CHAPTER 2
MATERIALS AND METHODS

This chapter describes the various materials and methods that are used to achieve the objectives of the present investigation.

2.1 RAW MATERIALS AND CHEMICALS

The commercial bauxite (50–55 wt.% Al₂O₃) was obtained from the Chatrapur region, coastal part of Orissa, India. Zircon sand (63 wt.% ZrO₂) and ilmenite (45.8 wt.% of TiO₂) were obtained from the Kanniakumari region, coastal part of Tamil Nadu, India. As received natural minerals such as bauxite, zircon sand and ilmenite were used as starting material respectively for the production of Al₂O₃, ZrO₂ and TiO₂ nanoparticles. Sodium hydroxide, hydrochloric acid, sulphuric acid, nitric acid, acetic acid, polyethylene glycol and ammonia chemicals of analar grade samples were received from Merck, Mumbai, India and used as received in the present investigation. Organic surfactant namely N-cetyl-N,N,N,trimethyl ammonium bromide and 4,5-dihydroxy-m-benzenedisulfonic acid disodium salt was received from Loba fine chemicals, Mumbai, India and used for nanoparticles preparation and dispersion. Tetraethyl orthosilicate (TEOS) was received from Aldrich and used for silicate sol-gel preparation without any further purification. All other chemicals were of analytical reagent grade and were used as received. Double distilled water was used throughout this investigation.
2.2 Synthesis of Al₂O₃ Nanoparticles

Bayer process was used to extract the synthetic Bayer liquor (sodium aluminium hydroxide) from bauxite which is used as the precursor for the synthesis of Al₂O₃ nanoparticles.

2.2.1 Extraction of Bayer Liquor from Bauxite

The commercial bauxite consists of 50 wt.% of Al₂O₃ was obtained from the Chatrapur region of Orissa, India and used as the starting material for synthesis of Bayer liquor. Table 2.1 presents the physical and chemical analysis of bauxite.

Table 2.1 Physical and chemical analysis of bauxite

<table>
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<tr>
<th>Physical Analysis</th>
<th>XRF Chemical Analysis</th>
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<td>Surface area (m²/g)</td>
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<td>Loss on Ignition (%)</td>
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</table>
The fine grained bauxite (25g) was roasted at 423 K for 1 h to remove the moisture content. The dry mixture, which consists of 66.67 wt.% of roasted bauxite and 33.33 wt.% of sodium hydroxide (Merck GR, 99.9%) was fused at 873 K for 3 h in a muffle furnace. Scheme 2.1 shows the fusion reaction of bauxite with sodium hydroxide. The fusion product was leached with 250 ml of double distilled water. The obtained solution mixture was adjusted to a pH value of 13 using 5N sodium hydroxide solution followed by vigorous magnetic stirring at 353 K for 1 h. Thus, the stirred solution was filtered using ordinary filter cloth followed by Whatman (Grade No.: 40) filter paper. Then, the filtrate (Bayer liquor) was used as a precursor for the synthesis of Al$_2$O$_3$ nanoparticles.

2.2.2 Precipitation Synthesis

The synthetic Bayer liquor (250 ml) was hydrolysed by the drop wise addition of 3M H$_2$SO$_4$ (Merck GR, 98%) solution under constant stirring which leads to precipitation of an amorphous hydrated aluminium oxide at pH 7. Scheme 2.2 represents the precipitation process of hydrous alumina from synthetic Bayer liquor. At

\[
\text{Fe}_2\text{O}_3\cdot\text{SiO}_2\cdot\text{TiO}_2 \cdot \text{Al}_2\text{O}_3\cdot3\text{H}_2\text{O} + \text{NaOH} \\
\text{Bauxite} \\
\downarrow \\
1. \text{Alkali fusion} \\
2. \text{Leached with DD water} \\
\downarrow \\
\text{NaAl(OH)}_4 + \text{Fe}_2\text{O}_3\cdot\text{SiO}_2\cdot\text{TiO}_2 \\
\text{Bayer liquor} \quad \text{Red mud} (\text{Residue})
\]

**Scheme 2.1 Schematic representation of the extraction of Bayer liquor from bauxite**

The fine grained bauxite (25g) was roasted at 423 K for 1 h to remove the moisture content. The dry mixture, which consists of 66.67 wt.% of roasted bauxite and 33.33 wt.% of sodium hydroxide (Merck GR, 99.9%) was fused at 873 K for 3 h in a muffle furnace. Scheme 2.1 shows the fusion reaction of bauxite with sodium hydroxide. The fusion product was leached with 250 ml of double distilled water. The obtained solution mixture was adjusted to a pH value of 13 using 5N sodium hydroxide solution followed by vigorous magnetic stirring at 353 K for 1 h. Thus, the stirred solution was filtered using ordinary filter cloth followed by Whatman (Grade No.: 40) filter paper. Then, the filtrate (Bayer liquor) was used as a precursor for the synthesis of Al$_2$O$_3$ nanoparticles.

2.2.2 Precipitation Synthesis

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this stage of the reaction, a characteristic white precipitate of Al(OH)$_{3-x}$H$_2$O was appeared. The resultant precipitate was aged at 353 K for 12 h. After the completion of ageing period, the precipitate was filtered using Whatman (Grade No.: 40) filter paper and washed for several times in double distilled water until it was free from sodium sulphate and unreacted components. Then, the precipitate was dried in a hot air oven at 393 K for 1 h. The precipitation of hydrous alumina was performed with three precipitants: a) 3M H$_2$SO$_4$, b) 6M HCl and c) 6M HNO$_3$. The above process was repeated for HCl and HNO$_3$. All the three synthesised samples (a, b and c) were calcined at 773 K for 6 h in a static air atmosphere with a heating rate of 5 K min$^{-1}$ and then cooled to room temperature inside the oven. Finally, the soft aggregates of the calcined samples were disaggregated by ball milling in a dry medium at 500 rpm for 4 h, using a planetary ball mill (PM 100; Retsch, Germany). The overall yield of alumina nanoparticles in the present precipitation process was 86±2% i.e., 10.8g out of 25g of bauxite with 50 wt.% of Al$_2$O$_3$.

\[
\begin{align*}
2\text{NaAl(OH)}_4 + \text{H}_2\text{SO}_4 &\xrightarrow{\text{Precipitation}} 2\text{Al(OH)}_3\cdot\text{H}_2\text{O} + \text{Na}_2\text{SO}_4 \\
\text{Bayer liquor} &\xrightarrow{\text{Precipitate}} \\
\text{Al(OH)}_3\cdot\text{H}_2\text{O} &\xrightarrow{\text{Dried at 393 K}} \text{Al(OH)}_3\cdot\text{H}_2\text{O} + \text{H}_2\text{O} \\
\text{Wet} &\xrightarrow{\text{Dry}} \\
2\text{Al(OH)}_3\cdot\text{H}_2\text{O} &\xrightarrow{\text{Calcined at 773 K}} \text{Al}_2\text{O}_3 + 5\text{H}_2\text{O} \\
\text{Dry} &\xrightarrow{\text{Al}_2\text{O}_3 + 5\text{H}_2\text{O}}
\end{align*}
\]

Scheme 2.2 Schematic representation of the synthesis of Al$_2$O$_3$ nanoparticles by conventional precipitation technique
2.2.3 Sol-Gel Process

A 250 ml of extracted Bayer liquor was cooled to room temperature. Organic surfactant namely N-cetyl-N,N,N,trimethyl ammonium bromide (Loba, 99%) was added into the Bayer liquor, which was maintained at 1 mM concentration. Six molar solution of acetic acid (Merck GR, 99%) is added to the Bayer liquor to initiate the flocculation and the effective flocculation was achieved in the pH range between 7.5 to 8.5. The sol-gel process was shown in Scheme 2.3. The obtained aluminium hydroxide gel was digested at 353 K for 28 h followed by drying at 423 K for 1 h in a hot air oven. Digestion led to control the nucleation of the gel. Then, the dried gel was washed with water to remove the organic surfactant and sodium acetate from the gel matrix. In order to reduce the agglomeration of the powder, water was replaced with ethanol, and then the gel was dried at 353 K for 1 h. The dried gel was fired at 773 K for 6 h in a stationary air atmosphere with a firing rate of 5 K min^{-1} to get nanosized Al₂O₃ particles. Ultimately, the fired samples of soft agglomerates were non-agglomerated using a planetary ball milling (PM 100, Retsch, Germany) in a dry medium at 500 rpm for 3 h. The total yield of present sol-gel process was 82±3% in lab scale.
2.2.4 Spray Pyrolysis

2.2.4.1 Preparation of Aluminium Nitrate Precursor

The extracted Bayer liquor (250 ml) was hydrolysed through the drop by drop addition of 6M HNO$_3$ (Merck GR, 69%) solution under constant stirring. An amorphous hydrated aluminium oxide was precipitated at pH 7. A characteristic white precipitate of Al(OH)$_3$.H$_2$O was appeared at this stage of the reaction. The obtained precipitate was filtered using Whatman (Grade No.: 40) filter paper and washed several times in double distilled water until it was free from sodium nitrate and unreacted components. Further, the precipitate (Al(OH)$_3$.H$_2$O) was dissolved in 500 ml of 1M HNO$_3$ solution to obtain the aluminium nitrate solution.
The schematic representation of the preparation of aluminium nitrate precursor was shown in Scheme 2.4.

\[
\begin{align*}
\text{NaAl(OH)}_4 + \text{HNO}_3 & \quad \xrightarrow{\text{Precipitation}} \quad \text{Al(OH)}_2\text{H}_2\text{O} + \text{NaNO}_3 \\
\text{Bayer liquor} & \quad \text{Precipitate} \\
\end{align*}
\]

\[
\begin{align*}
\text{Al(OH)}_3\text{H}_2\text{O} + 3\text{HNO}_3 & \quad \xrightarrow{\text{Dissolution}} \quad \text{Al(NO}_3)_2\text{4H}_2\text{O} \\
\text{Hydrated Aluminium Oxide} & \quad \text{Aluminium nitrate solution} \\
\end{align*}
\]

Scheme 2.4 Schematic representation of the preparation of aluminium nitrate precursor

2.2.4.2 Production of Al\textsubscript{2}O\textsubscript{3} Nanoparticles

The perfect uniform solution of aluminium nitrate was used as the starting precursor in spray pyrolysis to get nano Al\textsubscript{2}O\textsubscript{3} particles. The schematic diagram of automated spray pyrolysis experimental set-up used for mass production of nano Al\textsubscript{2}O\textsubscript{3} particles is shown in Figure 2.1. The present independent spray pyrolyser experimental set-up primarily consist of a) an atomiser which converts the starting solution into droplets, b) automated anti-blocking unit, c) tubular electric furnace with hot air blower, d) two fluid nozzle with compressed air inlet and sample feeding port, e) feed pump which facilitate the flow rate of precursor, f) reaction chamber, g) cyclonic sample collectors and h) purification system.
Figure 2.1 Schematic diagram of automated spray pyrolyser experimental set-up
The total automated experimental set-up is controlled by single control panel. The working features of automated system are explained in the following headings:

a) Atomiser

It consists of two fluid nozzle with different diameters such as 0.7 mm, 1.0 mm and 1.5 mm made up of titanium metal. The atomiser is used to convert the precursor solution into fine droplets called atomisation. The atomised droplets size depends on the nozzle size and pressure of compressed air. The atomised spherical droplets get decomposed to form spherical particles.

b) Automated Anti-block Unit

The blocking of nozzle has been anti-blocked by a sharp stainless steel rod (AISI 316L) which is automatically operated in a fixed interval of time. It is an essential process required for the continuous operation of the system.

c) Tubular Electric Furnace with Hot Air Blower

It consists of one main heater and one auxiliary heater (supporting heater) with temperature controller. The auxiliary heater is used to produce hot air up to the required temperature to air blower. The temperature of air flow has been monitored by inlet temperature controller which is present in hot air blower. An effective temperature sensor (Maxthermo, MC-2438) has been used to monitor the fixed temperature with an accuracy of ± 5 K. The blower speed is controlled employing rpm controller (Selec, PIC 101).
d) **Two fluid Nozzle with Compressed Air Inlet and Sample Feeding Port**

In spray pyrolyser, two way fluid nozzles is located at the top of reaction chamber which consists of one compressed air inlet port and one sample feeding port. The atomiser is formed by mixing the precursors with pressurised air at the edge of two fluid nozzles. The pressure of compressed air is regulated in PSI employing waaree pressure gauge regulator.

e) **Feed Pump**

Peristaltic feed pump with precise rpm controller (Selec, PIC 101) is used in the system to control the flow rate and uniform feeding of precursors in sample port. Adjustable speed pump is operated at a constant speed which is selected by the user. The pump is made up of stainless steel (AISI 316L) corrosion resistance material. The pump is capable to run continuously and it can maintain the performance of atomiser. The compressed fluid goes from initial stage to reaction chamber by constant and continuous manner and it has the ability to pump in respective direction with equal efficiency. The operation of the pump is controlled using control panel.

f) **Reaction Chamber**

A cylindrical stainless steel (AISI 316L) tubular reaction chamber is connected with hot air blower and two fluid nozzles which are located at the top of the chamber. At the other end of the reactor, three different cyclones are connected in a zigzag arrangement. It consists of four different parallel temperature zones which have been used to identify chamber temperature at different places. The atomised droplets get decomposed at the reaction chamber to form ultra fine spherical particles which are forced out to cyclones by internal air pressure.
g) **Cyclonic Sample Collectors**

The decomposed nanopowders have been collected on three different cyclonic collection ports. The tangential location of orifice develops a downward, spiraling flow of solid particles. The centrifugal force developed at the collection chamber walls in downward direction which is greater than that of gravity. This centrifugal force spins out the solid particles from the orifice. The solid particles strike and get deposited on the collector wall. The coarse, fine and ultra fine particles have been collected respectively at the initial, middle and end of collection port.

h) **Purification System**

It consists of two main parts such as reverse air jet filter and wet scrubber to avoid the fine particles enter into environments. The few uncollected ultra fine particles have been deposited by reverse air jet filter and the decomposed gas molecules like NO\textsubscript{2} have been dissolved in flow water at wet scrubber which prevents the air pollution. In addition, wet scrubber contains an outlet port to release the drain.

The method is based on atomising the precursor and injecting the spray into a tubular reaction chamber. The atomised droplets of the precursor are converted into nanosized oxide crystallites or nano sized entities during their flow through the tubular reaction chamber. The hot air is introduced into the reaction chamber followed by the precursors are sprayed into chamber with the use of two fluid nozzle along with compressor air inlet. The feed pump is used to control the flow rate of precursors and formation of atomiser. The formation of atomiser is controlled by controlling the pressure of compressed air. The sprayed and atomised nano entities are decomposed to obtain nano metal oxide powders which have been collected at different cyclones. The decomposed masses like H\textsubscript{2}O, NO\textsubscript{2} etc., are eliminated by ceramic water filter which is in the purification system. The above process is known as spray pyrolysis or aerosol
decomposition synthesis or droplet to particle conversion. The total process is automated using a single power control panel which controls the process automatically.

In spray pyrolysis, two stage reactions such as solvent evaporation and decomposition were frequently takes place in solution droplets. Figure 2.2 shows the automated spray pyrolysis experimental set-up. The spray pyrolysis set-up mainly consists of spray nozzle, stainless steel (AISI 316L) tubular reaction chamber and hot air blower assembly. The sprayer itself consists of two concentric nozzles (two fluid nozzle) with an outer nozzle of diameter 4 mm and an inner nozzle of diameter 1 mm. One end of the nozzle was connected to compressor air inlet and a reservoir (for holding the precursor) through silicone tube, while other end of the nozzle was connected with tubular reaction chamber which inturn connected with hot air blower and cyclones. An aqueous aluminium nitrate precursor was flow into the inner nozzle through the peristaltic feed pump. The feed pump was used to control the flow rate of precursor. The feed rate was optimised and maintained as 0.2 L h\(^{-1}\). Passage of the compressed air (30-40 PSI) through the outer nozzle was forced out the contents of the precursor in an inner nozzle. Thus, the precursor was atomised to generate spray. The formation of atomiser was controlled by controlling the pressure of compressed air. Then, the atomised nanosized entities of aluminium nitrate droplets were injected into hot air zone, generated through hot air blower in tubular reaction chamber. The temperature of reaction chamber was maintained in the temperature range of 673 to 773 K by adjusting the furnace temperature of hot air blower. In hot air zone, the atomised droplets were dried and the constituent aluminium nitrates were decomposed at 673 K to form nano sized Al\(_2\)O\(_3\) particles. The typical decomposition reaction of aluminium nitrate precursor in spray pyrolysis is given in Scheme 2.5.
Figure 2.2 Automated spray pyrolysis experimental set-up

I. Cyclone
II. Tubular Furnace with Air Blower
III. Two-Fluid Nozzle
IV. Peristaltic Feed Pump
After the completion of one full cycle, the nano Al$_2$O$_3$ particles obtained were collected in the cyclones. There are two main parts of cyclones which are used for the powder collection such as second and third cyclones. These two cyclones consist of fine powders which are in nano range. The collected samples were characterised as it is without post synthesis treatment such as customization and sintering of the particles. The present spray pyrolyser operating conditions yields 26 - 28g of nanopowder for the operation of the system for 8 h. The overall output of present mini-modal spray pyrolyser was 74±5%.

2.3 SYNTHESIS OF ZrO$_2$ NANOPARTICLES

The zirconyl nitrate solution was extracted from zircon sand using alkali fusion followed by the acid extraction which has been used as the precursor for production of ZrO$_2$ nanoparticles.

2.3.1 Extraction of Zirconyl Nitrate from Zircon Sand

Zircon sand (ZrSiO$_4$) obtained from the Kanyakumari region, a coastal part of Tamil Nadu, India was used as a starting material for precursor synthesis without further purification. Physical and chemical analysis of zircon sand is given in Table 2.2. Twenty five grams of zircon sand was powdered and roasted at 423 K for 1 h to remove the moisture content followed by boiling with 25 ml of concentrated
hydrochloric acid (Merck GR, 35%) at 323 K for 1 h on a hot plate. The water soluble metal chlorides which are present in the acid treated sand were removed by washing with double distilled water. The residue was further fused with about four times its weight (100g) of sodium hydroxide (Merck GR, 98%) at 873 K for 3 h. The alkali fusion and acid extraction reactions were shown in Scheme 2.6. The fused mass was cooled to room temperature and then, the formed hot cake was leached with water and filtered using ordinary filter cloth. The insoluble residues consist of zirconium hydroxide, which was dissolved in 250 ml of 6M nitric acid (Merck GR, 69%) and then filtered using ordinary filter cloth. The obtained clear filtrate was repeatedly evaporated to dryness and the residue was extracted by Whatman (Grade No.: 40) filter paper using 250 ml of double distilled water. The extracted zirconyl nitrate was used as the precursor for the synthesis of nano ZrO₂ particles.

\[
\begin{align*}
\text{ZrSiO}_4 + 4\text{NaOH} & \xrightarrow{\text{Alkali fusion}} \text{Na}_2\text{ZrO}_3 + \text{Na}_2\text{SiO}_3 + 2\text{H}_2\text{O} \\
\text{Fused mass} & \\
2\text{Na}_2\text{ZrO}_3 + 4\text{H}_2\text{O} & \xrightarrow{\text{Hydrolysis}} 4\text{NaOH} + 2\text{ZrO(OH)}_2 \\
\text{ZrO(OH)}_2 + 2\text{HNO}_3 & \xrightarrow{\text{Extraction}} \text{ZrO(NO}_3)_2 + 2\text{H}_2\text{O} \\
\text{Zirconyl nitrate} &
\end{align*}
\]

Scheme 2.6 Schematic representation of the extraction of zirconyl nitrate precursor from zircon sand
2.3.2 Precipitation Synthesis

The extracted zirconyl nitrate \((\text{ZrO(NO}_3)_2)\) precursor (250 ml) was hydrolysed by drop wise addition of 4M NaOH (Merck GR, 98%) solution while being constantly stirred and an amorphous hydrated zirconium oxide was precipitated at pH 7. At this stage of reaction, a characteristic white precipitate of \(\text{ZrO(OH)}_{2-x}\text{H}_2\text{O}\) appeared. The hydrous zirconia precipitation process was shown in Scheme 2.7. The resultant precipitate was aged in the mother liquor at a temperature of 298 K for 24 h in a bath at constant temperature. After the completion of the ageing period, the precipitate was filtered using Whatman (Grade No.: 40) filter paper and washed several times in double distilled water until the precipitate was free from sodium nitrate and unreacted components. Then, the precipitate was dried in a hot air oven at a temperature of 393 K for 1 h. The synthesis of nano zirconia particles was carried out

### Table 2.2 Physical and chemical analysis of zircon sand

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<th>Proportion</th>
<th>Component</th>
<th>Weight, %</th>
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<td>Bulk density ((\text{g/cm}^3))</td>
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<td>Apparent specific gravity</td>
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<td>Particle size ((\mu\text{m}))</td>
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<td>(\text{Hf})</td>
<td>01.50 ± 0.10</td>
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<tr>
<td>Loss on Ignition (%)</td>
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<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
at three different pH values such as 7, 10 and 13. The above process was repeated for pH 10 and 13.

\[
\text{ZrO(NO}_3\text{)}_2 + 2\text{NaOH} \quad \text{Precipitation} \quad \text{ZrO(OH)}_2 + 2\text{NaNO}_3
\]

\[
\text{ZrO(OH)}_2 \quad \text{Dried at 393 K} \quad \text{ZrO(OH)}_2 + \text{H}_2\text{O}
\]

\[
\text{ZrO(OH)}_2 \quad \text{Calcined at 773 K} \quad \text{ZrO}_2 + \text{H}_2\text{O}
\]

**Scheme 2.7 Schematic representation of the synthesis of ZrO}_2 nanoparticles by conventional precipitation technique**

All synthesised samples were calcined at different temperatures ranging from 773 - 1073 K for 6 h in a static air atmosphere with a heating rate of 5 K min\(^{-1}\) and then cooled to room temperature inside the oven. After calcination, the obtained samples of soft aggregates were disaggregated by ball milling in a dry medium at 500 rpm for 3 h, using a planetary ball mill (PM 100, Retsch, Germany). In the above process method yields 84±2% of ZrO\(_2\) nanoparticles i.e., 13.2g out of 25g of zircon with 63 wt.% of ZrO\(_2\) was obtained.
2.3.3 **Sol-Gel Process**

A 250 ml of the extracted zirconyl nitrate (ZrO(NO$_3$)$_2$) precursor was taken in a 500 ml glass beaker and cooled to room temperature. Subsequently, an organic surfactant namely N-cetyl-N,N,N,trimethyl ammonium bromide (Loba, 99%) was added into the precursor and it was maintained at 1 mM concentration. Then, the aqueous ammonia solution (5N) was added into the precursor to commence flocculation by hydrolysis of zirconyl nitrate. Effective flocculation was achieved at pH 7 and it continues with the addition of aqueous ammonia until pH 10 to obtain well dispersed zirconia sol. Scheme 2.8 represents the production process of nano zirconia from zirconyl nitrate employing sol-gel route. The zirconium hydroxide gel obtained was aged and digested at 353 K for 28 h followed by drying at 423 K for 1 h in a hot air oven. The digestion process was used to control the nucleation and growth of the gel. After the above process, the dried gel was washed with water to remove the organic surfactant and ammonium nitrate from the gel matrix. Subsequently, water was replaced with ethanol, and then the gel was dried at 353 K for 1 h to reduce the agglomeration of the powder during the calcination process. The synthesised sample was calcined at 773 K for 6 h in a static air atmosphere with a firing rate of 5 K min$^{-1}$ to obtain nano sized ZrO$_2$ particles. A planetary ball mill (PM 100, Retsch, Germany) was used to disagglomerate the soft agglomerates of calcined samples through ball milling at 500 rpm for 3 h in a dry medium. The present sol-gel processing method yields a total output of 80±2% of nano zirconia particles.
2.3.4 Spray Pyrolysis

A 250 ml of extracted zirconyl nitrate (ZrO(NO$_3$)$_2$) precursor was diluted to 500 ml using 250 ml of DD water and to get the true homogeneous solution of zirconyl nitrate which was used as the starting phase in spray pyrolysis. The working principle and operating conditions of automated spray pyrolyser experimental set-up are summarised in experimental section 2.2.4.2. The zirconyl nitrate precursor was used instead of aluminium nitrate precursor in the experimental section 2.2.4.2 and the procedure was repeated for production of ZrO$_2$ nanoparticles. The sprayed and atomised nano sized entities of ZrO(NO$_3$)$_2$ were decomposed at 673 - 773 K to obtain nano ZrO$_2$ particles. The feed rate was optimised and maintained as 0.15 L h$^{-1}$. A typical decomposition reaction of zirconyl nitrate precursor was given in Scheme 2.9. Subsequently, the nano ZrO$_2$ particles obtained were collected in the cyclones and the
samples were characterised as it is without any post synthesis treatments such as customization and sintering of the particles.

\[
\text{ZrO(NO}_3)_3 \xrightarrow{\text{Decomposition}} \text{ZrO}_2 + 3\text{NO}_2\uparrow + \text{O}_3\uparrow
\]

Scheme 2.9 Schematic representation of the decomposition reaction of zirconyl nitrate

The present mini-modal spray pyrolyser yields 32-34g powder for operation of the system for 10 h. The overall output for production of ZrO\(_2\) nanoparticles in spray pyrolysis was 72 ± 5%.

2.4 SYNTHESIS OF TiO\(_2\) NANOPARTICLES

The titanium sulphate solution was extracted from ilmenite employing acid extraction which is used as the precursor for production of TiO\(_2\) nanoparticles.

2.4.1 Synthesis of Titanium Sulphate Precursor from Ilmenite

The ilmenite which contains 49.2 wt.% of TiO\(_2\) obtained from Kanyakumari region, coastal part of Tamil Nadu, India was used as the starting material for precursor synthesis without any further purifications. Physical and chemical analysis of ilmenite are given in Table 2.3. The ilmenite ore about 25g was powdered and roasted at 423 K for 1 h to remove the moisture content followed by digestion with concentrated H\(_2\)SO\(_4\) in the temperature range of 473 - 573 K for 3 h in a furnace. After the reaction, the mixtures turned into dry cake. The mixture, which contained water soluble titanium and iron sulphates were leached with 250 ml of 1M H\(_2\)SO\(_4\). The acid extraction reaction was shown in Scheme 2.10. Iron powders were
added to the leached solution under stirring to reduce the ferric sulphate into ferrous sulphate. The solution was maintained at room temperature for 1 h to get the precipitated ferrous sulphate. Subsequently, the precipitated ferrous sulphate was removed by filtering the mixture and to get the titanium sulphate precursor.

Table 2.3 Physical and chemical analysis of ilmenite

<table>
<thead>
<tr>
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<td>Property</td>
<td>Proportion</td>
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<td>Bulk density (g/cm$^3$)</td>
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<tr>
<td>Loss on Ignition (%)</td>
<td>00.30</td>
</tr>
</tbody>
</table>

Scheme 2.10 Schematic representation of the extraction of titanium sulphate precursor from ilmenite
2.4.2 Precipitation Synthesis

The extracted titanium sulphate (Ti(SO$_4$)$_2$) precursor (250 ml) was hydrolysed by the drop wise addition of 4M NaOH (Merck GR, 98%) solution under constant stirring. An amorphous hydrated titanium oxide was precipitated at pH 7 and extends the addition of NaOH until pH 10 to control the nucleation and growth of hydrous titania during the aging period. A characteristic yellowish white precipitate of Ti(OH)$_{4-x}$H$_2$O appeared during the precipitation process. The production of hydrous titania from titanium sulphate by precipitation process was represented in Scheme 2.11.

The resultant precipitate was aged in the mother liquor at a temperature of 298 K for 24 h in a bath at constant temperature. After the completion of the ageing period, the precipitate was filtered using Whatman (Grade No.: 40) filter paper and washed several times in double distilled water until the precipitate was free from sodium sulphate and unreacted components. Then, the precipitate was dried in a hot air oven at a temperature of 393 K for 1 h. The sample produced was calcined at 573 K for 6 h in a static air atmosphere with a heating rate of 5 K min$^{-1}$ and then cooled to room temperature inside the oven. Ultimately, the calcined samples were ball milled in a dry medium at 500 rpm for 3 h using a planetary ball mill (PM 100; Retsch, Germany) which leads to the disaggregation of soft aggregates. The total yield output for precipitation process was $83\pm2\%$ i.e., 10.2g out of 25g of ilmenite with 49.2 wt.% of TiO$_2$. 
2.4.3 Sol-Gel Process

The extracted titanium sulphate (Ti(SO\textsubscript{4})\textsubscript{2}) precursor (250 ml) was cooled to room temperature. Organic surfactant namely N-cetyl-N,N,N,trimethyl ammonium bromide (Loba, 99\%) was added into the precursor and it was maintained at 1 mM concentration. After that, the aqueous ammonia solution (5N) was added into the precursor to begin the flocculation through hydrolysis of titanium sulphate. At pH 7, the complete flocculation was attained and continues the addition of aqueous ammonia until pH 10 to obtain well dispersed hydrous titania sol. Scheme 2.12 presents the above sol-gel process.
The obtained titanium hydroxide gel was digested at 353 K for 28 h followed by drying at 423 K for 1 h in a hot air oven. Digestion led to control the nucleation of the gel. The organic surfactant and ammonium sulphate were present in the gel matrix was removed by washing the dried gel with water. In order to reduce the agglomeration of the powder, water was replaced with ethanol, and then the gel was dried at 353 K for 1 h. The synthesised sample was calcined at 573 K for 6 h in a static air atmosphere with a firing rate of 5 K min\(^{-1}\) to get nano sized TiO\(_2\) particles. At last, the soft agglomerates of the fired samples were disaggregated by planetary ball milling (PM 100, Retsch, Germany) in a dry medium at 500 rpm for 3 h. The present sol-gel process yields an output of 77±3% of nano TiO\(_2\) particles.
2.5 BALL MILLING

Ball milling of soft aggregates and agglomerates of calcined samples were performed employing a planetary ball mill (PM100, Retsch Corporation, Germany) in a dry medium at 500 rpm for 3 h. Milling parameters such as ball to charge ratio (20:1) and rotational speed (500 rpm) as well as grinding time (3 h) were optimised. Milling was done in a 250 ml of zirconia grinding jar with protective jacket of zirconium oxide. Zirconium oxide balls of 10 mm were utilised for millings. The calcined samples were first placed in the jar at room temperature and atmospheric pressure and then sealed and imposed to milling. After grinding period, the jar was allowed to be cooled down to room temperature. The particles were collected from grinding jar and stored under nitrogen atmosphere to prevent particles agglomeration. The schematic representation of the ball milling used for the synthesis of nanopowders is shown in Figure 2.3.

![Figure 2.3 Schematic representation of the principle of ball milling](image-url)
2.6 PREPARATION OF SILICA SOL

The silica sol was prepared from tetraethyl orthosilicate, Conc.HNO₃ and ethanol. 2.5 ml of TEOS (Merck, 99%) and 90 ml of ethanol were mixed thoroughly under sonication for 10 minutes. A small quantity of polyethylene glycol (5 ml) was added to slow down the solvent evaporation. 2.5 ml of 69 % HNO₃ was then added drop wise with continuous stirring for 20 minutes and stirring was continued for 1 h to get stable silica sol.

2.7 PREPARATION OF NANO Al₂O₃ AND ZrO₂ FILLED SILICA SOL

The synthesised Al₂O₃ and ZrO₂ nanoparticles were individually dispersed in silica sol under sonication for 10 minutes and then the sonication was continued for 20 minutes to get stable dispersion of nano Al₂O₃ and ZrO₂ filled silica sol. In the present study, 0.1 to 0.5g of nano Al₂O₃ and ZrO₂ particles were individually dispersed in 100 ml of silica sol under sonication to obtain individual dispersions of nano Al₂O₃ and ZrO₂ filled silica sol.

2.8 DIP COATING

Dip coating was performed in the stable solution of nano Al₂O₃ and ZrO₂ filled silica sol and silica sol alone. The SS304 stainless steel substrates were coated by dipping into and withdrawing from the solution at a constant speed of about 1 mm s⁻¹. The coated substrates were allowed to dry for 1 h at ambient temperature. The coating was then heat treated by firing to 673 ± 25 K for 0.5 h followed by a second stage of firing at 1073 ± 25 K for 0.5 h using the heating rate of 5 K min⁻¹ and then allowed for furnace cooling. In order to deposit relatively thick coatings it was necessary to build up multiple layers with each layer fired separately to avoid cracking and delimitation. The thickness of nano filled silica film coating on steel specimen was controlled and varied by using layer by layer coating method. The stainless steel
substrate coated with one, three and six layers of nano Al$_2$O$_3$ and ZrO$_2$ filled silica and silica alone were prepared in the present study.

2.9 THICKNESS MEASUREMENTS

The film thickness was calculated by weight difference method known as gravimetric method using the equation 2.1. The film thickness is related to coating mass, coating area and density of the coating sol.

\[
T = \frac{m \times 10}{A \times d}
\]

where T is the film thickness in micrometers, m the mass of the coating in milligrams, A the area of the SS304 specimen in square centimeters, and d the density of the coating sol in grams per cubic centimeter.

2.10 CORROSION STUDIES

2.10.1 Acid Corrosion Studies

Anti-corrosive studies of stainless steel in acid media were performed using nano Al$_2$O$_3$ filled silica coated, silica coated and uncoated SS304 specimens. The conventional weight loss method was used to obtain the corrosion loss of coated and uncoated stainless steel in acid media. The sensitivity of the balance used in the study is 1×10$^{-5}$ g (CP225D, Sartorius AG, Bangalore, India). This method is the classical and still most reliable method for corrosion monitoring. The above method is also used for evaluation of surface protective coating. The weight losses of coated (W) and uncoated ($W_o$) SS304 specimens were estimated through weight difference between before and after immersion of specimens in corrosive media at a fixed time (24 h) interval. The change in weight is expressed in milligrams per square decimeter per day.
The percentage corrosion inhibition efficiency was measured using the equation 2.2 and the corrosion rate was calculated using the equation 2.3.

\[
\% \text{ IE} = \frac{W_o - W}{W_o} \times 100
\]

Corrosion rate = \frac{\text{Weight loss in mg}}{\text{Surface area in dm}^2 \times \text{Immersion period in days}}

The coated and uncoated stainless steel specimens were immersed in acid (1M HCl) solution for 24 h to determine the effect of nano coating against the corrosion of SS304 in acid media.

2.10.2 High Temperature Corrosion Studies

High temperature corrosion studies of stainless steel at 1273 K were performed using nano ZrO\(_2\) filled silica coated, silica coated and uncoated SS304 specimens. The coated and uncoated SS304 specimens were heated in supper temperature chamber furnace (Sandvick Asia Limited, Hosur, India) to study the high temperature oxidation behavior of SS304 at 1273 K. Isothermal oxidations of SS304 specimens were carried out in a static air at 1273 K for 100 h with weight measurements performed at regular intervals. Cyclic oxidation experiments with one cycle of heating at 1273 K for 60 min and cooling in air for 15 min were conducted for up to 100 cycles. After 25 cycles, rust (Fe\(_2\)O\(_3\)) of cooled specimens were cleaned using acetone and weight changes of the specimens were measured using digital balance with sensitivity of five decimal places (1×10\(^{-5}\)g).
2.11 PREPARATION OF SILICA REFRACTORY BRICK

2.11.1 Formulation of Batch Composition

A formulation was designed as per the standard method recommended for the manufacturing of the silica bricks for Coke Ovens. To meet the desired target properties, silica bricks were manufactured (Chrzan et al. 1924, Harako and Akahori 1994) by taking different quartzite fractions. Physical and chemical analysis of quartzite is given in Table 2.4. The crushed quartzite was sieved to separate out the coarse fraction (1.5 - 2.5 mm). The rest materials were grounded to get the middling (0 - 1.5 mm) and fine (0.075 - 0.2mm) fractions. Batches were formulated taking 25% coarse, 50% middling and 25% fine fractions. A constant quantity of hydrated lime powder (4%) and iron oxide (1%) were added as mineralizer. Sulphite lye/ Molasses (2 wt.%) were added for green binding.

Table 2.4 Physical and chemical analysis of quartzite

<table>
<thead>
<tr>
<th>Property</th>
<th>Proportion, %</th>
<th>Component</th>
<th>Weight, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apparent porosity (%)</td>
<td>0.20 ± 0.10</td>
<td>SiO₂</td>
<td>98.60</td>
</tr>
<tr>
<td>Bulk density (g/cm³)</td>
<td>2.65 ± 0.01</td>
<td>Al₂O₃</td>
<td>00.50</td>
</tr>
<tr>
<td>Apparent specific gravity</td>
<td>2.64</td>
<td>CaO</td>
<td>Trace</td>
</tr>
<tr>
<td>Loss on Ignition (%)</td>
<td>0.10</td>
<td>MgO</td>
<td>Trace</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fe₂O₃</td>
<td>00.30</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TiO₂</td>
<td>00.10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Na₂O</td>
<td>00.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td>K₂O</td>
<td>00.04</td>
</tr>
</tbody>
</table>
2.11.2 Mixing and Pressing the Formulated Batch

The coarse and middling fractions of quartzite were mixed properly for 20 minutes in a standard process. The fine fraction of quartzite along with the additives such as lime and iron oxide were added and mixed for another 10 minutes. A constant quantity of water was added for workability of green mix. Standard bricks of size 230×115×75 mm were pressed in a Friction Screw press of 150 ton capacity at a bulk density of 2.28 kg m$^{-3}$.

2.11.3 Drying and Firing Profiles

The brick was dried in a tunnel dryer at 383 K for 48 h. Dried bricks were fired in a silica kiln with proper firing schedule to a maximum temperature of 1723 K for 32 h. The major portion of the quartzite (95 wt.%) was transformed into cristobalite and tridymite phases during the firing process.

2.11.4 Incorporation of Micron and Nano Titania Particles in Silica Brick

The above process steps (2.11.1 - 2.11.3) were followed for the incorporation of micron and nano sized titania powders into silica bricks. The 0.25 - 1 wt.% micron sized rutile titania and 0.25 - 1 wt.% nano rutile titania were incorporated into silica bricks and the batches were formulated. In all the trials, the bulk density was maintained as 2.28 kg m$^{-3}$.

2.12 CHARACTERISATION

In this section, the different characterization techniques used in the present investigation are discussed briefly.
2.12.1 X-ray Powder Diffraction

The wavelengths of X-rays are nearly in atomic scale and hence, it is used to study crystalline structures at the atomic level. The X-ray diffraction method has been used for the fingerprint characterisation of crystalline materials and for the determination of their structure. Each crystalline solid has its unique characteristic X-ray patterns. These patterns are used for structure determination. Crystallinity and the crystalline phase of all the powder samples were determined by X-ray diffractometer (XRD, X’ Pert Pro, PANalytical, Almelo, the Netherlands) using CuKα as a radiation source (λ=0.15406 Å). Crystalline phases in the coatings were also identified using X-ray diffraction analysis. The samples were scanned in the 2θ range from 10° to 80° at a scanning rate of 5° min⁻¹. The average crystallite size of all the samples was calculated using the Scherrer’s formula as given in equation 2.4.

\[ D = \frac{k \cdot \lambda}{\beta \cdot \cos \theta} \]  

where \( D \) is the crystal size, \( k \) the Scherrer’s constant (\( k=0.9 \)), \( \lambda \) the wavelength of the CuKα source, \( \beta \) the full peak width at half of the maximum intensity (FWHM) after correction for instrument broadening contributions and \( \theta \) the peak position. The percentage composition of each phase was calculated from the integral peak intensity ratio (Ramamoorthy et al. 1999, Wanga and Zhoub 2000).

2.12.2 Particle Size Distribution

The particle size distribution (PSD) was determined with a submicron particle size analyser (Nanophox, Sympatec, Germany) according to the dynamic light scattering technique. It is used to determine the size distribution profile of small particles in suspension. The particle size of all the samples was measured in the range of 1 - 1000 nm at a scattering angle of 90°. The three dimensional photon cross
correlation technique was used for the simultaneous measurement of particle size and stability. The He-Ne laser with 10 mW maximum intensity was used as a light source at a wavelength of 632.8 nm. All the synthesised samples (Al$_2$O$_3$, ZrO$_2$ and TiO$_2$) were dispersed in an aqueous solution, which contains 5 mM 4,5-dihydroxy-m-benzenedisulfonic acid disodium salt (Loba GR, 99%) under sonication. To achieve a stable dispersion, the pH of colloidal solution was adjusted to pH 12 by adding a 0.1N NaOH (Merck GR, 98%) solution. The sonochemically dispersed stable colloidal solution was used to obtain the particle size distribution.

2.12.3 Fourier Transform Infrared Spectrometry

Fourier transform infrared spectroscopy (FTIR) is a powerful tool for identifying types of chemical bonds in a molecule by producing an infrared absorption spectrum. FTIR is used to identify the molecular fingerprint of solids, liquids and gasses. The wavelength of light absorbed is a characteristic absorption of chemical bond. The unknown sample has been identified through the comparison of FTIR spectrum of known compounds. Fourier transform infrared spectrum of all the samples was obtained on a PerkinElmer infrared spectrometer (Spectrum 100, PerkinElmer, USA) using KBr pellets. The KBr discs were made by pressing the mixture, which contained 10 mg of samples with 100mg of KBr at a pressure of 125 kg cm$^{-2}$.

2.12.4 Thermal Analysis

Thermo gravimetric analysis (TGA) is a technique in which the mass of a substance is monitored as a function of temperature. The sample specimen is subjected to a controlled temperature treatment in a controlled atmosphere which leads to structural and chemical composition changes such as fusion, melting, crystallisation, oxidation, decomposition, transition, expansion and sintering. The mass variations of the samples are monitored and the chemical composition has been determined using
thermal analysis. The sublimation temperatures of volatile substances were determined by differential thermal analysis (DTA). TG/DTA measurements were carried out using thermal gravimetric and differential thermal analysers (Diamond TG/DTA, PerkinElmer, USA). The samples were heated continuously with a rate of 10 K min\(^{-1}\) from 313 to 1473 K in a static air atmosphere. The obtained thermogram provides data on the chemical and physical transformations such as melting, sublimation, glass transition, crystal transition and crystallisation temperature of the samples.

2.12.5 **BET Surface Area Analysis**

BET theory explains the physical adsorption of gas molecules on a solid surface and it’s used to measure the specific surface area of a material. BET technique is developed by Stephen Brunauer, Paul Hugh Emmett and Edward Teller in year of 1938 and published an article about the BET theory (Brunauer et al. 1938). Gas sorption (both adsorption and desorption) at the surface of dry solid powders is the most commonly used method for determining the surface area of the nanomaterials. In a gas sorption method, the material is first heated and then degassed to remove previously adsorbed molecules. Thereafter, known doses of an inert gas, such as nitrogen, are introduced and the gas is adsorbed (or desorbed). The sample material is placed in a vacuum chamber at constant and very low temperature, and the pressure is varied in a wide range to obtain adsorption and desorption isotherms. Various amounts of gas molecules will be adsorbed or desorbed at different doses of the gas. As the area occupied by one gas molecule is known, an appropriate adsorption model can be used to determine the total surface area of the sample. The specific surface area (SSA) of all the samples were calculated according to the BET method (Brunauer et al. 1938) using the BET surface area analyser (Autosorb AS-1MP, Quantachrome, USA). The samples were degassed under vacuum at 568 K for 3 h to remove the physisorbed moisture. The physisorption analysis was done with N\(_2\) adsorption–desorption measurements at liquid nitrogen temperature (77 K). Very low temperature is used to avoid any thermally
induced changes on the surface of the particles. The desorption pore size distribution, average pore diameter and total pore volume were calculated according to the Barret–Joyner–Halenda (BJH) method (Barrett et al. 1951). The specific surface equivalent diameter (DBET) of spherical particles (Tok et al. 2006) was calculated using the relationship is given in equation 2.5.

\[ D_{\text{BET}} = \frac{6}{AE \rho} \]  

2.5

where AE is the specific surface area, \( D_{\text{BET}} \) the particle diameter and \( \rho \) the theoretical density of the particles.

2.12.6 Energy Dispersive Spectroscopy

Qualitative and surface quantitative elemental analysis, X-ray line scans and mapping of the samples were performed with an energy dispersive spectrometer (EDS, JED-2300, JEOL, Japan). The elemental EDS analysis (JED 2300, JEOL) was performed at randomly selected areas on the solid surfaces of each being approximately 20 \( \mu \text{m} \times 20 \mu \text{m} \) in dimension. EDS mapping was carried out at 1000 X magnification with an applied voltage of 18 kV under vacuum condition of \( 3.5 \times 10^{-5} \) mbar.

2.12.7 X-ray Fluorescence Spectrometry

X-ray fluorescence spectrometry (XRF) is the characteristic emission of fluorescent (secondary) X-rays from a material that has been excited by bombarding with high energy X-rays. This phenomenon is widely used as a fast, accurate and non-destructive method for chemical and elemental analysis. XRF is used to identify and determine the concentration of the elements present in solid, powder and liquid
samples. XRF is a semi-quantitative technique used for chemical mapping of samples under ordinary atmospheric conditions. Qualitative and quantitative elemental analyses of natural minerals and nanopowder samples were performed using X-ray fluorescence spectrometry (XRF, EDX-720, Shimadzu, Japan). The powder samples were analyzed directly without any preparation.

2.12.8 Chemical Analysis

The chemical purity of the alumina samples were determined through wet chemical analysis by the ethylenediaminetetraacetic acid (EDTA) titration method according to the Indian Standard procedure (IS 1760, Part 3, 1992). The chemical purity of the zirconia samples were determined through wet chemical analysis using EDTA titration method (Sinha and Das Gupta 1967). The weight percentage and purity of titania samples were determined spectrophotometrically by the hydrogen peroxide method at \( \lambda_{\text{max}} = 410 \text{ nm} \) (Mahmoud et al. 2004 and Vogel, 1978).

2.12.9 Optical Emission Spectrometry

Optical emission spectrometry employing arc/spark excitation is the reference technique for rapid and reliable quantitative elemental analysis of solid metallic samples. The single components of the spark emitted light intensity are integrated and the integrated intensity is transformed into a concentration through a calibration curve. Elemental analysis of coated and uncoated stainless steel specimens were performed using arc/spark optical emission spectrometry (OES, ARL 4460, Thermo Scientific, USA).

2.12.10 Electron Microscopic Analysis

The principle of SEM is the scanning of the surface of a solid material in a raster pattern with a high energy beam of electrons as source. The energy of the
electron beam can range from a few hundred eV to 100 keV. The surface morphology of the samples was inspected using a scanning electron microscope (SEM, JSM-6390LV, JEOL, Japan) with an accelerating voltage of 25 kV. The powder samples were attached into an adhesive carbon tape supported on metallic disks. Sample surfaces were then observed at different magnifications and the respective images were recorded. SEM images are formed using secondary electron beam (SEI) which produce magnification details up to 300,000X with low vacuum resolution of 15 nm. The microstructure and morphological features of coated and uncoated SS304 specimens were also inspected using SEM micrographs. The primary particle size and its morphology were obtained through transmission electron microscopic images using a transmission electron microscope (TEM, CM200, Philips, USA) operating at 120 kV. TEM images are formed using transmitted electrons which produce magnification details up to 1,000,000X with resolution better than 10 Å. The images can be resolved over a photographic film.

2.12.11 Atomic Force Microscopy

Atomic force microscopy provides a three dimensional profile of the surface on a nanoscale by measuring forces between a sharp probe (<10 nm) and surface at very short distance (0.2-10 nm). The probe is supported on a flexible cantilever. The AFM tip (probe) gently touches the surface and records the small force between the probe and the surface. The amount of force between the probe and sample is dependent on the spring constant (stiffness) of the cantilever and the distance between the probe and the sample surface which is described using Hooke’s Law. The deflection of the probe (force) is generally measured using a beam bounce method. A semiconductor diode laser is bounced off the back of the cantilever into a position sensitive photodiode detector. The photo detector measures the bending of cantilever during the tip is scanned over the sample. The measured cantilever deflections are used to generate a map of the surface topography. The surface topography of coated and
uncoated SS304 specimens were obtained by tapping mode imaging using atomic force microscopy (AFM, Innova, Veeco, USA).

2.12.12 Characterization of Fired Silica Bricks

The silica bricks were characterised by their physical, chemical, mineralogical and thermo mechanical properties which were studied as per the standard specification laid in DIN (Deutsches Institute for Normung) 1089 part 1. Apparent porosity and bulk density were determined by boiling water method as described in DIN 51056 part 1. Cold crushing strength (CCS), refractoriness under load (RUL), reversible thermal expansion (RTE) and creep in compression (CIC) were determined as described respectively in DIN 51067, DIN 51053 part 1, DIN 41045 and DIN 51053 part 11. Further, the chemical analysis was carried out according to DIN 51001. CCS was measured in a CCS testing machine (1515, Toni Technik, Germany). Refractoriness under load (RUL) and creep in compression (CIC) were determined in a refractory testing machine (RUL 421, Netzsch, Germany). Thermal expansion of silica brick was measured by Dilatometer (402C, Netzsch, Germany). The microstructure and morphological features of silica bricks with and without nano titania were studied by optical microscope (12 MEST, Leitz Laborlux, Germany). The phase conversion and dispersion of silica bricks with and without nano titania were studied employing X-ray diffractometer (PW1730, Phillips, USA).

2.13 SUMMARY

In this chapter, the complete experimental procedures used for the synthesis of Al\textsubscript{2}O\textsubscript{3}, ZrO\textsubscript{2} and TiO\textsubscript{2} nanoparticles from natural minerals employing different methods have been discussed. The methodology used for the preparation of nano Al\textsubscript{2}O\textsubscript{3} and ZrO\textsubscript{2} filled silica sol and its coating on SS304 were explained briefly. The experimental procedures used for the preparation of silica refractory brick with and
without TiO$_2$ nano additive have been discussed. The characterisation details such as XRD, EDS, XRF, FTIR, PSD, BET, AFM, SEM, TEM and OES used for the characterisation of the samples are discussed in detail. The necessary experimental details used for characterisation of fired silica brick in the present investigation have also been explained. SEM micrographs and weight loss measurements of coated and uncoated SS304 play a key role in identifying the acid and high temperature oxidation corrosion properties of the SS304 specimens. Using all the above mentioned characterisation techniques, one can explore the purity, particles size, morphology, structural and textural properties of the all synthesised nano metal oxide samples. Thus, the optimisation of the processing methods for the production of different metal oxide nanoparticles such as Al$_2$O$_3$, ZrO$_2$ and TiO$_2$ for different industrial applications can be achieved easily using the above procedures.