Chapter II

Experimental and Characterization Techniques

2.1 Chemicals Used

1. Titanium tetraisopropoxide (Fluka, Switzerland, 99.99%)
2. Tetraethylorthosilicate (Fluka, Switzerland, 99.99%)
3. Alumina (A16SG, ACC-Alcoa, Kolkata, 99.9%)
4. Lanthanum Nitrate (IRE, India, 99.99%)
5. Cerium Nitrate (IRE, India, 99.99%)
6. Acetic Acid (S D Fine Chemicals, India)
7. Propan-2-ol AR (S D Fine Chemicals, India)
8. Sodium hydroxide LR (Qualigens India Ltd.)
9. Nitric Acid 69% GR (Merck, India)
10. Polyethylene glycol 300 LR (S D Fine Chemicals, India)
11. Glycerol AR (S D Fine Chemicals, India)
12. Methylene Blue (Qualigens India Ltd.)
2.2 Experimental Methods

2.2.1 Synthesis of Nanocrystalline Titania

In the present study nanocrystalline titania is prepared by a modified sol-gel technique. Acetic acid is used as stabilizing agent against hydrolysis. Acetic acid modifies the co-ordination sphere of titania and makes it more stable against hydrolysis. Further, dopants were added to the partially hydrolyzed titanium tetraisopropoxide solution as their respective nitrates.

2.2.1.1 Synthesis of Undoped TiO$_2$ Sol

Titanium tetraisopropoxide (TTIP) was used as received. Ti$^{4+}$ moiety owing to its extremely high reactivity with water requires a pre-stabilization against hydrolysis. Therefore glacial acetic acid was used as a stabilizing / catalyzing agent. Titanium isopropoxide stabilized with acetic acid usually follows a condensation pattern producing linear chains and enclosing small pores that result in high surface area. This is because the acid-catalyzed condensation is directed preferentially toward the ends rather than the middles of chains. Synthesis started with the addition of titanium tetraisopropoxide (3.56g) to glacial acetic acid (7.16 ml). Glacial acetic acid modifies the coordination sphere of titanium to a more stable state. Dropwise addition of 78.85 ml deionized water accomplished the hydrolysis under vigorous stirring conditions. The solution is then stirred for homogenization for a period of 3 h. After trial and error methods, the titanium tetraisopropoxide/acetic acid/water mole ratio was fixed as 1:10:350.
2.2.1.2 Synthesis of La₂O₃-doped TiO₂ Sol

Lanthanum nitrate hexahydrate [La(NO₃)₃·6H₂O, 99.99%] was used as such. In a typical experiment for the preparation of 1% La₂O₃-doped TiO₂, stoichiometric quantity of lanthanum nitrate solution (0.53 ml) was added dropwise to the TiO₂ solution prepared as discussed in section 2.2.1.1 after 1h stirring. Stirring continued for 2 more hours to ensure the homogeneity of the mixture. Separately, 0.1, 0.5, 2.0, 5.0 and 10 wt. % LaO₃ doped TiO₂ compositions were also prepared by the same procedure (Figure 5).

2.2.1.3 Synthesis of CeO₂-doped TiO₂ Sol

Cerium nitrate hexahydrate [Ce(NO₃)₃·6H₂O] was purified by filtration and made up to 5% aqueous solution. The solid content was accurately measured by gravimetric method. For preparing 1% CeO₂-doped TiO₂, stoichiometric quantity of cerium nitrate solution (0.53 ml) was added dropwise to the partially hydrolysed titanium tetraisopropoxide solution prepared as discussed in section 2.2.1.1 after 1h stirring. Stirring continued for 2 more hours to ensure the homogeneity of the mixture. Separately, 0.1, 0.5, 2.0 and 5.0 wt. % of CeO₂ were also prepared by the same procedure (Figure 5).

2.2.1.4 Synthesis of SiO₂ Sol

Tetraethylorthosilicate was used as received. In case of silica, the lower reactivity of Si⁴⁺ moiety little demands the presence of stabilizing agent compared to Ti⁴⁺ moiety. However, anhydrous isopropanol was used as a solvent to make the polar water and non-polar alkoxide compatible in the
Titanium tetraisopropoxide + Acetic Acid

Deionised water 1 hr stirring

Titanium Isopropoxide Solution

Stirring 2 hr

Doped Titania Solution

3 hr stirring 8 days aging

Co-doped Titania Sol

Particle Size Analysis

Dried at 70°C

Doped-Titania Xerogel

FTIR, TG, DTA

Calcination

Doped-Titania Powder

FTIR, BET Specific Surface Area, XRD, TPD, Leaching Study, TEM, Photoactivity Evaluation

Figure 5: Flow chart for the preparation of doped TiO₂ powder
Isopropanol was distilled to remove the water content adsorbed to it. Alkoxide-isopropanol-water ratio was fixed as 1:4:16 in all the synthesis procedures of silica in the present work. In a typical experiment, tetraethylorthosilicate (3.45g) dissolved in anhydrous isopropanol (5.08 ml) was hydrolysed by the dropwise addition of 0.001N-deionized water (4.77 ml). Stirring for a period of 3 h ensured homogeneity of the sol.

2.2.1.5 Synthesis of $\text{SiO}_2$-$\text{La}_2\text{O}_3/\text{CeO}_2$ Co-doped $\text{TiO}_2$ Sol

Dropwise addition of the stoichiometric quantity of silica sol, prepared as per section 2.2.1.5, to the $\text{La}_2\text{O}_3$ doped TiO$_2$ sol (Section 2.2.1.2) accomplished the formulation of co-doped composition. A ratio of 94:1:5 percentage TiO$_2$:La$_2$O$_3$/CeO$_2$:SiO$_2$ (wt %) was selected as the catalyst composition. The homogeneous distribution of the SiO$_2$ phase in the La$_2$O$_3$ doped TiO$_2$ sol was ensured by appropriate stirring. Repeated particle size measurements at various intervals of stirring were carried out to see the distribution of sol particles.

2.2.1.6 Synthesis of $\text{Al}_2\text{O}_3$ Sol/Suspension

The finer fraction of alumina was separated after suspending it in deionized water. pH of the suspension was adjusted to be 3.5 till a stable colloid is obtained. The average particle size of the sol was measured to be 275

2.2.1.7 Synthesis of $\text{Al}_2\text{O}_3$-$\text{La}_2\text{O}_3$ Co-doped $\text{TiO}_2$ Sol

The mixed sol was prepared by adding calculated volume of the Al$_2$O$_3$ suspension (corresponding to 10 wt % of the total mixed oxide concentration) to the 1% La$_2$O$_3$-doped TiO$_2$ sol, synthesised as per section 2.2.1.2, after 1 h
stirring and the mixture was stirred further for a period of 5 hrs. The coating precursor sols were prepared by the addition of 0.5 % PVA and 0.1% glycerol to the above sol. This was labelled as TLA10.

Aging for a period of 8 days followed by concentrating over a steam bath and subsequent drying at 70°C in an air oven produced the doped titania xerogel. Annealing of the xerogels at different temperatures ranging from 100-1100°C, and soaking for a period of 3 hours have been carried out in an ambient pressure and normal oxygen atmosphere. Heat treatment was done in a stepwise manner, i.e., RT to 200°C (2°C/min), 200 to 500°C (3°C/min) and 500 to higher temperature (5°C/min). The xerogels were characterized by various methods. The detailed description is provided in the following section.

2.2.2 Leaching Process

5% aqueous NaOH solution was used for leaching. 2 g 5% SiO₂-1% La₂O₃-doped TiO₂ powder calcined at 700°C was dropped into 30 ml NaOH solution. It is then heated to about 70°C. Stirring the mixture for 1h in this stature accomplished the leaching. The sodium silicate formed as slag was removed by decanting and the slurry was subsequently washed several times (20 times) to remove the sodium impurity. The complete removal of NaOH was primarily confirmed by pH measurement (washed till the pH becomes ≤7). The leached samples were dried in an air oven at 70°C and subsequently heat treated at 300°C to remove any residual precipitates formed due to the action of NaOH.
A list of total samples prepared for the study is provided in Table 4. Apart from these samples, the ones incorporated with silica are used for leaching.

<table>
<thead>
<tr>
<th>TiO₂</th>
<th>La₂O₃</th>
<th>CeO₂</th>
<th>SiO₂</th>
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<tbody>
<tr>
<td>100</td>
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<td>1</td>
<td>5</td>
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</tbody>
</table>

All the compositions are in weight percentage
All the silica-incorporated samples were undertaken leaching

2.2.3 Fabrication of Nano Titania Coatings by Dip Coating

The film fabrication was carried out on pre-treated glass slides obtained from micro slides corp. Dip coating was employed for the fabrication of films from precursor sols such as titania, doped titania and co-doped titania samples. The precursor sols were again modified with the addition of 0.5% PEG and/or 0.5% glycerol to study their effect on the film formation and also to compare with the optimized compositions employed in this work. The coated glass slides were subsequently dried at room temperature for 1 h followed by heating in an electric air oven at 70°C for another 1 h. The samples were annealed to
400°C at a heating rate of 1°C/min. and soaked further for 3 h. The detailed film fabrication procedure is provided below.

**Pre-treatment of Glass Slides:** The micro slides (size: 75 mm long x 25 mm wide x 1.35 mm thick) were obtained from Polar Industrial Corporation, Mumbai. The pre-treatment of the slides was necessary to remove the Na impurity and to make the glass perfectly wetting. The glass slides were first boiled in Conc. H$_2$SO$_4$ for 1 h followed by thorough washing with distilled water to remove the acid completely. H$_2$SO$_4$ will selectively extract the free-Na ions embedded in the glass slides (sheet glass) and convert it into soluble sodium sulphate. The glass slides were then ultrasonicated in a 80:1 water-isopropanol mixture for 10 minutes and subsequently dried in an oven at 100°C followed by heat treatment at 400°C to remove the organic impurities on the surface if any. The glass slides were kept in the oven at 100°C till the time of coating. The coatings were carried out using dip coating as well as spin coating technique.

**Dip Coating Technique:** KSV Dip coater [KSV Dip coater D, Model 1000IUD, KSV Instruments Ltd., Finland] as well as the one fabricated locally was used for dip coating. Dip coating was carried out using the pre-treated glass slides kept at 100°C by a dipping-withdrawing process. Coating was done with different withdrawal speeds such as 0.6, 1.8, 3.0, 4.2 and 6.6 cm/min with a view to study its effect on the film thickness of coatings. The dip coating using the locally fabricated equipment was carried out by keeping the glass
slides in the glass vessel containing the sol and allowing the sol to drain out in a slow controlled manner through the bore drilled at the bottom of the vessel. The speed of coating (withdrawal speed) was measured manually using a scale and stopwatch. The schematic diagram of the coating equipment is provided in Figure 6.

Figure 6: Schematic representation of the dip-coating unit fabricated.

The coating formulations used in the present study are given in Table 5. All the compositions are in wt % only (if not stated otherwise).
Table 5: List of coating formulations used in the present research

<table>
<thead>
<tr>
<th>TiO₂</th>
<th>La₂O₃</th>
<th>CeO₂</th>
<th>SiO₂</th>
<th>GLY*</th>
<th>PEG**</th>
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</thead>
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<td>1</td>
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<td>--</td>
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<td>5</td>
<td>--</td>
<td>1</td>
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</table>

* GLY – Glycerol; **PEG – Poly (ethylene glycol)

The coating formulations were restricted to the above compositions for clarity of discussion and interpretation, even though more compositions have been attempted on a trial and error basis.

2.2.4 Fabrication of Nano Titania Coatings by Spin Coating

A drop-spin coating technique was employed for the film fabrication. Pretreated glass discs were mounted on the rotating disk and the precursor sols were dropped into it at a rotation speed of 2000 RPM. The speed was increased to 4000 RPM and kept for 1 minute for evaporation of the solvent. The coated discs were dried in an air oven at 70°C for 1h and subsequently annealed to 400°C at a heating rate of 1°C/min. and soaked further for 3h. The 1°C heating
rate was selected after trial and error method since this rate and soaking at 400°C for 3 h gave almost similar film characteristics with the ones obtained for bulk powders heat treated at 700-800°C with a heating rate of RT to 200°C (2°C/min), 200 to 500°C (3°C/min) and 500 to 800°C (5°C/min).

Leaching of coated glass slides was performed by the immersion of coated glass substrates in 5% NaOH aqueous solution for a period of 1 h at 70°C. The glass slides were taken out and washed several times with deionized water to remove the sodium impurity. 1, 2, 5 and 10% NaOH solutions were used for leaching study and the 5% NaOH solution was selected for the detailed analysis.

2.2.5 Photoactivity Evaluation

Methylene blue (MB) degradation experiments were done in presence of UV light (360 nm) in a Rayonet Photoreactor (The Netherlands). The photoreactor is made up of 24 UV lambs of 360 nm wavelength arranged in concentric circular fashion. The solution/mixture can be stirred using the magnetic stirrers provided in the platform and also the base can be rotated to make sure that the solution is exposed to maximum light throughout the irradiation. A mixture of aqueous solutions of 15 ml MB (0.16 mg/100 ml) and 10 ml TiO₂ (0.32 mg/100 ml) were kept in the photoreactor for UV irradiation. The mixture was exposed to UV light for a period of 5 hrs. UV-Vis spectra were recorded at regular time intervals of irradiation such as after 5 min, 15
min, 30 min, 1 h, 2h, 3h and 5 h. Similarly, photodegradation was done under sunlight as well.

The photoactivity of coated samples was also evaluated by similar experiments. Photoactivity evaluation of the coatings was done by UV light exposure of the Titania coated glass slides immersed in the methylene blue solution (2μl). The degradation profiles were drawn by plotting the maximum absorbance of the main intensity peak (664 nm) of methylene blue at regular intervals of UV exposure. In fact all the samples are calcined at 400°C at a heating rate of 1°C/min and soaked for a period of 3 h.

The flow chart for the preparation of the co-doped TiO₂ powder is provided in Figure 7 and those for the co-doped TiO₂ coatings are provided as Figures 8 and 9. The total samples prepared for the present study are labelled as provided in Table 6 and these codes are used for further discussions.
Table 6: Total samples prepared for the study and their abbreviations

<table>
<thead>
<tr>
<th>Sample</th>
<th>Abbreviation</th>
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<tbody>
<tr>
<td>TiO$_2$-1% La$_2$O$_3$</td>
<td>TL-1</td>
</tr>
<tr>
<td>TiO$_2$-1% La$_2$O$_3$-1% PEG</td>
<td>TL-PEG1</td>
</tr>
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<td>TiO$_2$-1% La$_2$O$_3$-0.5% PEG</td>
<td>TL-PEG0.5</td>
</tr>
<tr>
<td>TiO$_2$-1% La$_2$O$_3$-1% GLY</td>
<td>TL-GLY1</td>
</tr>
<tr>
<td>TiO$_2$-1% CeO$_2$</td>
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<td>TiO$_2$-1% CeO$_2$-1% PEG</td>
<td>TC-PEG1</td>
</tr>
<tr>
<td>TiO$_2$-1% CeO$_2$-1% GLY</td>
<td>TC-GLY1</td>
</tr>
<tr>
<td>TiO$_2$-1% SiO$_2$</td>
<td>TS-1</td>
</tr>
<tr>
<td>TiO$_2$-5% SiO$_2$</td>
<td>TS-5</td>
</tr>
<tr>
<td>Chemically leached- TiO$_2$-5% SiO$_2$</td>
<td>TSN</td>
</tr>
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<td>TiO$_2$-1% CeO$_2$-5% SiO$_2$</td>
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</tr>
<tr>
<td>TiO$_2$-1% La$_2$O$_3$-5% SiO$_2$-1%PEG</td>
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</tr>
<tr>
<td>TiO$_2$-1% La$_2$O$_3$-5% SiO$_2$-1%PEG</td>
<td>TLS-PEG0.5</td>
</tr>
<tr>
<td>Chemically leached- TiO$_2$-1% La$_2$O$_3$-5% SiO$_2$</td>
<td>TLSN</td>
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</tbody>
</table>
Titanium tetraisopropoxide + Acetic Acid

Deionised water 1 hr stirring

Tetraethylorthosilicate + Isopropanol

Deionised water 3 hr stirring

Titanium Isopropoxide Solution

Stirring 2 hr

Titania-Silica-RE Oxide Solution

3 hr stirring 8 days aging

Co-doped Titania Sol

Dried at 70°C

Co-doped Titania Xerogel

Calcination

Co-doped Titania Powder

RE Nitrate Solution

Particle Size Analysis

FTIR, TG, DTA

FTIR, BET Specific Surface Area

XRD, Leaching Study, TEM, Photoactivity Evaluation

Figure 7: Flow chart for the preparation of co-doped TiO₂ powder
Titanium tetraisopropoxide + Acetic Acid

Deionised water
1 hr stirring

Tetraethylorthosilicate + Isopropanol

Deionised water
3 h stirring

Titanium Isopropoxide Solution

RE Nitrate Solution

2 hr stirring
Particle Size Analysis
Dip Coating, Spin Coating

Titania-Silica-RE Oxide Solution

Particle Size Analysis
Dip Coating, Spin Coating

3 hr stirring
8 days aging

Co-doped Titania Sol

Particle Size Analysis
Dip Coating, Spin Coating

Dried at 70°C
Calcination at 400°C

Co-doped Titania Coating

AFM
UV-Vis Spectral Analysis

Figure 8: Flow chart for the preparation of co-doped TiO₂ coating
Figure 9: Flow chart for the preparation of Al$_2$O$_3$-La$_2$O$_3$ co-doped TiO$_2$ powder and coating
2.3 Characterization Techniques

2.3.1 Particle Size Analysis

The technique of dynamic light scattering (DLS) is ideally suited for the determination of the size of particles in the nanometre size range. The Malvern Zetasizer, Malvern Instruments Ltd, Malvern UK uses patented optics that provides exceptional levels of sensitivity and allows the determination of the size of samples that contain very small particles and/or particles that are present at very low concentrations. In addition, the backscatter optics allows for the measurement of samples at much higher concentrations than is possible using conventional DLS instruments using a 90° detection angle. Since the samples are stable sols, no deflocculant is added to the sample in the present case. Instead the measurement is done as such.

2.3.2 Fourier Transform Infrared Spectroscopy (FTIR)

The Fourier transform infrared spectra of gels and calcined samples were recorded in Nicolet Magna-560-IR Spectrometer (USA) to study the dehydroxylation and bonding characteristics of the gels and calcined powders. The disc samples were prepared using KBr.

2.3.3 Thermogravimetry (TG)

Thermogravimetry is a technique whereby a sample is continuously weighed as it is heated at a constant, preferably linear rate. The decomposition
features of the gel samples were characterized using the Shimadzu-TGA 50H in nitrogen atmosphere at a rate of 10°C/min up to 1000°C.

### 2.3.4 Differential Thermal Analysis (DTA)

In differential thermal analysis, the sample temperature is continuously compared with a reference material temperature, the difference in temperature being recorded as a function of furnace temperature as the sample is heated or cooled at a uniform rate. The gel samples were characterized using the Shimadzu-50H DTA in nitrogen atmosphere at a heating rate of 10°C/min.

### 2.3.5 X-ray Diffraction (XRD)

The X-ray powder diffraction patterns of the calcined samples were recorded in Philips Diffractometer (PW1710), The Netherlands, using Ni filtered Cu Kα radiation. The samples for XRD were prepared by smearing the powder on a clean glass plate coated with silicon grease and the smeared powder on the glass plated was pressed using another glass plate to get a plane surface. Most of the samples prepared for this study are scanned between 20 to 60° 2θ values with a step speed of 2.4°/min.

The percentage of rutile (X) in the samples was estimated from the respective integrated peak intensities using the equation.

\[ X = (1 + 0.8 \frac{I_A}{I_R})^{-1} \]

Where \( I_A \) and \( I_R \) are the X-ray intensities of the anatase and (101) and rutile (110) peaks respectively. Crystallite sizes were calculated from the peak widths using the Scherrer equation. 488
\[ \Phi = k \lambda / (\beta \cos \theta) \]

Where \( \Phi \) is the crystallite size, \( k \) the shape factor (a value of 0.9 was used in this study), \( \lambda \) the X-ray radiation wavelength (1.540 Å for CuKα) and \( \beta \) is the full line width at half-maximum height of the main intensity peak after subtraction of the equipment broadening.

### 2.3.6 Nitrogen Sorption Studies (BET Specific Surface Area Analysis)

The phenomenon of higher concentration of any molecular species at the surface than in the bulk of a solid (or a liquid) is known as adsorption. The solid that takes up a gas or vapour or a solute from a solution is called the adsorbent while the gas or the solute, which is held to the surface of the solid is called the adsorbate. The variation of adsorption with pressure at a given constant temperature is generally expressed graphically and is known as adsorption isotherm.

**Adsorption isotherms**

The relationship between the magnitude of adsorption and pressure can be expressed mathematically by an empirical equation known as Freundlich adsorption isotherm, \( a = Kp^n \), where \( a \) is the amount of the gas adsorbed per gram of the adsorbent at pressure \( p \), \( K \) and \( n \) are constants depending upon the nature of the gas and the adsorbent. It is possible to divide the adsorption isotherms into major five different types (Figure 10).
Figure 10: Types of adsorption isotherms, Brunauer, Deming, Deming, and Teller classification together with stepped isotherm

(1) Type I corresponds to unimolecular adsorption. The volume of the gas adsorbed approaches a limiting value; just enough to complete a unimolecular layer even when the gas pressure is very high. Microporous solids also show similar behaviour.

(2) Type II and Type III isotherms, the amount of adsorption keeps on rising in each case with increase in pressure. This is attributed to the formation of additional layers of physically adsorbed gas molecules.

(3) Type IV and Type V have been observed in cases where there is a possibility of condensation of gases in the minute capillary pores of the adsorbent at pressures even below the saturation pressure, 'Po' of the gas. There is not only the formation of multimolecular adsorbed layers of gas molecules but also condensation of some of the gas molecules within the
narrow capillary pores of the adsorbent known as capillary condensation of
the gas.

(4) Type III and Type V are special isotherms showing by gases having less
interaction with solids. Type VI is a stepped isotherm not included in the
classical classification

Nitrogen sorption studies of the samples were carried out using
Micromeritics BET surface area analyzer (Gemini Model, 2360). The calcined
samples were preheated in a flow of nitrogen for about 3 hours at around 200°C
to remove all the volatiles and chemically adsorbed water from the surface.
Adsorption studies were carried out at liquid nitrogen temperature.

_Determination of Specific Surface Area_

The specific surface area is usually determined using the BET equation.
The Langmuir theory of adsorption is restricted to the formation of a
monomolecular layer of gas molecules, on the solid surface and disregards the
possibility for multilayer adsorption. But in the BET theory it is assumed that
multilayer adsorption can take place since the solid surface possesses uniform
localized sites.
The BET equation is

\[
\frac{P}{P_0} = \frac{1}{V} + \frac{C}{V_m} \left(\frac{P}{P_0}\right)
\]

Where, 

\[V = \text{volume of the gas adsorbed at the pressure 'P'}\]

\[V_m = \text{volume adsorbed when the surface of the solid is}
\text{completely covered with a monolayer of adsorbed gas molecules.}\]
C = \text{a constant depending upon the nature of the gas.}

Since 'C' and 'V_m' are constant for a given gas solid system, a plot of \( PV(P_0 - P) \) against \( (P/P_0) \) should give a straight line. So \( V_m \) can be calculated.

The total surface area of the sample can be calculated using the equation. Surface area, \( S = V_m NA/M \), Where, \( N = \text{Avogadro number, } A = \text{cross sectional area of a single molecule of the adsorbate, } M = \text{Molecular weight of the adsorbate.} \)

**Determination of Total Pore Volume**

The liquid equivalent of the designated volume adsorbed is the total pore volume (cc/g), \( V_{\text{tot}} = (V_a) \times (D) \), Where \( V_a = \text{volume adsorbed at } P/P_0 0.99, \)

\( D = \text{density conversion factor.} \)

**Average Pore Size**

Assuming the pores are of cylindrical shape and open at both ends, the average pore size of a given sample is calculated using the equation,

\[
\text{Average pore size} = \frac{4V_p}{S_{\text{BET}}}
\]

\( V_p = \text{pore volume, } S_{\text{BET}} = \text{BET multipoint surface area.} \)

**Pore Size Distribution Curves**

Pore size distribution curves are determined from adsorption/desorption isotherms making use of Kelvin equation, which relates the equilibrium vapour pressure of a curved surface, such as that of a liquid in a capillary or pore, to the equilibrium pressure of the same liquid on a plane surface.
\[
\ln \frac{P}{P_0} = -\frac{2\gamma V}{rRT} \cos \theta,
\]
where \(P\) is the equilibrium vapour pressure of the liquid contained in a narrow pressure of radius \(r\) and \(P_0\) is the equilibrium pressure of the same liquid in a plane surface. The terms \(\gamma\) and \(\bar{V}\) are the surface tension and molar volume of the liquid respectively, and \(\theta\) is the contact angle of the liquid. When nitrogen is used as the adsorbate at its boiling point of 77 K, the Kelvin equation can be written as,
\[
r_k = \frac{4.15}{\log(P/P_0)} \text{ (Å)}
\]
\(r_k\) is the radius obtained from Kelvin equation, which differs from actual pore size since condensation occurs to a core of pore that was already covered by an adsorbed layer. The thickness of the adsorbed layer can be obtained by comparing the absorption layer with a nonporous one. However, \(t\), the statistical thickness, can also be determined by Halsey equation, which for nitrogen can be written as,
\[
t = 3.54 \left[ \frac{5}{2.303 \log \left( \frac{P_0}{\bar{P}} \right)} \right]^{1/3}
\]
A procedure involving only the wall area and based on the cylindrical pore model put forward by Pierce and modified by Orr and Dall Valle was used for the determination of pore size determination. The additional area of multilayer exposed during each step of desorption is calculated from the volume and radius from a cylindrical model. For the speedy calculation a
computer programme was written using Visual Basic and used for all the analysis of the isotherms.

2.3.7 Temperature Programmed Desorption of Ammonia (TPD)

Ammonia TPD is a method for identifying the strength of acidic sites of the sample. A known weight of NH$_3$ is adsorbed at room temperature on the sample taken in the reactor. The NH$_3$ desorbed at different temperatures is determined by titrimetry. About 0.5 g of the sample was loaded into a microcatalytic reactor and degassed in a stream of nitrogen at a temperature of 300°C for 30 minutes. The reactor was then cooled to room temperature and 20 ml NH$_3$ was injected through the sample. The gases emerging from the reactor outlet was scrubbed into known quantity of standard sulphuric acid for 15 minutes and the eluted ammonia was estimated volumetrically using the equation:

Amount of ammonia desorbed = \( (N_{NaOH} \times \Delta V) \times \frac{17}{(w \times 1000)} \) (mmol/g)

Where, \( w \) = weight of the catalyst in mg/g

The experiment was repeated similarly at different temperatures 100,200,300,400,500,600 and 700°C. The desorption of ammonia at relatively lower temperatures 100 - 250°C was considered as occurring from weak Brønsted acid sites, while that occurring at high temperatures 250-650°C was considered as occurring from Lewis acid sites. The schematic representation of the locally fabricated TPD set up was provided in Figure 11.
A = Cylinder  
C = Sample as pellet  
D = Furnace  
E = Standard sulfuric acid

Figure 11: Schematic representation of TPD set up

2.3.8 Transmission Electron Microscopy (TEM)

TEM has become the primary tool for the observation of crystal defects, second phase precipitates, elucidation of the crucial role of intrinsic and extrinsic dislocations, grain boundaries, interfaces, line and planar defects. Surface morphology on a nanometer scale is obtained from TEM.
When high-energy electron beam passes through the thin specimen, the transmitted beam is ejected on the fluorescent screen. This transmitted beam gives structural information of the specimen. The TEM gives very high resolution (in the order of 1Å) and very high magnification (~1 million times). However, this is obtainable for thin specimens only (~100Å). The bulk specimen need necessary thinning by various techniques like ion milling, electropolishing etc. depending on the nature of the material. The powder specimen is suspended in water or any other medium generally in the ratio 1:100 or 1:1000. Ultrasonic stirring is necessary for agglomerated samples. A drop of the suspension is placed on the grid supported by carbon or plastic films. The suspensions form a hemispherical drop on the grid. With time the liquid is evaporated and the powder is adhered to the supporting film. The grid is dried and ready for observation under TEM.

TEM of selected samples in the present work were taken in JEOL 3000EX with acceleration voltage 300kV and a resolution of less than 0.2nm. Diffraction patterns have a camera length of 80 cm. The powder was dissolved in ethanol, and homogenized in ultrasonic bath for 5 min. Then the 3mm carbon-coated Cu-grid for TEM-observation was dipped into this dispersion, so that the powder particles were stacked on the grid. Since they are so small, they are translucent for the electron beam. The upper limit for this critical thickness would be about 250 nm. Dr. Wilfried Wunderlich of Nagoya Institute of Technology, Nagoya, Japan did the TEM analysis for the present work.
2.3.9 UV-Vis Absorption/Transmission Spectroscopy

The photodegradation capacity of titania samples were measured by taking absorption spectra of the UV exposed titania-methylene blue mixture solutions. The solution was centrifuged and the solution is taken for the measurement to avoid scattering of light due to titania particles. In case of coated films, transmission spectra were recorded in the transmission mode. The UV-Vis absorption/transmission spectra of the titania-methylene blue mixture solutions were recorded using Shimadzu UV 2401 PC UV-Vis spectrophotometer.

2.3.10 Atomic Force Microscopy (AFM)

The surface morphology of the spin coated glass surface was determined by AFM imaging. A Multimode head with a Nanoscope IV controller from Digital Instruments (Santa Barbara) was used in contact mode for all imaging. Repeat scans were used to confirm that the scanning was not affecting the surface. For non-symmetrical features, two sets of orthogonal scans were used to confirm that the observed features are real and not due to the scanning direction of the tip. Prof. Frank J. Berry and Dr. Sharon Moore of Open University, UK, did the AFM analysis for the present thesis work.