Chapter 3

Physico-Chemical Characterization

Abstract

This chapter deals with the characterization techniques. The physico-chemical characterization of metal incorporated titania systems by the three routes namely Sol-gel, Hydrothermal and EISA route were done. A detailed investigation was performed by different techniques such as X-Ray diffraction analysis (XRD), Infra-Red spectroscopy (FTIR), Surface area and Pore volume measurements (BJH). Thermogravimetric analysis (TG/DTA), Energy dispersive X-Ray analysis (EDX), Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and UV-Vis diffuse reflectance spectroscopy (UV-vis.DRS). The evaluation of acid sites were done by the technique known as temperature programmed desorption of ammonia (TPD) and chemical catalytic activity studies such as liquid-phase reactions analyzed by gas chromatography (Chemito 1000 GC, FID detector). Prior to the study of these techniques, the optimization of calcination temperature was done using X-Ray diffraction analysis (XRD), Surface area measurements (BET) and thermogravimetric analysis (TG) in sol-gel route.
3.1.0 Optimization of the calcination temperature

Catalyst characterization is a lively and relevant discipline in catalysis. In heterogeneous catalysis, the reaction occurs at the surface. Catalyst and catalytic surfaces need to be characterized with reference to their physical properties and by their actual performance as a catalyst [1]. A thorough characterization of the prepared systems was undertaken using various spectroscopic as well as quantitative methods. The selection of calcination temperature is of critical importance in catalysis. The crystalline phase formation also depends on the calcination temperature. It has been reported that the transition of amorphous titania to crystalline titania takes place at 350°C for pure titania [2-4]. An earlier study on the kinetics of the anatase to rutile transformation has shown that the transformation involves an overall contraction or shrinking of the oxygen structure and a cooperative movement of ions. The transformation needs to overcome both the strain energy for the oxygen ions to reach their new configuration and the energy necessary to break the Ti-O bonds as the titanium ions redistribute. A high activation energy is required for this purpose (over 420 KJ/mol) and so the phase transition takes place at a temperature around 500°C [5]. Also the phase transformation is generally accompanied with the crystal growth. In the present case, the titania samples calcined at 450°C contain the prominent characteristic peaks of anatase [6] than calcined at other temperatures in sol-gel route. Also the surface area seems to decrease as the calcination temperature is increased. A crystal size of about 10-11 nm is believed to be the optimum size for photocatalytic applications [7]. Significant difference in crystallite size was observed for the crystallite size of the samples calcined at temperatures other than 450°C. TG graph also confirms the calcination temperature to be 450°C (723K). Comparing Fig. 3.1 and Table 3.2, the crystallinity of nanocrystals increased.
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(XRD became sharper, and FWHM decreased) as the calcination temperature is increased. At higher calcination temperatures, the crystallite sizes formed are larger in size (Table 3.2), which can be attributed to the thermally promoted crystallite growth. These results were in agreement with the previous results reported by Yu et al. [8]. So the calcination temperature was optimized to be 450°C.

![Fig 3.1 XRD of Titania catalysts at 400°C](image1)

![Fig 3.2 XRD of Titania catalysts at 500°C](image2)

![Fig 3.3 XRD of Titania Catalysts by Sol-Gel route at 450°C](image3)
Table 3.1 Surface area (m²/g) of Titania Catalysts by Sol-Gel route

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>400°C</th>
<th>450°C</th>
<th>500°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>56</td>
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<td>T2</td>
<td>70</td>
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<td>22</td>
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<td>T3</td>
<td>96</td>
<td>95</td>
<td>83</td>
</tr>
<tr>
<td>T4</td>
<td>71</td>
<td>43</td>
<td>27</td>
</tr>
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</table>

Table 3.2 Crystallite size (nm) of Titania Catalysts by Sol-Gel route

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>400°C</th>
<th>450°C</th>
<th>500°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>8.9</td>
<td>12.3</td>
<td>16.5</td>
</tr>
<tr>
<td>T2</td>
<td>6.3</td>
<td>9.1</td>
<td>14.8</td>
</tr>
<tr>
<td>T3</td>
<td>7.9</td>
<td>11.7</td>
<td>14.8</td>
</tr>
<tr>
<td>T4</td>
<td>7.2</td>
<td>10.6</td>
<td>15.1</td>
</tr>
</tbody>
</table>

Fig 3.4 TG/DTA graph of Titania Catalyst by Sol-Gel route at 450°C
3.2.0 Characterization Techniques

A brief discussion of the characterization methods adopted was described below. The prepared systems were characterized by the following methods such as

1. Small and wide angle XRD
2. FT-IR
3. N\textsubscript{2} adsorption/ desorption analysis (BJH)
4. TG/DTA
5. EDX
6. SEM
7. TEM
8. XPS
9. TPD
10. UV-Vis.DRS
10. Liquid-phase reactions were analyzed by GC.

3.2.1 X-Ray Diffraction Analysis (XRD)

3.2.1.1 Wide Angle XRD

X-ray diffraction (XRD) by crystals is the most widely employed method for determining the three dimensional structure of solid substances. Recording X-ray diffraction pattern of powdered polycrystalline samples by powder diffractometer method has many applications like qualitative phase analysis, quantitative phase analysis, determination of unit cell parameters, study of orientation and determination of particle size. The X-ray diffraction patterns of the catalysts were recorded using a Rigaku D-max C X-ray diffractometer using Ni filtered CuK\textalpha\ radiation source (\(\lambda=1.5406\text{Å}\)) in the range of 10-80° at a scan rate of 0.1°sec\textsuperscript{-1} using Bragg-Brentan configuration. The anatase peaks of the systems were confirmed by comparing with JCPDS data files. The percentage of phase formed was
determined from integrated peak at $\theta = 25.3$ (101) for anatase and peak at $\theta = 27.4$ (110) for rutile.

![XRD of Titania catalysts](image1)

**Fig 3.5 XRD of Titania catalysts**

**Fig 3.6 XRD of Titania catalysts**

Sol-Gel route  EISA route

![XRD of Titania catalysts by Hydrothermal route](image2)

**Fig 3.7 XRD of Titania catalysts by Hydrothermal route**

The wide-angle XRD patterns showed increasing intensity of the (101) anatase peak alone with slight narrowing of the peak width in Hydrothermal route. Instead of controlling the pore formation, the presence of the block copolymer seems to retard an excessive anatase crystal growth. The XRD patterns of titania and metals incorporated titania (Ag, Ce and Cu) were given in Fig 3.8-3.10. Anatase type structure is kept in all, indicating that the metals are merely placed on the surface of the crystals without being covalently anchored into the crystal. Pure titania
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shows characteristics peaks at 2θ values 25.5, 37.4, 47.9 and 53.0 corresponding to the crystal planes (101), (004), (200) and (211) according to JCPDS data. The small characteristic peaks of Ag were seen at 38.2, 44.4 and 64.6 for the planes (111), (200), and (220) indicating that Ag metal exists on the TiO₂ surface as very fine metal particles and is supported by TEM images. JCPDS peaks for Ce is 29.8(020), 32.9(110), 34.4(021), 37.3(111) and for Cu 43.3(111), 50.4(200). Less intense diffraction peaks of metal particles of Ag at 34.2 and 44.4, Ce at 29.8 and 32.9, Cu at 43.2 and 50.4 suggesting that these are well dispersed on the TiO₂ surface. It may also be noted that the background of the X-ray pattern is flat indicating that TiO₂ is crystalline. Apparent full width at half maximum intensity (FWHM) was determined on (101) and (004) X-ray diffraction lines of anatase phase, as a measure of crystallinity. The crystallite size of the metals incorporated samples in different routes were estimated from line broadening of anatase (101) diffraction peak using Sherrer's equation is recorded in Table 3.3.

<table>
<thead>
<tr>
<th>Sol-Gel Route</th>
<th>Hydrothermal Route</th>
<th>EISA Route</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst</td>
<td>Crystallite Size(nm)</td>
<td>Catalyst</td>
</tr>
<tr>
<td>T1</td>
<td>12.3</td>
<td>THT1</td>
</tr>
<tr>
<td>T2</td>
<td>9.1</td>
<td>THT2</td>
</tr>
<tr>
<td>T3</td>
<td>11.7</td>
<td>THT3</td>
</tr>
<tr>
<td>T4</td>
<td>10.6</td>
<td>THT4</td>
</tr>
</tbody>
</table>

Table 3.3 Crystallite size (nm) of Titania Catalysts
Fig 3.8 XRD of TiO$_2$/0.6\%Pt catalyst by Hydrothermal route

Fig 3.9 XRD of TiO$_2$/0.6\%Pd catalyst by Hydrothermal route
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Fig 3.10 XRD of 0.6% Au/TiO$_2$ catalyst by Hydrothermal route

All the prominent peaks at 2θ values 25.5 are assigned to anatase crystal phase. A weak broad peak at 39.8 for d value 2.26 A is that of Pt metal in Fig 3.8. The presence of Pt observed at 0.6% loading concentration at diffraction angle of 39.8° indexed to (111) plane, however the peak intensity is relatively weak, presumably due to the combination of its low content and small particle size. The crystallite size of the noble metals incorporated samples estimated from line broadening of anatase (101) diffraction peak using Sherrer equation is shown in Table 3.4. The Palladium shows a weak reflection at 40.13 having a d value of 2.25A. An intense peak at 38.18 of (111) plane is that of gold metal deposit over titania surface. The relatively wide width of the peaks indicates small crystallite size, which was estimated to be approximately between 11-13 nm using Scherrer’s equation from the XRD peak broadening analysis at (101) [10]. It is worth to note that the crystallite size was in the range of 11-13 nm, which is known to be optimum for photocatalytic activity. This is because a very small crystallite size causes a blue shift in the light absorption spectrum and favors surface recombination of the photo-exited holes and electrons while a larger crystallite size exhibits lower surface area and thus a smaller number of catalytic active sites per unit mass of catalyst.
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It should also be noted that films made of nano size TiO$_2$ particles coated on substrates may exhibit resistance to abrasion and good mechanical stability [13]. So an optimum particle size as mentioned by Y.Q.Wang et al is required[7]. The UV–vis absorption band edge which is a strong function of the reactivity of the catalysts, reveals that the crystallite size of noble metals (0.2-1.0%) incorporated catalysts prepared by the hydrothermal method is about 11–13 nm while that of pure TiO$_2$ is 10 nm.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>0.2%</th>
<th>0.6%</th>
<th>1.0%</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$/Pt</td>
<td>10.8</td>
<td>12.2</td>
<td>13.0</td>
</tr>
<tr>
<td>TiO$_2$/Pd</td>
<td>10.6</td>
<td>11.4</td>
<td>10.0</td>
</tr>
<tr>
<td>TiO$_2$/Au</td>
<td>12.1</td>
<td>13.0</td>
<td>13.2</td>
</tr>
</tbody>
</table>

Table 3.4 Crystallite size (nm) of noble metals/ TiO$_2$ Catalysts

3.2.1.2 Small Angle XRD

Figures below show the small-angle (SA) XRD patterns of the resultant titania after the assembly and subsequent calcination at 450°C. The patterns imply that the calcined powder has a long-range mesophase order. It should be noted that we could not determine the mesophase structure from this single peak. However, the N$_2$ adsorption-desorption analysis supports the conclusion that we have mesoporous order, as shown in Fig3.18-3.21 [14]. Mesoporous structure TiO$_2$ should be an even more effective catalyst because of its large surface area and porous frameworks [15-19]. Recently, Zhang et al. found that TiO$_2$ microspheres with porous structures have higher photocatalytic activity and are easy to be recovered and used repeatedly [20]. The breakthrough will open a novel pathway for the elevation of the photocatalysis of TiO$_2$ materials. The mesoporous materials have high surface area and high pore volume because of the large
dimensions of the pores and titania in a mesoporous state has high surface area in a continuous structure which makes the electron transfer easier, resulting in increased photocatalytic activity. However, the metal/TiO$_2$ catalysts show the same type of peak, characteristic of mesoporous materials which indicates that the deposition of metal oxides and the subsequent reduction in H$_2$ did not induce a collapse of the meso structure.

![Fig3.11 SAXRD of Titania Sol-Gel route](image1)

![Fig3.12 SAXRD of Titania EISA route](image2)

![Fig3.13 SAXRD of Titania in Hydrothermal route](image3)

Except for the titania catalyst from sol-gel route, all patterns are similar and exhibit a single diffraction peak corresponding to d-spacings of
5.54, 5.48 and 5.25nm respectively. Small angle XRD gives peaks at 2θ values 1.5, 1.8 corresponding to the crystal plane (200) characterizing long-range meso order [21]. This single strong diffraction peak in the small-angle region indicates the presence of meso structure in samples. Meso-structures with more or less regular in diameter and packed at random (well ordered arrangement) often display a single peak in low-angle XRD. Although others have already demonstrated that similar single-reflection products still have short-range hexagonal symmetry [22, 23] those single strong diffraction peaks of the calcined samples may just indicate the presence of mesostructure. No obvious peak is observed on small-angle XRD patterns for the sample calcined at 700°C [24] and 400°C for films by Stucky et al [25] suggesting the complete collapse of the mesoporous framework.

3.2.2 Fourier Transform Infra Red Spectroscopy (FTIR)

Infrared absorption spectroscopy is a rapid, economical and non-destructive physical method universally applicable for structural analysis. The technique is so versatile that it can be used both as a source of physical parameters of crystal lattice determinations and for eliciting purely qualitative relationship between samples. The number, position, bandwidth and intensity of adsorption bands may be correlated with the electronic and molecular structure. It also provides important information about the intermolecular forces acting between the atoms in a molecule, intermolecular forces in condensed phase and nature of chemical bond.

Infrared spectroscopy is a direct method for monitoring transitions between quantized vibrational levels induced by absorption of light in infrared region. A vibration that interacts with the electromagnetic field absorbs the radiation into the molecule, the interaction being provided by an oscillating dipole moment. The spectrum is generally recorded by passing a beam of polychromatic infrared light through a sample and monitoring the radiant power transmitted light at each frequency of 99
source. The technique can be applied to solids as crystals or powder, liquids as solutions or melt, gases, films and adsorbed species. IR analysis can be used to almost any type of samples as long as the material is composed of compounds. Areas of application include catalysis, polymer chemistry, fast reaction dynamics, charge transfer complexes etc. Its utilization is spreading to other areas like layer thickness measurements, reflectivities and refractive index. The use of IR spectroscopy for samples is controlled by the constraints of overall symmetry of unit cell and local site symmetry of each atom within the unit cell.

FT-IR spectra was measured by the KBr technique over the wave number range 400-4000 cm\(^{-1}\) by using ABB BOMEM (MB Series) FT-IR spectrophotometer. Figures 3.14-3.16 show FTIR spectra of mesoporous titania catalyst as well as metal incorporated titania catalysts thermally treated at 450\(^\circ\)C in air flow. FTIR spectra shows broad bands around 3500 cm\(^{-1}\) are due to \(-\text{OH}\) stretching vibrations of free and hydrogen bonded surface hydroxyl groups in titania\[26-28\]. The adsorption bands at 1630 cm\(^{-1}\) are arising from the bending vibrations of physisorbed water molecules in the catalysts\[29\]. After deposition of metals, a clear increase of the OH bands is observed. This surface hydroxylation is very advantageous for the photocatalytic activity of anatase because it provides higher capacity for oxygen adsorption\[30,31\]. Intensive and broad bands appearing at 565 cm\(^{-1}\)-660 cm\(^{-1}\) is that of fundamental vibrations of TiO\(_2\)nano crystals i.e., stretching vibrations of Ti-O bonds\[32\]. It is obvious that \(-\text{OH}\) gps are more on the hydrothermally prepared catalysts which clearly indicates the adsorption capacity of the prepared catalysts and the result is enhanced photocatalytic activity. Figure 3.17 is FT-IR spectra of noble metals incorporated titania catalysts with the fundamental vibrations and peaks at 2362 cm\(^{-1}\) is due to asymmetric stretching of CO\(_2\) adsorbed from the atmosphere.
Fig 3.14 FT-IR spectra of Titania catalysts by Sol-Gel route

Fig 3.15 FT-IR spectra of Titania catalysts by EISA route

Fig 3.16 FT-IR spectra of Titania catalysts by hydrothermal route

Fig 3.17 FT-IR spectra of noble catalysts/TiO₂ by hydrothermal route
3.2.3 N\textsubscript{2} Adsorption-Desorption analysis (BJH)

3.2.3.1 Surface area

The Brunauer, Emmett and Teller (BET) method has been adopted as standard procedure for surface area determination of powdered catalysts. Adsorption of nitrogen gas at its boiling point is generally used for surface area measurements using BET method. The BET theory of adsorption is an extension of Langmuir model to multi layer adsorption. The basic assumptions of BET model are

1. Heat of adsorption for adsorbate-adsorbant system does not change with surface coverage which means that all the adsorption sites on a given surface are energetically homogeneous.
2. Adsorption is multilayer and the heat of adsorption of second and subsequent layers are the same as heat of condensation of adsorbate
3. Dynamic equilibrium occurs within each layer

The BET equation is conveniently expressed in the form,

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

where \( P \)-adsorption equilibrium pressure, \( P_0 \)-standard vapour pressure of adsorbate, \( V \)-volume occupied molecules adsorbed at equilibrium pressure, \( V_m \)-volume of adsorbate required for monolayer coverage and \( C \)-a constant related to heat of adsorption.

A plot of \( \frac{P}{V(P_0 - P)} \) against \( \frac{P}{P_0} \) is a straight line with slope \( \frac{C - 1}{V_m C} \) and intercept \( \frac{1}{V_m C} \). From the slope and intercept, \( V_m \) can be calculated and the specific surface area can be calculated using the relation,

\[ A = \frac{V_m N_0 A_m}{W \times 22414} \]

Where \( N_0 \)-the Avagadro number, \( A_m \)-the molecular cross sectional area of adsorbate (for \( N_2 \) being \( 0.162 \text{nm}^2 \)) and \( W \)-the weight of the sample.
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The linearity of BET plot is severely restricted within the P/P₀ range of 0.005-0.30. A very high or low C value will create considerable error in calculating the effective adsorbate surface area. High C values are likely to be associated with localized monolayer adsorption or with micropore filling. N₂ Adsorption-Desorption measurements at 77K were made using a Micromeritics Tristar 3000 surface area & Porosity analyzer. This helps to determine structural characteristics of TiO₂ materials including Brunauer, Emmett, and Teller (BET) surface area, porosity, pore size and pore distribution in the mesoporous range, using nitrogen adsorption and desorption isotherms. The catalysts were purged with nitrogen gas for 4 h at 350°C using Flow reactor 060 (Micromeritics).

<table>
<thead>
<tr>
<th>Method</th>
<th>Catalyst</th>
<th>Crystal size (nm)</th>
<th>Surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Pore diameter (nm)</th>
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</thead>
<tbody>
<tr>
<td>Sol-gel Route</td>
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</tr>
<tr>
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<td></td>
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<td>95</td>
<td>0.133</td>
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<td></td>
<td>T4</td>
<td>10.6</td>
<td>43</td>
<td>0.097</td>
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</tr>
<tr>
<td>Hydrothermal Route (HT)</td>
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</tr>
<tr>
<td></td>
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<td></td>
<td>THT3</td>
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<td>132</td>
<td>0.453</td>
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<tr>
<td></td>
<td>THT4</td>
<td>12.1</td>
<td>125</td>
<td>0.389</td>
<td>8.8</td>
</tr>
<tr>
<td>Evaporation Induced Self Assembly Route (EISA)</td>
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<td>63</td>
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</tr>
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<td></td>
<td>TEA2</td>
<td>10.5</td>
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<td>0.253</td>
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</tr>
<tr>
<td></td>
<td>TEA3</td>
<td>10.8</td>
<td>88</td>
<td>0.329</td>
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<tr>
<td></td>
<td>TEA4</td>
<td>18.4</td>
<td>24</td>
<td>0.165</td>
<td>24.6</td>
</tr>
</tbody>
</table>

Table 3.5 Surface Properties
In the publications of Song et al, the synthesis and characterization of TiO$_2$ nanoparticles with anatase mesostructure have been reported. His findings describe that this kind of materials which is a combination of the properties of nano scale powders and mesoporous materials contribute much to the photocatalytic and photoelectron chemical performances [33,34].

Crystallite size, calculated using scherrer equation from the (101) reflection of anatase is given in the Table3.5. Total Pore Volume is determined using adsorption branch at the single point of P/P$_0$ =0.989. Pore diameter, estimated using BJH model of the desorption branch [35]. The physicochemical characterization data of the systems were given in the table 3.5-3.7. The specific surface area values of different systems observed to follow the general trend that, as the surface area increases the pore diameter decreases for all the catalysts prepared by different routes. The surface area, pore diameter and pore volume values suggests the mesoporous nature of the catalysts. The pores are formed by interstitial spaces between anatase particles. A crystal size of about 10-11 nm is reported to be the optimum size for photocatalytic application [36]. Reported surface area in HT route for pure TiO$_2$ calcined at 400°C is 98 m$^2$/g, pore volume 0.24 cm$^3$/g and pore diameter 8.01 nm [37]. In this work, HT route prepared TiO$_2$ catalyst calcined at 450°C gives a specific surface area of 110m$^2$/g, pore volume 0.369cm$^3$/g and pore diameter 9.9 nm higher than the reported value. Antonelli and Ying have used different surfactants such as alkyl phosphate anionic surfactants in EISA method and obtained 200m$^2$/g, 3.2nm, calcined at 400°C) [38]. Reported surface area in EISA route for ammonia modified TiO$_2$ catalyst is 340 m$^2$/g, pore volume is 0.28 cm$^3$/g and pore diameter is 3.4nm as given in table 3.6 [39]. But the surface area obtained in this work for non-treated EISA route catalysts
were 63 m$^2$/g, pore volume is 0.28 cm$^3$/g and very large pore diameter is obtained which is about 13.0 nm [40-42]. As already stated above, the difference observed in surface area is due to the remarkably larger pore size of the catalyst. In the case of TiO$_2$/Cu catalyst a pore size of about 24.6 nm is obtained. Kesong Liu et al reported that large pore size depends on the molar ratio of the precursor to the surfactant which is the structure-directing agent and the synthesis process [43]. In the investigated range of metal loading content, the surface area obtained from the different routes decreased in the following order: HT > EISA > SG. The surface areas and pore sizes of the obtained samples allow for comparison with the following results: [a] Stone and Davis (300 m$^2$/g, 2.4 nm, calcined at 400°C), [b] Blanchard et al. (350 m$^2$/g, 2.1 nm, calcined at 350°C). Surface area decreases with increase in calcination temperature and in this work all the systems were calcined at a temperature of 450°C. The mean pore diameter of the SG and HT photocatalysts remained almost identical to that of the TiO$_2$ support, while the total pore volume decreased in similar trend to the surface area which is optimum for the photocatalytic reactions. The pore diameter of the EISA photocatalysts remained almost different with low degradation in the reactions. Since ammonia modified TiO$_2$ metals catalysts given in table 3.6 showed less efficiency in the application reactions, these catalysts were not considered for further studies, may be due to the lower crystallite size and larger pore diameter. Also at temperatures of about 450°C, the conversion decreased due to oxidation of NH$_3$ by oxygen. [38,43,44].
### Table 3.6 Surface Properties of Ammonia modified TiO₂ metals catalysts

<table>
<thead>
<tr>
<th>Method</th>
<th>Catalyst</th>
<th>Crystallite size (nm)</th>
<th>Surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Evaporation Induced Self-</strong></td>
<td>TEA1 NH₃</td>
<td>8.74</td>
<td>138.31</td>
<td>0.448</td>
<td>10.64</td>
</tr>
<tr>
<td><strong>Assembly (EISA) Route</strong></td>
<td>TEA2 NH₃</td>
<td>9.85</td>
<td>89.46</td>
<td>0.457</td>
<td>17.69</td>
</tr>
<tr>
<td></td>
<td>TEA3 NH₃</td>
<td>9.83</td>
<td>131.41</td>
<td>0.405</td>
<td>9.87</td>
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<tr>
<td></td>
<td>TEA4 NH₃</td>
<td>7.49</td>
<td>64.16</td>
<td>0.365</td>
<td>20.69</td>
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</tbody>
</table>

### Table 3.7 Surface Properties of noble metals/TiO₂ catalysts

<table>
<thead>
<tr>
<th>Method</th>
<th>Catalyst</th>
<th>Crystallite size (nm)</th>
<th>Surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Hydrothermal Route (HT)</strong></td>
<td>TiO₂</td>
<td>10.0</td>
<td>97</td>
<td>0.257</td>
<td>9.80</td>
</tr>
<tr>
<td></td>
<td>TiO₂-0.2%Pt</td>
<td>10.8</td>
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<td>0.269</td>
<td>10.5</td>
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<td></td>
<td>TiO₂-0.6%Pt</td>
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<td>0.230</td>
<td>9.1</td>
</tr>
<tr>
<td></td>
<td>TiO₂-1.0%Pt</td>
<td>13.0</td>
<td>99</td>
<td>0.257</td>
<td>12.8</td>
</tr>
<tr>
<td></td>
<td>TiO₂-0.2%Pd</td>
<td>10.6</td>
<td>104</td>
<td>0.265</td>
<td>10.2</td>
</tr>
<tr>
<td></td>
<td>TiO₂-0.6%Pd</td>
<td>11.4</td>
<td>103</td>
<td>0.257</td>
<td>11.0</td>
</tr>
<tr>
<td></td>
<td>TiO₂-1.0%Pd</td>
<td>10.0</td>
<td>100</td>
<td>0.261</td>
<td>9.9</td>
</tr>
<tr>
<td></td>
<td>TiO₂-0.2%Au</td>
<td>12.1</td>
<td>94</td>
<td>0.210</td>
<td>11.0</td>
</tr>
<tr>
<td></td>
<td>TiO₂-0.6%Au</td>
<td>13.0</td>
<td>91</td>
<td>0.245</td>
<td>11.2</td>
</tr>
<tr>
<td></td>
<td>TiO₂-1.0%Au</td>
<td>13.2</td>
<td>88</td>
<td>0.215</td>
<td>10.1</td>
</tr>
</tbody>
</table>

In the case of noble metals/ TiO₂ catalysts prepared by hydrothermal route and calcined at 450°C possess optimum crystallite size and pore
diameter as in table 3.7, were efficient catalysts for the photocatalytic degradation reactions. Pd catalysts show the highest surface area\(^{[45-49]}\). In the investigated range of metal loading content, the surface area obtained from the HT method decreased in the following order: 0.2% > 0.6% > 1.0%. Pore volume shows the general trend.

### 3.2.3.2 Isotherm plots

Figure 3.18-3.19 shows the \(N_2\) adsorption-desorption isotherms of pure mesoporous titania and metal incorporated mesoporous titania outgassed at 350°C for 4h under \(N_2\) flow in the three routes. Except sol-gel route, the isotherms of the calcined mesoporous titania and metal incorporated mesoporous titania by HT and EISA routes are type-IV according to IUPAC classification and exhibit a H2 hysteresis loop that is associated with plate like particles, which is typical for mesoporous materials\(^{[50]}\). In the \(N_2\) adsorption-desorption isotherms these samples showed type-IV character with a characteristic inflexion around \(P/P_0\) in the range 0.6-0.7 for each isotherm indicating capillary condensation in the mesopores. The high steepness of the hysteresis indicates, the high order of mesoporosity. The isotherm of the modified samples slightly decreases due to the metal present on the support (Figure 3.19) whereas the porosity of modified samples slightly increase compared to the blank support. However, the TiO\(_2\)/metals samples show the same type of hysteresis, which indicates that the deposition of metal oxides and the subsequent reduction in H\(_2\) atmosphere did not induce a collapse of the mesostructure. Catalysts in HT route show narrow pore size distribution with a maximum pore diameter of 11.4nm and in the deposition of noble metals12.8nm. For large pore mesoporous materials by EISA type IV isotherm with a clear H\(_2\) hysteresis loop is reported \(^{[51,52]}\). It is reported that the non-treated catalysts prepared by EISA route, shows less photocatalytic activity although anatase
is present in the structure due to the loss of mesoporosity [53]. The stabilizing effect of NH₃-treatment on mesoporous titania by EISA method is also reported [54] and is discussed above. However, it is surprisingly found in this work that the non-treated catalysts in EISA route were mesoporous in nature even after calcination and reduction. The photocatalytic activity was correlated to the formed mesoporous structures (results follows) and found to be less than the catalysts by HT method. So HT route is selected to be the best route for the incorporation of noble metals in TiO₂ catalysts.

In each isotherm three well-defined stages may be identified. First, a slow increase in N₂ uptake at low relative pressure corresponding to monolayer–multiplayer adsorption. Then, a sharp step at intermediate relative pressures indicative of capillary condensation within the mesopores. And a plateau with a slight inclination at high relative pressures associated with multilayer adsorption on the external surface. While, the end point of the hysteresis loop at around a relative pressure (P/Pₒ) of 0.6 is indicative of the presence of a large pore mesostructure, which to our knowledge has not been reported for titania synthesised using this type of template [55–57].
Chapter 3

Hydrothermal route

Fig. 3.18 Isotherms of titania catalysts prepared by different routes

Sol-Gel route

Fig. 3.19 Isotherm plots of metal incorporated titania catalysts by different routes
In the case of noble metals catalysts, the isotherms exhibit typical type IV pattern with hysteresis loop, characteristic of mesoporous materials according to the classification of IUPAC [58] discussed above. A steep hysteretic loop is observed, which is typical for mesoporous materials that exhibit capillary condensation and evaporation [59]. Higher loading blocks the pores, is evident from the curves as 1% loading reduces the steepness from the other [60]. Therefore an optimum loading of 0.6% metal, which gives the isotherm characteristic of mesoporous materials was taken for further studies.

It can be assumed that in this neutral hydrothermal route, the block-copolymer P123 works as a nanocrystallite segregating agent rather than a pore structure template as in the usual mesoporous materials synthesis. In this case, the titania particles were surrounded by block copolymers creating steric stabilisation which is attributed to the di-block hydrophilic characteristic of the Pluronic P123 [61]. The aggregation mechanism is driven by the surface charge potential. The subsequent removal of the block copolymer leads to interstitial pores structural arrangements resulting in the formation of uniform mesopores due to surface charge balanced interaction between coated composite particles. Therefore, the pore formation from interstitial spaces between particles is well controlled, and generates uniform mesopores. It is also observed that the length of the hydrothermal treatment has no significant effect, neither on the surface area nor the pore volume and pore size. But increasing the hydrothermal temperature generates a bigger pore size, thus decreasing the surface area as well as the pore volume [62]. This phenomenon can be related to densification due to the anatase crystal growth. The change in the hysteresis attributes to the presence of the incorporated metal particles on the surface of TiO₂. The crystallite size ranges from 10-13 nm, which fairly covers the requirement.
for the photocatalytic activity. The pore diameter is observed to be higher, in such cases the surface area seems to show a decrease and can be related to the densification due to the anatase crystal growth[63]. This affirms the mesoporous nature of the catalysts and in certain cases only, the pore volume is enhanced while the general pore size characteristic maintained.

![Isotherm plots of different wt% Pt/TiO₂ catalysts](image)

Fig. 3.20 Isotherm plots of different wt% Pt/TiO₂ catalysts
Physico – Chemical Characterization

Fig. 3.21 Isotherm plots of noble metals/TiO₂ catalysts
3.2.3.3 Pore volume measurements

Fig. 3.22 Pore Volume Graphs of Pt, Pd, Au/ TiO$_2$ catalysts
Tuning the hydrothermal temperature in the self-assembly process controls the pore size. The maximum pore volume is contributed by 100 Å size pores. Mesopores are in the range of 20 to 200 Å size. This stemmed from the stabilization of capillary condensation, indicating the good homogeneity of the sample and fairly small pore size since the $P/P_0$ position of the inflection point is related to the pore size. The pore size distribution obtained with BJH method is noticeably narrow, confirming good quality of the sample. The textural properties of the photocatalysts prepared by the hydrothermal method is observed to be the best. The higher the loaded metal content, the larger the decrease in the BET surface area of all the samples \[64,65\]. The mean pore diameter of the photocatalysts remained almost identical to that of the TiO$_2$ support, while the total pore volume decreased in similar trend to the surface area. It may be concluded that such the small amount of loaded metal disturbed the mesopore volume by depositing at the outer and near the outer surface of the TiO$_2$ aggregates, while maintaining the general pore size characteristic.

3.2.4 Thermogravimetric Analysis/Differential Thermal Analysis (TG/DTA)

Thermogravimetric analysis is a well established technique in catalysis for evaluating the thermal stability of the catalyst. It finds widest applications in the determination of different parameters on preparation of catalyst, nature and composition of active phase, effect of added promoters or presence of impurities on the catalyst, dispersion of active phase and active phase support interactions, nature and heterogeneity of active sites on catalyst surface, mechanistic aspects of the reaction under investigation, transient chemical changes that occur on the surface, catalyst deactivation and regeneration. This can also be used for quality control and catalyst
characterization through finger print spectra of different batches of the same catalyst. The technique involves the pursuit of weight of sample over a period of time while its temperature is raised linearly. Recording analytical data and the temperature curve with provision for controlled heating of sample is carried out. In a thermo gravimetric curve (TG), horizontal portions point out regions where there is no weight change, where as weight loss is indicated by curved portions. In derivative thermo gravimetric curve (DTG) plateaus correspond to zero weight change. Any decomposition of the sample is indicated by a dip in the curve and hence provide an idea about species lost during heating step. Differential thermal analysis curve (DTA) exhibits endothermal peak and exothermal peaks indicating changes in the catalyst.

TG/DTA were done on a Perkin Elmer Pyris Diamond thermogravimetric/differential thermal analyzer instrument under nitrogen atmosphere at heating rate of $20^\circ\text{C}/\text{min}$ from room temperature to $800^\circ\text{C}$ with samples mounted on an alumina sample holder. TG- DTA profiles of some representative samples are given. Weight loss below $100^\circ\text{C}$, which is visible in the case of all the samples, is due to evaporation of hydrated water. An exotherm exhibited by TiO$_2$ can be proposed as being due to a phase transition from an amorphous into a crystalline form. It is clear from all the thermograms that there is no apparent weight loss after $400^\circ\text{C}$, which confirms the thermal stability. So the catalysts can be prepared at a lower temperature.
Furthermore, DTA profiles exhibit an endothermic peak centered at around 115 °C and an exothermic peak in the range 400–425 °C. The former is due to the loss of water adsorbed at the surface particle [66], whereas the latter can be attributed to amorphous to anatase transformation [67]. In some cases a small exothermic peak at 290 °C is observed which is usually
assigned to the loss of organic residue [67,68]. In any case, crystallization seems to have been completed at 450°C which prompted to choose such a value as calcination temperature. TG/DTA of a representative sample in noble metal catalysts is given below.

![TG/DTA of 0.6%Pt/TiO₂ catalyst](image)

**Fig.3.24** TG/DTA of 0.6%Pt/TiO₂ catalyst

### 3.2.5 Energy Dispersive X-ray Analysis (EDX)

The stoichiometry of the compositions of the prepared catalysts were checked by EDX analysis and the results obtained are given in Table 3.8 and 3.9. As the first part of the research is to select a suitable route for the preparation, only 6.0 wt% of metals like Ag, Ce and Cu are incorporated to the TiO₂ matrix on a theoretical basis. It has been found that there is expected agreement between the experimentally obtained weight percentage of the elements and the theoretically calculated weight percentage. The EDX analysis performed on the catalysts clearly reveals the occurrence of various elements incorporated. Intensity of the spectra correlates to the amount of element (wt %) present in the catalysts. Data shows that effective promotion of Ag has been occurred on TiO₂ surface.
Composition (wt%) of noble metals incorporated in TiO$_2$ surface increases up to 0.6% in metal loading and then decreases.

<table>
<thead>
<tr>
<th>Route</th>
<th>TiO$_2$/Ag</th>
<th>TiO$_2$/Ce</th>
<th>TiO$_2$/Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TiO</td>
<td>Ag</td>
<td>TiO</td>
</tr>
<tr>
<td>Sol gel</td>
<td>97.76</td>
<td>3.24</td>
<td>97.69</td>
</tr>
<tr>
<td>Hydrothermal</td>
<td>96.92</td>
<td>3.08</td>
<td>97.60</td>
</tr>
<tr>
<td>EISA</td>
<td>96.40</td>
<td>3.60</td>
<td>96.41</td>
</tr>
</tbody>
</table>

Table 3.8 EDX values (Wt %)

| wt% of        | TiO$_2$/Pt | TiO$_2$/Pd | TiO$_2$/Au |
| noble metals  | TiO  | Pt   | TiO  | Pd  | TiO  | Au  |
| Incorporated  |      |      |      |     |      |     |
| 0.2           | 99.90 | 0.10 | 99.89 | 0.11 | 99.85 | 0.15 |
| 0.6           | 99.58 | 0.42 | 99.55 | 0.45 | 99.48 | 0.52 |
| 1.0           | 99.30 | 0.70 | 99.35 | 0.65 | 99.21 | 0.79 |

Table 3.9 EDX values (wt %)

3.2.6 Scanning electron microscope analysis (SEM)

In addition to crystal structure (crystal phase and degree of crystallinity) of TiO$_2$, which is among the parameters determining its intrinsic catalytic properties, its structural properties are also important. This is because catalyst morphology can affect the transport of reactants and products to or from the catalytic active sites as well as the light absorbance for the photo-excitation of the catalyst and the generation of electron–holes pairs. The surface morphology of the catalysts were observed from the SEM images. It is to be noted that after the metal...
incorporation, the surface morphology changes. This is attributed to the observed phenomenon to the poly layer behavior of TiO$_2$ particles with a wide size (and shape) distribution. Here the thickness of the cake vary in the range of 100-300 $\mu$m. It can be observed that the surface is uneven and the structure is very compact. The compactness of the TiO$_2$ cake could confirm the explanations by Xi and Geissen concerning the mechanism of cake build-up at low catalyst concentrations [69]. The morphologies are noticeably dependent on the preparation procedure and the composition. The TiO$_2$/noble metals showed a highly porous and particulate surface.
EISA Route

Fig3.25  SEM images of TiO$_2$ and Ag/TiO$_2$ catalysts by different routes
3.2.7 Transmission Electron Microscopy (TEM)

3.2.7.1 TEM and HRTEM micrographs

Transmission electron microscopy (TEM) images shown below reveals the mesoporous nature of the titania catalyst in different routes. The images clearly indicate cubic ordered structure for titania catalysts prepared by Hydrothermal route, and regions of ordered structure prepared by EISA route, consistent with XRD data which showed broad, low intensity diffraction peaks for the mesoporous phase. The cubic structured mesoporous titania had higher stability than the hexagonal structure\cite{70} and could be formed with a high content of nanocrystalline anatase with conservation of the meso-order. The high crystallite content was monitored by both X-ray diffraction together with dark field Transmission Electron Microscopy. From the images, it is clear that the incorporated metal was formed within the mesopores of titania. The XRD and TEM data are similar to those found by other researchers for porosity materials\cite{71-75}. TEM images show the mesoporous nature of the titania catalyst as well as it indicates cubic crystalline structure for metal loaded titania catalyst, consistent with XRD data. The dark spots are metal particles within titania.
The observed particle size of TiO$_2$ and Ag, Ce, and Cu incorporated TiO$_2$ catalysts were 10-13 nm is in good accordance with the crystallite size estimated from XRD. Results were given in tables 3.5 and 3.6. This crystal size is believed to be the optimum size for photocatalytic application [76].

![TEM images of TiO$_2$ and Ag/TiO$_2$ catalysts prepared by different routes](image)

(a) Hydrothermal Route

(b) EISA Route

Fig3.27 TEM images of TiO$_2$ and Ag/TiO$_2$ catalysts prepared by different routes
Fig. 3.28 HRTEM images of TiO$_2$ and Ag/TiO$_2$ catalysts prepared by different routes.
Figures 3.27 and 3.28 show TEM and HRTEM images of the TiO$_2$ powders prepared at a pH 6.6 slightly higher than the isoelectric point of titania (IEP) which is 5.8, respectively. It could be observed from Fig. 3.27(b) that the nano crystallite showed an agglomerated status, and mesoporous structures without a long-range order in EISA route catalysts. Fig.3.28 (b) shows the corresponding HRTEM image of the sample. It is clear that EISA route prepared catalysts indicate only regions of ordered cubic crystalline structure. But the Fig. 3.27(a) Fig.3.28 (a) show TEM and HRTEM images of the TiO$_2$ powders prepared at a pH 6.6 slightly higher than the iso electric point of titania (IEP) by Hydrothermal route. It could be observed that mesoporous structures with long-range order is there and it shows clear lattice fringes, which allowed for the identification of crystallographic spacing. The fringes of 0.35 nm is that of the (101) crystallographic plane of TiO$_2$ anatase. HRTEM micrographs show the ordered crystalline structure of titania as well as the mesoporous nature. Compared with the other TiO$_2$ preparations, these TiO$_2$ nanoparticles prepared from Hydrothermal route have several advantages, such as being in fully pure anatase crystalline form, having fine particle size with more uniform distribution and high-dispersion ability either in polar or non-polar
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solvents, stronger interfacial adsorption and easy coating on different supporting material. The dark spots are the metal particles within titania. The white spots in Fig 3.29 SA Electron Diffraction pattern are silver particles embedded within titania matrix.

Fig 3.30 TEM images TiO₂ and Pt, Pd, Au/TiO₂ catalysts

The bright-field TEM images obtained in the case of noble metals on the same area of the TiO₂ sample shows the uniform, rounded rectangular shape of the anatase particles is clearly given in the histogram Fig 3.29. Majority of TiO₂/Pt particles occupy a crystallite size of about 12.1 nm, TiO₂/Pd of 11.6 nm, TiO₂/Au of 13.0 nm whereas that of TiO₂ is
10.0 nm, i.e., size of the noble metals incorporated TiO₂ catalysts estimated from the TEM images was about 10-13 nm, which was in good agreement with the values calculated from XRD pattern using the Scherrer equation (Refer Table 3.6). The image clearly shows that the pores are formed by interstitial spaces between anatase particles. The small crystallite anatase seed had experienced crystal growth during the second hydrothermal treatment and calcination processes, as demonstrated by the formation of larger crystal size (~10–11 nm) in the dark-field image. This crystal size is believed to be the optimum size for photocatalytic application [76].

Fig 3.31 A histogram of particle size of TiO₂ and noble metals/TiO₂
Fig 3.32 HRTEM micrographs of TiO$_2$ and Pt,Pd,Au/TiO$_2$

Selected TEM images showing parallel (above) and perpendicular (below) views of the channels in location of the metal nano clusters. HRTEM micrographs show the ordered crystalline structure of titania as well as the mesoporous nature. The dark spots are the metal particles within titania.
3.2.8 X-ray photoelectron spectroscopy (XPS)

As far as XPS results are concerned, the binding energies of the most intense peaks of the various samples are listed in Table 4.0. The origin of the binding energy is the Fermi level. Only the values relative to the powders containing a definite amount of metal are given since, for most of the samples, the amount of different metal loadings did not affect the binding energies.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Scan Details</th>
<th>Ti, 2p\textsubscript{3/2}, 2p\textsubscript{1/2} eV</th>
<th>O, 1s eV (shoulder)</th>
<th>Metal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/TiO\textsubscript{2}</td>
<td>Survey Scan</td>
<td>464.93</td>
<td>534.51(sh)</td>
<td>878.59</td>
</tr>
<tr>
<td></td>
<td>High resolution</td>
<td>460.10 (Ti\textsuperscript{4+}) 465.89</td>
<td>531.58</td>
<td>931.79,951.78</td>
</tr>
<tr>
<td>Pt/TiO\textsubscript{2}</td>
<td>Survey Scan</td>
<td>466.26</td>
<td>528.31(sh)</td>
<td>66.27</td>
</tr>
<tr>
<td></td>
<td>High resolution</td>
<td>459.75 (Ti\textsuperscript{4+}) 465.54</td>
<td>531.04</td>
<td>73.38,76.38, 81.81,83.70</td>
</tr>
<tr>
<td>Pd/TiO\textsubscript{2}</td>
<td>Survey Scan</td>
<td>461.54</td>
<td>533.96(sh)</td>
<td>338.23</td>
</tr>
<tr>
<td></td>
<td>High resolution</td>
<td>459.94 (Ti\textsuperscript{4+}) 466.61</td>
<td>531.25</td>
<td>337.60,342.89</td>
</tr>
<tr>
<td>Au/TiO\textsubscript{2}</td>
<td>Survey Scan</td>
<td>459.87</td>
<td>533.52(sh)</td>
<td>86.53</td>
</tr>
<tr>
<td></td>
<td>High resolution</td>
<td>459.05(Ti\textsuperscript{4+}) 464.94</td>
<td>532.40</td>
<td>83.96, 87.48</td>
</tr>
</tbody>
</table>

Table 4.0 Binding energy values from the XPS scan spectra

At some places, C 1s peak with binding energy value of 286.08 eV was referred to as the standard value for the surface adventitious carbon.
Thus if we include this correction the binding energy values observed in present study will be shifted to higher side by 0.02 eV. During the linear increase of the surface M/Ti ratio, a monolayer coverage of the surface by the dopant oxides is formed. Thereafter, the XPS signal increases very slowly because, due to the electron mean free path limitations, the probability of detecting electrons from a level below the monolayer decreases noticeably. The trend shown in, indicates similar dispersion among the different metal doped samples. In all cases, the monolayer coverage is reached in correspondence of the specific metal loading (6wt% in Cu and 0.6 wt% in noble metals). Above this loading, bigger oxide particles or thicker oxide layers are likely formed. Generally, the larger information depth, determined by the higher kinetic energy of 3d and 4f photoelectrons of the metal, may account for the different behaviour observed in the samples.

![XPS spectra of Ti in Cu/TiO₂.](image)

The Ti 2p XPS spectra showed two prominent peaks, one at 460.1 eV and other at 465.89 eV in the case Cu loaded titania. These were assigned to the Ti 2p₃/₂ and Ti 2p₁/₂ states. These doublet peaks were due to
the spin-orbit splitting of Ti 2p [77]. The above values corresponded to the 4+ oxidation state of Ti. Thus in the prepared samples titanium had 4+ oxidation state with stable Ti-O bond. Binding energies or Ti 2p\textsubscript{3/2} peak clearly correspond to Ti\textsuperscript{4+} in TiO\textsubscript{2} structure. The peak was characterized by a narrow width and it is indicative of Ti(IV) [78]. Subtraction of the normalized Ti 2p spectra did not allow to detect any reduced Ti\textsuperscript{3+} ions in the samples. The binding energy shifts were smaller for the doped samples. These shifts of Ti core level signal, which were attributed to Ti 2p peaks of Cu-Ti-Cu or O-Ti-Cu suggested the successful incorporation of the metal into the titania matrix. For the pure titania these peaks were observed at 458.9 and 464.7 eV respectively (not shown), which were contributions from O-Ti-O in TiO\textsubscript{2} [79-81]. For the other samples such as Pt, Pd, Au the Ti 2p\textsubscript{3/2} binding energy was found at 459.75 eV, 459.94 eV, 459.05 eV and Ti 2p\textsubscript{1/2} states as 465.54 eV, 466.61 eV, 464.94 eV respectively. The XPS results indicated that the types of special peaks for Ti 2p in the metal-TiO\textsubscript{2} systems did not change much.

![XPS spectra of O in Cu/TiO\textsubscript{2}](image)

Fig 3.34 XPS spectra of O in Cu/TiO\textsubscript{2}.

For oxygen, the 1s XPS spectra was de-convoluted using Gaussian multi-peak fitting program gives a peak at a binding energy 531.58 eV for Cu loaded titania samples. Neither the amount nor the type of transition metal modifies the oxygen peaks typical of bare TiO\textsubscript{2}. The valence band of
TiO$_2$ consisted mainly of the O 2p state, which is hybridised with the Ti 3d state \[82,83\]. Fitting of the oxygen region produced the O 1s peak at 531.58 eV for Cu/TiO$_2$ samples and the other at 531.04 eV, 531.25 eV, 532.40 eV. The shoulder at higher binding energy in the survey scan spectrum was associated with hydroxyl groups or adsorbed on the TiO$_2$ surface corresponding to O$_2^-$ and to OH$^-$ respectively. Although the first O 1s peak (TiO) did not change in most of the samples, the shoulder observed in the survey scan of Cu/TiO$_2$ for O, being the second peak (TiOH) changed in various ways. Reports give that the larger the second peak, the greater the hydrophilic properties. Then it is clear from the spectra that, the hydrophilicity was greatest for Pd-TiO$_2$ \[84\]. Therefore, from the O/Ti ratio values, it is expected the existence of a certain number of oxygen vacancies. The presence of this oxygen deficient structure was already reported in TiO$_2$ samples impregnated with different inorganic acids \[85-89\].

![Survey Scan Cu/TiO$_2$](image)

**Fig. 3.35 XPS Survey Scan spectra of Cu/TiO$_2$.**

XPS spectra corresponding to Cu loaded TiO$_2$ calcined at a temperature of 450°C shown in figure 3.35. The determination of the nature and oxidation state of Cu species (Cu$^0$, Cu$_2$O, CuO and Cu(OH)$_2$) is normally accomplished using XPS technique and in particular by means of
the Cu 2p$_{3/2}$ peak study. The appearance of spin-orbit split Cu 2p$_{3/2}$ and Cu 2p$_{1/2}$ with their shake-up satellites which indicates that Cu$^{2+}$ species are formed on titania matrix. The Cu surface content and binding energy of Cu 2p$_{3/2}$ peaks indicate the good dispersion of metal into TiO$_2$ matrix. The XPS peak intensity ratio of I$_{Cu2p}$/ I$_{Ti2p}$ is only 0.085 which is less than that of the threshold indicating highly dispersed CuO on TiO$_2$ surface [90]. The modification of the electron properties of TiO$_2$ induced by the presence of Cu$^{2+}$ species appears to be not particularly beneficial for the photooxidation of organic substrates but could justify the photoefficiency of Cu-doped TiO$_2$ samples for CO$_2$ photoreduction [91].

![Fig.3.36 High resolution XPS spectra of Cu in Cu/TiO$_2$.](image)

The main Cu 2p$_{3/2}$ peak for CuO is shifted by 1.3±0.2 eV above that for the metal and Cu$_2$O, and by a further 1.2±0.15 eV for Cu(OH)$_2$, allowing chemical differentiation [92,93]. The samples containing copper were characterized by a Cu 2p$_{3/2}$ binding energy of 931.78eV. This value
and the presence of the satellite peak on the high binding energy side between 20 eV from the primary photoelectron are indicative of Cu(II) [94]. The presence of Cu(II) determines a broadening of all the features and an increase of the intensity of the low energy states. This perturbation may arise from a larger involvement of the copper d electrons in the molecular orbital, due to the large d occupancy of the Cu (II) species [95].

Fig. 3.37 High resolution XPS spectra of Cu in Cu/TiO$_2$. 
The binding energy of the Cu 2p₃/₂ peak at around 931.78 eV together with the characteristic shake-up feature at a binding energy of 951.78 eV are indicative of Cu²⁺ species [96] while slightly lower binding energy (932 eV) and the absence of shake-up peaks is characteristic of Cu¹⁺ [97]. The shake-up peaks indicate a clear surface oxidation process for Cu during calcination. Large shake-up lines up to 20 eV apart from the main Cu 2p₃/₂ peak were observed, this phenomenon is quite similar to the results of Schon [98] and Novakov [99] who observed the satellite peaks and explained as a result of multiple excitation, but is different from that of Frost et al. [100] who observed that all cuprous compounds did not have any satellite peaks. Furthermore, a major difference between Cu¹⁺ and Cu²⁺ species is the prominent satellite structure on the high binding energy side of the copper core lines for Cu²⁺ species, with two strong shake-up peaks above the principal Cu 2p line. These satellites have been attributed to shake-up transitions by ligand-to-metal 3d charge transfer. This charge transfer cannot occur in Cu¹⁺ compounds and metallic Cu because of their completely filled 3d shells. The results point out that the copper species is present as Cu²⁺ in Cu/TiO₂ though the existence of a small fraction of Cu¹⁺ cannot be discarded. In this case, the absence of shake-up peak appears in very low extent pointing out the presence of small amounts of Cu¹⁺ together with Cu²⁺ species. Thus, a considerable stabilization of Cu₂O species upon calcination is taking place for this system. Colon et al. in the reports observed a similar trend for Cu/TiO₂ showing an important effect of sulphuric acid in the initial precursor solution [101].
Fig. 3.38 XPS Survey Scan spectra of Pt/TiO₂.

The XPS analysis on the Pt 4f\(\text{5/2}\) and 4f\(\text{7/2}\) regions deposited on TiO₂ is shown in Fig. 3.38. No noticeable difference was observed in the region of Ti 2p and O 1s between Pt/TiO₂ and other samples. The surface Pt concentration profile is closely correlated with that of photocatalytic activity in which the Pt loading rapidly increases the activity in initial deposition stage, and then starts to be saturated.

Fig. 3.39 High resolution XPS spectra of Pt in Pt/TiO₂
The de-convolution of the Pt spectra reveals that there exists the main Pt species as Pt$^0$. The Pt 4f$_{5/2}$ and 4f$_{7/2}$ binding energies for each species were assigned to 73.38 and 76.38 eV for Pt$^0$ respectively. The normalized concentration profiles of Pt$^0$ species are almost identical. Whereas, a previous study [102-104] suggested that the photocatalytic activity increases with lowering Pt oxidation state. This is in contrast with the fact that most photocatalytic reactivities of Pt/TiO$_2$ are optimized at a few percent, here 0.6 wt% of Pt concentration [105,106].

Fig. 3.40 XPS Survey Scan spectra of Pd/TiO$_2$.

This implies that the active oxidation state of the incorporated Pd as shown in Figure 3.40.
Two Pd states can be distinguished in these spectra: (i) Pd $3d_{5/2}$ of metallic Pd, which corresponds to the peak at 337.6 eV (ii) the peak at 342.89 eV corresponds to the Pd $3d_{3/2}$ of metallic Pd. The XPS of Pd 3$d$ spectrum with the binding energies of Pd $3d_{5/2}$ and Pd $3d_{3/2}$ lying at about 337.6 and 342.89 eV, respectively, suggest the presence of the Pd$^{0}$ species. This means that metallic state of Pd nanoparticles are stable in the catalyst and the presence of Pd nanoparticles enhances the photocatalytic activity, the reduction of it is worthy of remark in applying Pd nanoparticles to, as reported by Shouji et al. [107].
The Au 4-f emission from the figure reveals that the two sharp peaks 83.96 eV and 87.48 eV are consistent with the Au$^0$ state[108-110].
3.2.9 Ultraviolet Diffuse Reflectance Spectroscopy (UV-Vis DRS)

The measurement of radiation in the ultraviolet region reflected from a material surface constitutes the area of spectroscopy known as ultraviolet diffuse reflectance spectroscopy (UV-DRS). The technique is widely used for the study of solid or powdered solid samples although it can be used for the study of liquids or paste-like materials also. Since only the surface of the sample is responsible for reflection and adsorption of incident radiation, it is used in the chemistry and physics of surfaces. The most appropriate theory treating diffuse reflections and transmission of light scattering layers is the general theory developed by Kubelka and Munk [111,112]. For an infinitely thick, opaque layer the Kubelka-Munk equation can be written as

\[ F(\alpha) = \frac{(1-R_\alpha)^2}{2R_\alpha} = k/s \]

where \( R_\alpha \) is the diffuse reflectance of the layer relative to a non-absorbing standard such as MgO, \( k \) is molar absorption coefficient of sample and \( s \) is the scattering coefficient.

In catalysis the information given by DRS mainly includes the active phase-support interactions, chemical changes during modification procedure leading to active phase and nature of active surface species. Metal centered (d-d) transitions and charge transfer (CT) transitions can be clearly differentiated by UV-DRS and assignment of these gives a picture about the oxidation state and coordination environment of the transition metals.

Absorbance measurements as well as band gap are taken in a Spectro UV-VIS Double Beam UVD-3500, Labomed, Inc. DRS studies of the catalysts prepared is carried out to calculate the band-gap. Absorbance measurements of the UV irradiated dye solution with the catalyst is also
taken in UV-vis Spectrophotometer. The UV–vis absorption band edge is a strong function of the crystallite size of nanosize TiO$_2$ catalyst. The band gap of semiconductor nano materials will increase with the decrease of particle size and this leads to the shift of the absorption edge to a higher energy; this is the so-called quantum size effect. Enough reports are there to support that the band gap between the valance band and the conduction band of semiconductor increases with decreasing particle size [113]. The band gap is a strong function of titania particle size for diameters less than 10nm because of the well known quantum size effect [114]. The interface interaction (matrix support effect) and changes in the coordination and ligand environment and the inter atomic distances of titania micro domains also results in the changes in the band gap absorption edge [115-122].

The UV–vis absorption spectrum of the catalysts prepared by different routes is shown in Fig 3.45. The onset of absorption of wavelength (l) and the corresponding band gap energy (Eg) of TiO$_2$ material is well known to be l = 388 nm and Eg = 3.2 eV for anatase phase, respectively [123]. Charge-transfer from the valence band (mainly formed by 2p orbitals of the oxide anions) to the conduction band (mainly formed by 3d t2g orbitals of the Ti$^{4+}$ cations) occurs (O$_2^-$→Ti$^{4+}$)[124]. In the present work, characteristic band for the tetrahedrally co-ordinated titanium appear at about 390 nm in all the routes. Extrapolating the spectral curve, the band gap energy of the TiO$_2$ catalyst prepared by Hydrothermal route was measured to be Eg = 3.1 eV corresponding to l = 390 nm which is in agreement with other research results [125,126]. The difference in Eg = 0.1 eV is the blue shift compared to bulk anatase TiO$_2$ particles indicated a size of TiO$_2$ crystallites smaller than 10 nm (Refer Table 3.5) due to so called quantum size effect [127]. However, the XRD and TEM data are similar to those found by UV–vis spectroscopy for pure TiO$_2$ prepared by
Hydrothermal route. Similar results were reported by other researchers also [128-130].

Fig 3.44 UV-vis DRS spectra of Titania Catalysts prepared by different routes
3.2.9.1 Determination of Band gap of semiconductor

Modification of titania with other metal ions has a significant impact on the electronic properties of titania. And a direct relationship with the percentage of metal loaded and the band gap energy of titania is obtained in the present study.

Band gap of semiconductor can be estimated by

1. UV-vis.DRS spectra
2. Photocurrent measurement and
3. Cyclic voltammeter measurements

From UV-Vis.DRS, \[ E = \frac{h \times c}{\lambda} \]

\[ B.G \ (eV) = \frac{1240}{\text{Absorption onset (nm)}} \]

The measurements show that upon metal incorporation, the wavelength of catalysts were shifted to higher wavelength region, i.e., a progressive shift in the wave length onset to the visible region is observed in the case of all the metal loaded catalysts in different routes. In Hydrothermal route, band-gap energy of TiO\(_2\) is 3.1 eV, TiO\(_2\)/Cu is 3.06 eV, TiO\(_2\)/Ce is 2.3 eV and TiO\(_2\)/Ag is 2.1 eV according to KM equation corresponding to the wave lengths 390 nm, 405 nm, 539 nm and 590 nm. In Fig 3, observed that ceria and copper metal incorporated TiO\(_2\) catalysts shifts entirely to the visible region with a band-gap around 2.3 eV and 3.06 eV respectively and TiO\(_2\)/Cu catalyst shows an abnormal absorbance in the visible region like TiO\(_2\)/Au in figure 3. But the presence of ceria not only increased the surface area of mesoporous TiO\(_2\) nanoparticles, but also inhibited the mesopores collapse and the anatase-to-rutile phase transformation. This may be attributed to the presence of cerium oxide distributed on the TiO\(_2\) matrix, which is in turn beneficial for effectively enhancing surface area of TiO\(_2\) as reported in table 3.5. The addition
of copper and gold ions and subsequent UV irradiation cause significant changes to the absorption spectrum of TiO$_2$ resulting in high absorbance from 400 nm to entire visible region which is characteristic of surface plasmon absorption (SPR)[133,134]. An absorption corresponding to the surface plasmon band of gold is observed. A band at 550 nm is characteristic of surface plasmon absorption of Au [135]. It is accounted with the presence of loosely bound conduction electron present or this absorption is ascribed to a collective oscillation of the free conduction band electrons of the gold and copper particles in response to optical excitation [136,137]. The band is strongly dependent on the shape and size of the gold clusters [138,139]. Such an absorption edge red shift for the gold modified titania materials depends directly on the Au load. This phenomenon is because, the surface electromagnetic waves that propagate in a direction parallel to the metal/dielectric (or metal/vacuum) interface (SPR). The actual SPR signal can be explained by the electromagnetic 'coupling' of the incident light with the surface plasmon of the copper or gold layer. This is the basis of many standard tools for measuring adsorption of material onto planar metal (typically gold and silver) surfaces or onto the surface of metal nanoparticles. About CuO, Larsson and Andersson also reported that the surface area of the TiO$_2$ support could also be stabilized by addition of CuO to the TiO$_2$ system[140]. Silver catalyst shows an absorbance of lower value and a high shift to the visible region. In noble metal incorporation, metallisation extends the light absorption to longer wave lengths. It shows that the lower energy transitions are possible. This is because the metal clusters give rise to localized energy levels in the band gap of TiO$_2$ into which valence band electrons of TiO$_2$ are excited at wavelengths longer than 390 nm. It is clear from fig.3.56 and 3.57 that onset absorbance measurements that the wave length of all the catalysts shift entirely to the
visible region from 390 to 600nm. 0.6 wt.% Pd content shows the highest shift.

Fig 3.45 Band gap of Catalysts in Hydrothermal Route

Fig 3.46 UV-vis DRS (Abs) spectra of Pt/TiO$_2$ Catalysts of different compositions
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Fig 3.47 UV-vis DRS (R%) spectra of Pt/TiO$_2$ Catalysts

Fig 3.48 UV-vis DRS (Abs) spectra of noble metal/TiO$_2$ Catalysts
3.2.10 Study of Acid-base property

3.2.10.1 Temperature programmed desorption of ammonia (TPD)

Temperature programmed desorption (TPD) has become a powerful tool for the characterization of catalysts. Ammonia is used frequently as a probe molecule because of its small molecular size, stability and strong basic strength [141]. Ammonia can be adsorbed on an oxide surface through hydrogen bonds or through dipolar interaction yielding the total acidity (Bronsted and Lewis type) of the system [142]. The total acidity measurements of catalysts have been carried out by step-wise temperature programmed desorption of NH$_3$. The acid strength distribution is classified depending on the desorption temperature; region 373-473 K is for weak, 474-673 K is due to medium, and 674-873 K is due to strong acid sites [143]. It is attempted to correlate the conversion with total acidity obtained from ammonia TPD measurements and got a very good correlation between activity of reactions such as Epoxidation of...
cyclohexene and Hydroxylation of phenol carried out in liquid phase conditions over acidic sites supporting the suggested mechanism as in Figure 3.50.

Fig 3.50 Mechanism of Temperature programmed desorption of ammonia
Fig 3.51 Temperature programmed desorption (TPD) of ammonia

Strong acidity is observed in the case of TiO₂-Ce catalyst than pure TiO₂ and TiO₂-Cu catalysts. Weak acidic sites are richer in TiO₂–Cu. The redox properties of Ceria and Copper enhance the oxidation reactions. In the case of TiO₂-Cu catalyst, the difference might be related to the stabilization of Cu₂O species and the higher surface area with respect to pure TiO₂[144]. The results of the FTIR spectroscopic measurements of samples pretreated with ammonia presented by Busca et al.[145,146] showed that pure TiO₂-anatase exhibited only Lewis acidity. Since the Brønsted acid sites are absent on the surface of pure TiO₂ [147-149], it can be concluded that they originate from the incorporation of oxides of Ce and Cu. Ammonia molecules chemisorbed on Lewis acid centers are thermally more stable than ammonium ions[150]. The broad temperature range, in which ammonia desorbs from the surface of the pure mesoporous titania suggests the presence of Lewis centers that are characterized by various

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acidic strength. The redox properties of Ceria and Copper enhances the oxidation reactions. This stabilization of Cu$_2$O species in doped TiO$_2$ could be related to the presence of oxygen vacancies generated in the preparation procedure. However, incorporation of Cu significantly increases the surface area with respect to the former ones. This higher surface area values might be attributed to the effect of surfactant that thermally decompose during calcinations at a temperature lower than 450$^\circ$C, increasing the porosity of surface and that the preparation route also improves the Cu loading effect of TiO$_2$. Reports on lewis acidity were given by Busch et al. and Davis et al. [151,152]. The reaction parameters that influence both conversion and selectivity can be optimized in such a way to get maximum catalytic efficiency. Present systems show good conversion and selectivity when compared to the reported catalysts systems. All the experimental observations suggest that structural properties of the photocatalysts such as distribution of ions in the TiO$_2$ matrix and/or on the surface, aggregation/deaggregation and metal-assisted network formation as well as the dispersity of metal are important factors for the photocatalytic activity of these materials[153]. The point of zero charge represents the pH value at which the coverage of H$^+$ equals the coverage of OH$^-$. The pzc is closely related to the surface acidity of a solid and its knowledge allows to evaluate the propensity of a surface to become either positively or negatively charged as a function of the pH. The pzc values of the powders containing Cr, Mo, V and W decrease significantly with increasing the metal content [154] indicating a surface enrichment of species with an acid behaviour as CrO$_3$, MoO$_3$, V$_2$O$_5$ and WO$_3$. For the samples containing Co, Cu and Fe the pzc moves to a value more basic than that of the support[155]. A change in the surface acidity of oxides mixed with other oxides was already reported in the literature. In particular, Connell and Dumesic [156,157] studied the case of mixed oxides
in which an incorporation of the "guest" cation takes place onto the surface of the oxide support. The authors hypothesized that the formal charge on the supported cation is, in some case, not balanced by surface coordination of lattice oxide anions. In this way the coordinatively unsaturated cations are able to behave as surface Lewis acid centres, which strength depends on the electronegativity of the guest metal cation. The absence of Brønsted acidity in the powders containing chromium is at variance with the results of a previous study carried out following the adsorption of ammonia on Cr-loaded TiO$_2$ [158]. The difference can be due to the higher basicity and lower size of ammonia that allow to distinguish among different surface acid sites.
References


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