in technological applications. The method of preparation of core shell and composite particles is a new direction in engineering. Recently, attempts have been made to prepare core shell (coated) and composite nanoparticles of organic-organic, organic-inorganic, inorganic-inorganic materials.

Coated nanoparticles are essentially defined as the particles containing a core and a shell and have dimensions in the nanometer range. Core-shell/composite nanoparticles often exhibit improved physical and chemical properties over their single-component counterparts, and hence are potentially useful in a wide range of applications. These core and shell nanomaterials can increase the luminescence quantum yield due to improved passivation of the surface and can be more physically robust than the bare organically passivated clusters. The scientific interest arises from the diverse attributes of core and shell nanoparticles as a model building block towards functional materials, including 1) size dispersity, 2) core and shell processability, 3) solubility, 4) stability and tenability, 5) capability of self assembly and 6) reactivity involving optical, electronic, magnetic, catalytic and chemical/biological phenomena. These core shell nanoparticles have applications in the areas such as microelectronics, quantum dots, optics, magnetic, photoactive devices and so on. The controlled synthesis of novel, uniform and stable core-shell and composite nanoparticles has been remained as a technical challenge for many years.

1.5.Various methods for Synthesis of nanoparticles :

The synthesis and study nanoparticles, has become a major interdisciplinary area of research over the past 10 years. The size, morphology as well as the properties of nanoparticles basically depends on the methods of preparation. All the processes can be broadly divided into two processes, physical methods and chemical methods.

❖ Chemical techniques:

- Chemical precipitation
- Sol-gel technique
- Polymeric precursor
- Micro emulsion
- Hydrothermal synthesis
- Combustion synthesis.
- Dc Arc Plasma Process
- Rf Plasma Process
- Plasma Rapid Solidification Technology
- Reactive Electrode Submerged Arc

❖ Physico-chemical technique :

- Spray pyrolysis
- Gas condensation
- Freeze drying
- Ultrasonic methods.

1. Chemical precipitation method

Formation of a separable solid substance from a solution, either by converting the substance into an insoluble form or by changing the composition of the solvent to diminish the solubility of the substance in it. The distinction between precipitation and crystallization lies largely in whether emphasis is placed on the process by which the solubility is reduced or on that by which the structure of the solid substance becomes organized.

2. Vapor-phase synthesis

Formation of nanoparticles takes place in gas phase. In this synthesis technique the condensation of atoms and molecules is carried out. The vapor phase synthesis is not new and many multinational companies have been using flame reactors for decades for producing large quantities of nanoparticles. The flame reactors were used for forming various nanoparticles such as carbon black and titanium dioxide.

3. Simple solution combustion method:

In this process a metal nitrate and a organic compound is used as a oxidizer and fuel respectively. The exothermic combustion of the fuel leads to the release of a large amount of energy which is used to convert the metal salt to metal oxide. This method has been used for the preparation of nanosize alumina, ceria, yttria, zirconia, CeO_2-ZrO_2, t-ZrO_2-Al_2O_3 and Y_2O_3-ZrO_2 etc. using corresponding metal nitrate, ammonium nitrate and glycine redox mixtures. The process is fast (instantaneous) and yields high purity, homogenous crystalline products with desired composition and structure.

1.6 Applications of Nanoparticles :

In recent years, nanoparticles, coated and composite nanoparticles has been used in various fields of science, engineering and industrial applications by virtue of their specific, novel and useful properties. Some of these applications are described briefly as follows.

A. Heterogeneous catalysis

Heterogeneous catalysis represents one of the oldest and common applications of nanoparticles. Catalytic properties of nanoparticles are enhanced due to presence of large fraction of the reactive atoms that reside on the surface. There are many applications of metal, oxide and semiconductor nanoparticles in important area of applications such as three way catalysis, fuel cells, cracking and reforming.

B. Optical and Electronic Applications

Semiconductor nanoparticles have unique optical and electrical properties. These are used for preparing computer chips, laser diode, photo emitter, and transducer. Nanostructured semiconductors are known to show various non-linear optical proper ties. These semiconductors are also used as window layers in solar cells.

C. Paints and coatings

Nano-sized particles are used as pigments in paint industries. Carbon black, an amorphous form of carbon, is used in rubber, pigments and ink. The use of nanoparticles, such as SiO_2, TiO_2, $CaCO_3$ and ZnO in coatings industry provide long lasting coating. The coatings are useful for detective applications such as finger print identifications.

D. Metal and ceramics

Ceramic nanoparticles have widespread applications in the material processing technology. The nanostructured metals can be used for fabrication of different cutting tools and devices. These also extensively used in magnetic recording tapes.

E. Drug delivery

Nanocapsules have several advantages as a delivery system over the micro particles because of their targeted surfaces, easy penetration into the arterial wall and the ability to cross the blood-brain barrier.

1.7 OBJECTIVE OF THIS STUDY

The main objective of the present study include

1. To synthesize zirconia by pH controlled precipitation method.
2. To synthesize silica nanospheres by stober method.
3. To Coat the silica spheres with zirconia nanoparticles.
4. To study and evaluate the catalytic properties of the SiO_2@ZrO_2 nanoparticles.

1.8 ORGANIZATION OF REPORT:

This report has been organized in four chapters .The present chapter is an introductory chapter, chapter two describes the experimental method used for preparation of zirconia coated silica composites nanoparticles. The result obtained has been discussed in chapter three. The main finding of this work has been summarized in chapter four.

CHAPTER-2

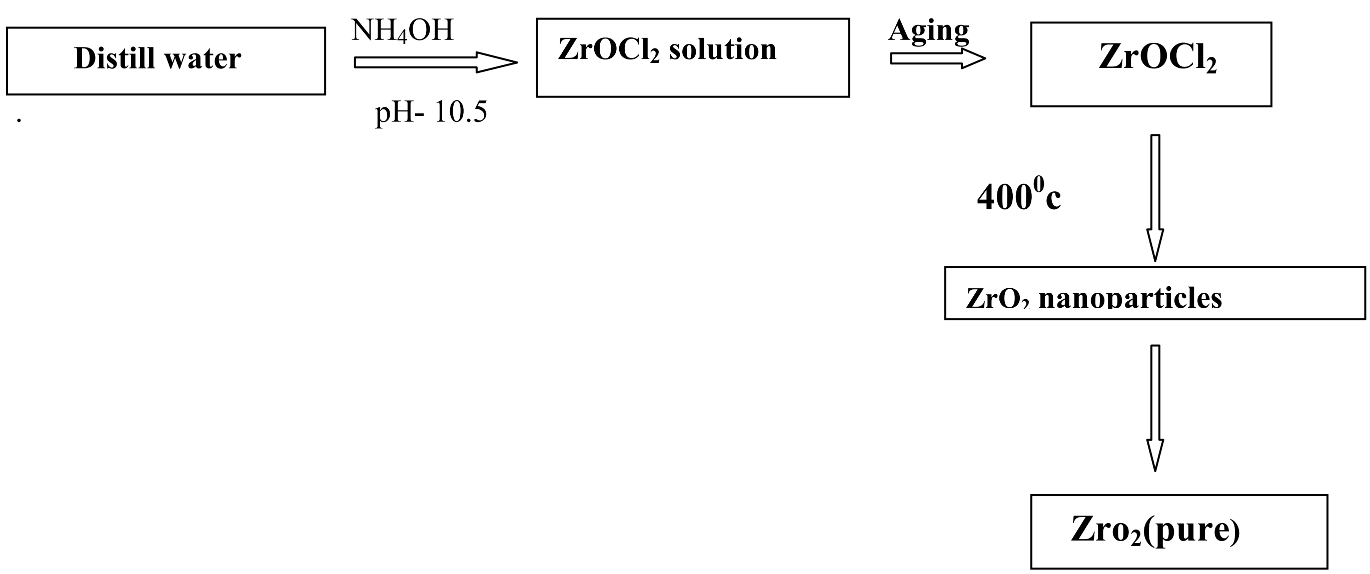
Experimental Details :

2.1 Materials: The chemicals used in this experiment are $ZrOCl_2$. $8H_2O$, Tetra ethyl orthosilicate (TEOS), concentrated NH_4OH and ethanol solution. All the chemicals are used as received, without further purification. Distilled water was used throughout the experiment.

2.2. Synthesis of zirconia nanoparticles:

200 ml of distilled water was taken in a one litre beaker over a magnetic stirrer with constant stirring. Then NH_4OH was added to adjust the pH about 10.5, After maintaining the pH, 13.05 gm of $ZrOCl_2$ solution was added in a dropwise manner with constant stirring and also maintain the pH of reaction mixture. Then the resulting nanoparticles was filtered and it was washed with hot distill water for 4-6 times. Finally, the nanoparticle was kept in oven at 100^0C for 12 hour followed by calcination at 400^oC for 2 h at.

Schematic representation:



2.3.Synthesis of silica nanoparticles by stober method

Silica particles were prepared by a simple one-step protocol which involves the condensation of tetraethyl orthosilicate (TEOS) in ethanol: water mixture under alkaline conditions at room temperature.

First 20 ml of ethanol was taken in a 50ml beaker, and then 2ml of TEOS was added followed by 4ml of concentrated NH_4OH. After that it was stirred for 8 hour. The mixture thus obtained was centrifuged to get the silica nanoparticle.

Schematic representation:

$$\text{ETHANOL} + \text{TEOS} + NH_4OH \xrightarrow{\text{Stirring for 8 hrs}} \text{centrifuge} \longrightarrow SiO_2$$

2.4.Coating of zirconia on Silica nanoparticle

In order to prepare silica nanoparticles, we have used the Stober synthesis in which first 20 ml of ethanol was taken in a 50 ml beaker then simultaneously 2ml of TEOS was added followed by 4 ml of NH_4OH and stirring was done for 8 hrs. After the obtained mixture was centrifuged, the silica nanoparticles were dispersed in distill water and $ZrOCl_2$ was added by making the medium alkaline by addition of NH_4OH to maintain the pH at 10-10.5 .The solution mixture thus obtained was filtered and it was dried at 100°C and then calcined at 400°C for 2 hr.The product was silica spheres which were coated by zirconia nanoparticles.

2.5. Characterization of the nanoparticles

The synthesized nanoparticles are characterized by the following techniques

X-ray diffraction

The X-ray diffraction patterns of the samples were recorded on a Siemens D-500 diffractometer using Ni-filtered CuK_α radiation. The XRD measurements were carried out in the 2θ range of 20-70^o with a scan speed of 2 degrees per minute using Bragg-Brantano configuration.

Scanning Electron Micrograph

Scanning electron microscopy pictures were taken using JEOL JSM-5300 microscope (acceleration voltage15 kV). The sample powders were deposited on a carbon tape before mounting on a sample holder for SEM analysis.

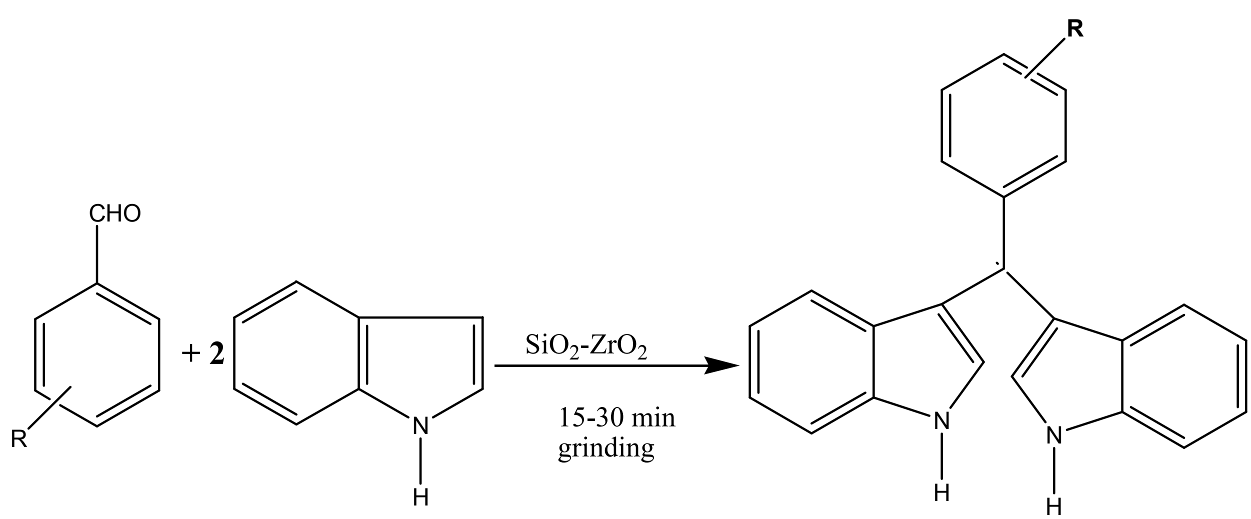
IR Specroscopy

The IR spectra of the samples were recorded (as KBr pellets) were recorded using a Perkin-Elmer infrared spectrophotometer with a resolution of 4 cm^{-1}, in the range of 400–4000 cm^{-1}.

2.6.Catalytic organic synthesis reactions by using SiO_2@ZrO_2:

Synthesis of bis(indolyl) methane synthesis by click chemistry

The synthesis of bis(indolyl) methane was performed by mixing two mmol of indole and 1 mmol of aromatic aldehyde in presence of SiO_2-ZrO_2 catalyst (Scheme 1). The mixture was grinded by a mortar and pestle for the required amunt of time. During the process the reactants change to liquid form and then solidified. The formation of the product was monitored by TLC. After completion of the reaction, the reaction mixture was treated with 15 ml of dichloromethane and then the catalyst was filtered. The product were recovered from dichloromethane solution and then recrystallized.



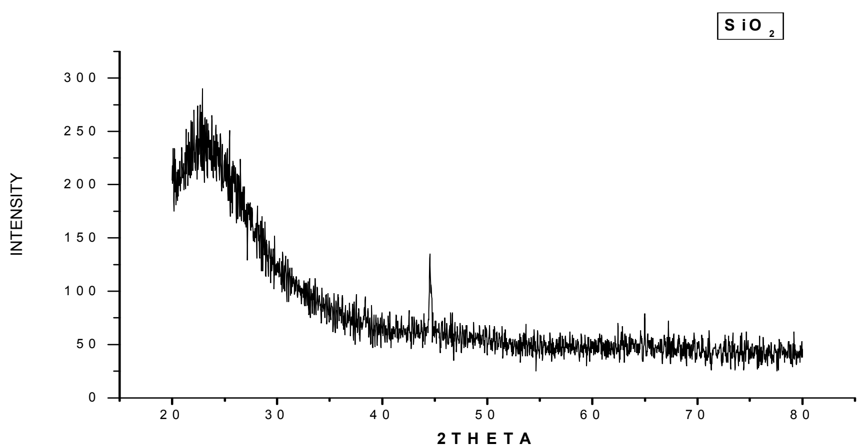
(Scheme 1)

CHAPTER - 3

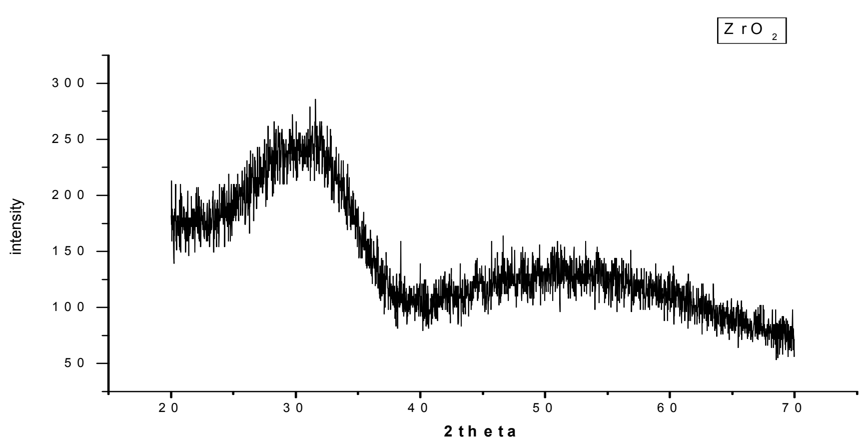
RESULT AND DISCUSSIONS

3.1 XRD study

The X-ray diffraction pattern of the silica, zirocnia and the solica coated zirconia nanoparticles are shown in figure 1.



(a)



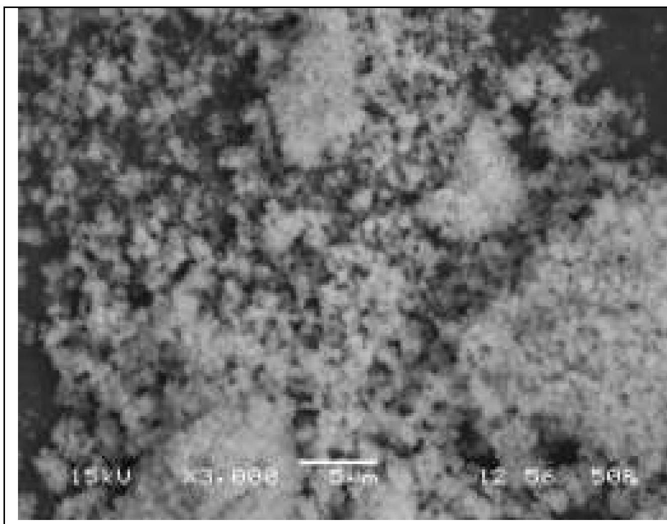
(b)

Figure 1. The XRD patterns of (a) silica, (b) Zirconia coated silica nanoparticles

The pure zirconia prepared by this method was found to be well crystalline in nature with the peak positions corresponding to the presence of monoclinic phase. The silica prepared by the Stobber method in contrast is purely amorphous in nature. No well defined peaks are observed in case of the pure silica as well as he zirconia coated silica nanoparticles.

3.2 SEM/EDX

SEM/EDX analysis are done for silica and zirconia coated silica nanoparticles synthesized by stober's synthesis and subsequent modification. Figure 2 shows the SEM and the EDAX profile of the pure silica particles prepared by the Stober method. Te silica particles are of uniform size however, there are considerable agglomeration of the particles along the grain boundary resulting in the formation of the secondary particles. The EDX analysis also indicates the presence of elemental Si and O in the sample with a relative proportion corresponding to the SiO_2 particles.



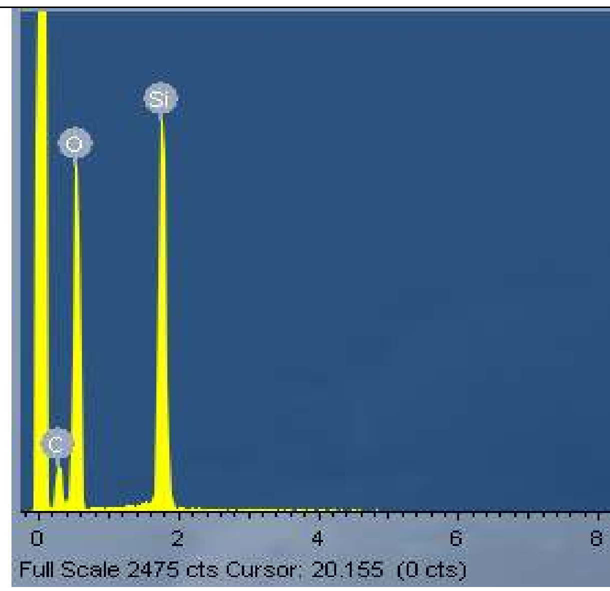


Figure 2. The SEM-EDX of silica particles

The SEM-EDX analysis of the SiO2-ZrO2 nanoparticles are presented in figure 3. The coated particles shows a completely disordered morphology which is different from the silica paticles. The EDX analysis indicate the present of silica as well as the zirconia particles in the composite sample.

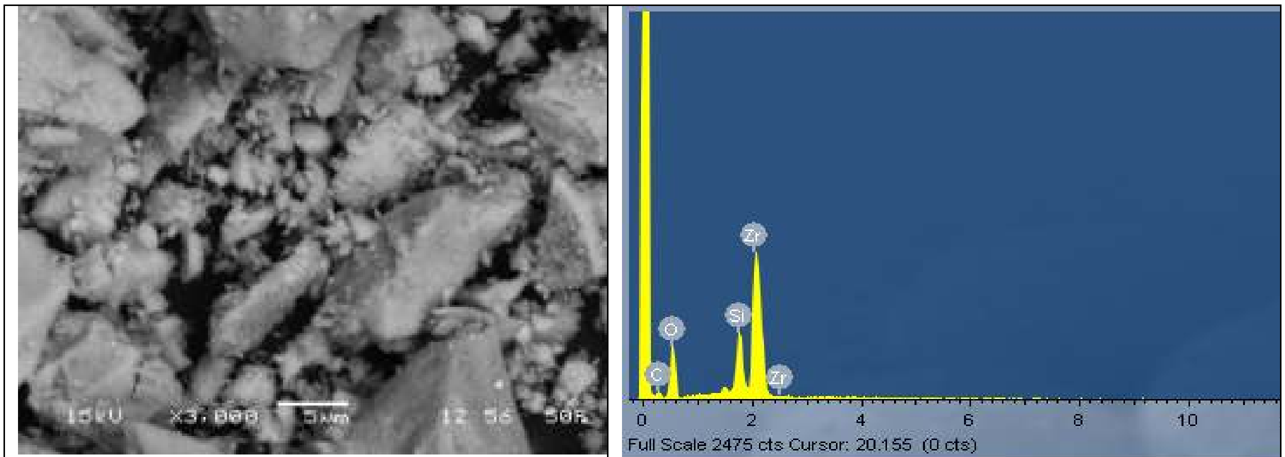


Figure 3. The SEM-EDX of SiO_2-ZrO_2 particles

3.3 IR spectroscopy :

The IR spectra of the zirconia coated silica particlde is shown in figure 3. The prominent band in the region of 3400-3600 cm^{-1}, corresponds the structural O-H stretching of the nanomaterials. In the bending mode region two bannds are observed in the range of 1500-1700 cm^{-1}, which is due to the O-h bending. In addition, the band at 900 cm^{-1}-1000cm^{-1} can be assigned to the Zr—O bond.

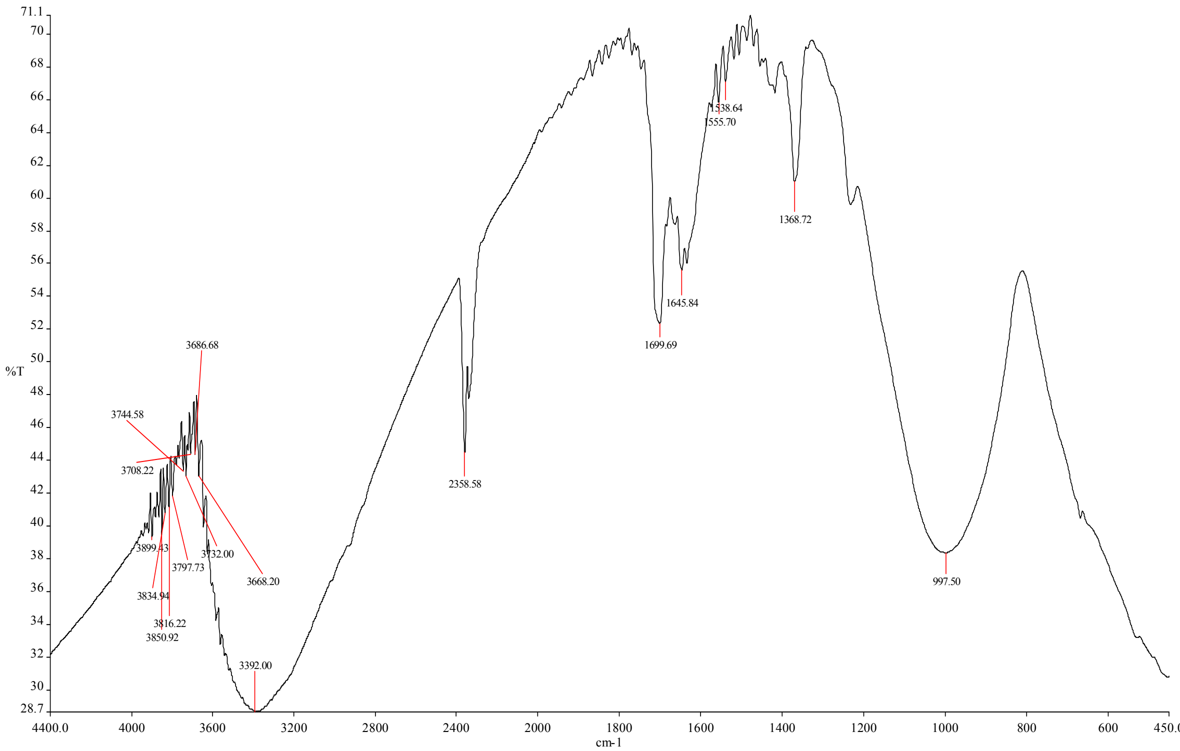
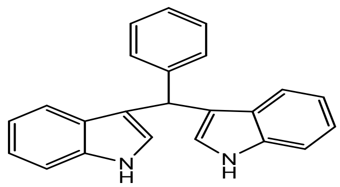
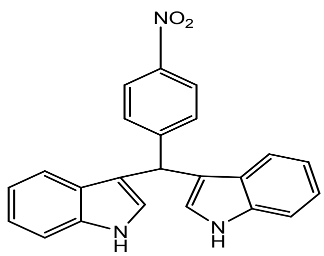
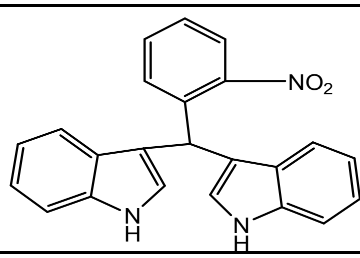
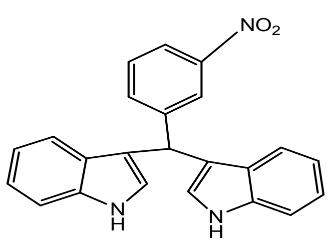
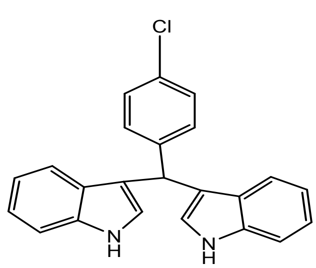


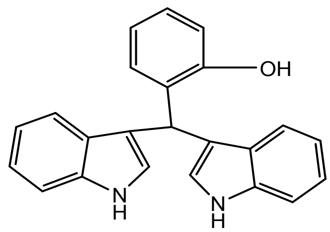
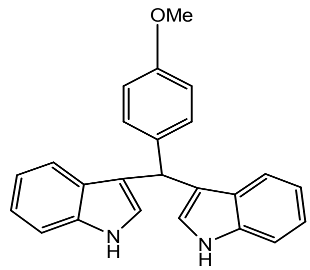
Figure 4. IR spectra of ZrO_2 coated SiO_2 nanoparticle

3.4 Catalytic studies

The SiO_2 @ ZrO2 nanoparticles was used as a environmental friendly catalyst for the synthesis of bis(indolyl)methane. It was observed that the catalyst is quite active for the reaction with good yield of the products are obtained with in 10-30 minutes of mechanical grinding (Table 1). The electrophilic substitution reaction on indole with aldehyde give excellent yields in presence of the catalyst and the catalyst was found to be recyclable.

Table 1. Synthesis of bis(indolyl) methane in presence of SiO2@ZrO2 catalyst

Sl no	Aldehyde	Product	Time (min)	Yield (%)	IR (cm^{-1})
1	C_6H_5		**30**	**65**	**3052, 1599, 1490, 792**
2	4-$NO_2C_6H_4$		**20**	**72**	**3052, 1593, 1506, 1487, 873**
3	2- $NO_2C_6H_4$		**20**	**90**	**3052, 1596, 1510, 1499, 886**
4	3- $NO_2C_6H_4$		**20**	**85**	**3052, 1595,**
5	4-Cl C_6H_4		**30**	**93**	**3052, 1617, 1486, 856, 786**

6	2-OH C6H5		**25**	**71**	**3454, 3050, 1156, 1610, 1434, 862**
7	4-OMeC6H5		**40**	**83**	**3053, 1608, 1454, 1244, 837**

Chapter 4.

CONCLUSION :

The main conclusion of the present work is as follows

- Silica nanoparticles and zirconia coated silica nanoparticles were prepared by Stober method.and various subsequent methods.
- The XRD study of pure ZrO_2 shows well crystalline characteristics with the presence of 100% monoclinic phase.
- The coated nanoparticles are found to be amorphous in nature.
- SEM study indicate the particles to possess disorder morphology with the particle are attached to each other through grain boundary to form agglomerated structure.
- The zirconia coated silica nanoparticles were used as a efficient catalyst for the synthesis of Bis(indolyl) methane under solvent free condition.
- The Bis(indolyl) methane were obtained with high yield and purity using the silica coated zirconia nanoparticles as catalyst .

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