Chapter 2

Synthesis and investigation of dependence of photoactivity of titania with different anatase/rutile phase ratio
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There are inconsistent claims about the photocatalytic activity of the different phases of titania. In fact the complex nature of interaction between the catalyst and reactant phases and the photons inherit it naturally. This chapter reports the synthesis of a set of anatase, rutile and mixed phase (anatase + rutile) titania nanomaterials through simple sol-gel technique. The physico-chemical characterization results of the samples with the detailed analysis have been presented to understand the material. The photocatalytic activities of the samples were assessed under both UV and visible radiation flux using an aqueous pollutant probe. The study carried out on a series of mixed phase titania with varying ratio of anatase-rutile phases (A/R ratio) including the pristine phases helped the present work in correlating the A/R ratio with their unique photocatalytic response to UV and visible radiation. These results helped in formulating a model reported herein as “Interface model”. The model attempt to explain the high activity of mixed phases along with its dependence on A/R ratio under UV and visible light irradiation wavelength ranges.

2.1. Introduction

The ongoing research on titania photocatalysis may be divided in to three general areas based on the main activity being undertaken by different researchers. These are: (1) exploration of the probability of synthesis of highly UV/Visible active titania photocatalysts using different techniques, (2) investigation of different methods to reduce the electron-hole recombination of titania and (3) identification of potential applications of titania photocatalysts in the development of different systems and devices.

The synthesis, characterization and photoactivity of titania nanoparticles has been thoroughly studied and accounted in a number of excellent reviews [1-2]. A large number of studies correlated their results to either the pristine phase or the
dominant phase of titania and the dopants among other characteristics ignored the presence impact of other phases of titania. Recently impact of synergy of the phases in a mixed phase titania on its performance as photocatalyst has been investigated by many researchers [1-20]. The investigations mainly focused on studying and correlating the physico-chemical characteristics of mixed phase photocatalysts with their photoactivity under either UV or visible light irradiation. The enhanced activity of mixed phases compared to its pristine phases has been explained through different models explaining the causality relationships [4, 5, 8-9]. Out of these models, two models which have gained popularity are referred to as “rutile sink” model and “rutile antenna” model [4]. The approach in these models is based on the investigation of the relative position of conduction band edges in two phases in intimate contact and the existence of trap levels in the bulk. In “rutile sink” model proposed by Bickley et al. [5] the anatase phase is considered to be the collector of incident photons and rutile as the sink for photo-excited electrons diffusing into the rutile region. The photo-excited electrons go to the conduction band edge of rutile phase which is at lower energy level compared to anatase. It must be noted that “rutile sink” model was based on the experiments conducted under UV light illumination. Consequently the role of rutile region in contributing charge carriers was apparently ignored because of high level of recombination of photo-generated energetic carriers in the region under UV illumination. This model didn’t consider activity of mixed phase under visible light. This was followed by a work by Hurum et al. [4] wherein they proposed a model called “rutile antenna” model.

The small visible light activity exhibited by mixed phase titania may be explained by considering rutile as a collector of incident photons because of its smaller band gap. Also it needs a lower energy level on the anatase side for enabling the photo-generated electrons on the conduction band edge of the rutile side to cross-over to anatase side. Hurum et al.[4], through a series of experimental studies conducted under visible light irradiation established the existence of a large number of electron trapping sites in the anatase side. This was supported by the Time-resolved Photo-acoustic Spectroscopic (TRPAS) study by Leytner and Hupp[20] which exhibited the existence of electron trapping sites 0.8 eV below the conduction
band edge of anatase phase. Here the role of interface becomes very important. The electron will not move to the other region unless it is energetically favored and more probable. It is to be noted that the behavior of the interfacial quantized levels of the anatase and rutile phases under UV and visible light irradiation will be different due to their band gap difference. Anatase shows activity only under UV while rutile may be activated by visible light also.

The main aim of the work reported in this chapter is to synthesize a set of anatase, rutile and mixed phase employing sol-gel technique. Pristine and mixed crystalline phases were obtained by calcining the resulting gel at various temperatures. Photoactivity of the samples in UV and visible light was investigated by monitoring the degradation of phenol. Also an attempt was made to explain the high activity of mixed phase titania in terms of a model based on the interfacial phenomena to have a better understanding of the differential UV and visible light activity of the mixed phase catalysts as well.

2.2. Experimental

2.2.1. Materials synthesis

The reagents used for the synthesis of the TiO$_2$ were titanium iso-propoxide [Ti(OCH(CH$_3$)$_2$)$_4$], iso-propyl alcohol [(CH$_3$)$_2$CHOH], and nitric acid (HNO$_3$). Titanium iso-propoxide was obtained from Himedia (India). Isopropyl alcohol and nitric acid were from Merck (India). All the reagents were of analytical grade and double distilled water was used in all the processes.

Many researchers synthesized titania using different methods [21-25]. In this work titanium dioxide samples were prepared using sol-gel method as shown in the flow chart in Figure 2.1. Initially titanium iso-propoxide was mixed in the isopropyl alcohol in 1:10 ratio to prepare the titanium sol. Thereafter, 1 ml of concentrated HNO$_3$ was added to the solution. Finally, a small amount (0.8ml) of water was added drop wise under constant stirring. The solution was left for aging for 12 hrs at room temperature under constant stirring. Finally the gel was heated at a ramping rate of 4 $^\circ$C/min and calcined at 600 $^\circ$C, 650 $^\circ$C, 675 $^\circ$C, 700 $^\circ$C, 750 $^\circ$C, 800 $^\circ$C and 850 $^\circ$C (hereafter referred to as sample T60, T65, T67, T70, T75, T80 and T85, respectively)
for 1 hr each to get the samples.

Figure 2.1: Flow chart of titania synthesis using sol-gel technique

2.2.2 Characterization

X-ray diffraction (XRD) patterns were recorded on diffractometer (Rigaku Miniflex, Japan) using Cu Kα radiation at 30 kV and 450 W and scan rate of 0.05 2θ per sec. The crystallite size of the nanoparticles were calculated using Scherrer formula [6]

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

(2.1)

where D is the crystallite size, λ is the wavelength of the X-ray radiation (Cu Kα =0.15406 nm), k is the shape factor (0.9), β is the full width at half maxima of the most intense peak and θ is the diffraction angle. The anatase to rutile phase mass fraction and anatase-to-rutile ratio(A/R) of the samples are calculated using Spurr’s equation [26]

\[ f_a = (1 + 1.26 \frac{I_a}{I_r})^{-1} \]  

(2.2)

\[ f_r = (1 - f_a) \]  

(2.3)
where \( f_a, f_r \) are the anatase and rutile fraction and \( I_o, I_r \) are the integrated intensities of the most intense peaks of rutile (110) and anatase (101) respectively. Scanning Electron Microscopy (SEM) images were taken using Scanning Electron Microscope (Joel 6390LV, Japan) operated at an accelerating voltage of 15kV. Energy Dispersive X-ray analysis (EDAX) was done using the EDAX attachment (Oxford Instruments, UK) to the same system. The catalyst materials were evaluated for their respective spectral response from UV-Visible diffuse reflectance spectra (UV-DRS) using UV-Vis diffuse reflectance spectrophotometer (Shimadzu UV-2200, Japan). Also the band gap of the samples were calculated using Tauc’s equation [12]

\[
\alpha h\nu = A(h\nu - E_g)^n
\]

where \( \alpha \) is the absorption coefficient, \( E_g \) the energy gap, constant \( A \), is different for different transitions, \( (h\nu) \) is energy of photon and \( n \) is an index which assumes the values 1/2, 3/2, 2 and 3 depending on the nature of the electronic transition responsible for the reflection. The trap states were identified from PL spectra using photoluminescence spectrometer (Perkin Elmer LS55, USA). FTIR studies were done to identify the functional groups using FTIR spectrometer (Nicolet Impact 1-410, USA).

2.2.3 Photocatalytic test:

The photocatalytic activities of the prepared materials were studied in batch reactor mode under UV (\( \lambda < 380 \) nm, Medium Pressure Mercury Arc Lamp (MPMA), 250W, SAIC, Chennai) and visible (\( \lambda > 380 \) nm, 1N1203R, 1000W, Philips) light intensities of 42.5 W/m² and 750 W/m², respectively. The intensity measurement was made using a research radiometer (International light, USA with detectors SD 005, SD 033). The solution used for the testing of the visible photocatalytic activity was phenol. The catalytic material loading of the experiment was kept at 0.5 g/l and the average reactor temperature was maintained at 28 °C. The experiments were carried out by simultaneous exposure of each of the catalysts T60 to T85 each in 30 ml of phenol of 1 mM concentration under stirred condition. The schematic diagram of the batch reactor setup with spectral distribution of sources is given in Figure 2.2.
ensure adsorption-desorption equilibrium each of the solutions were kept in dark for 2 hrs before exposing them to irradiation. The samples were taken from the reactor after every 30 min of exposure. The spectral responses of the centrifuged sample solutions were checked at the wavelength of 270 nm (corresponding to absorption maxima of phenol) using UV-Visible spectrophotometer (Shimadzu 1700, Japan). The rate constants were calculated using the pseudo first order kinetics equation

\[ k_t = \ln \frac{C}{C_0} \]  

(2.6)

where \( k \) is the rate constant, \( t \) is the time and \( C \) is the final concentration and \( C_0 \) is the initial concentration. The photonic efficiency is calculated using the following equation [27]

\[ \xi = \frac{V \Delta C}{J A \Delta t} \]  

(2.7)

where \( V \)=volume (l); \( \Delta C \)= change in concentration (M); \( J \)=flux of photons; \( A \)=illuminated area (m²); \( \Delta t \)=change in time (sec).

The flux of photons \( (J) \) was calculated using the equation

\[ J = \frac{I a}{N_A h c} \]  

(2.8)
where \( I = \text{light intensity}; \ \lambda = 600 \text{ nm}; \ \mathcal{N}_A = \text{Avogadro constant}; \ h = \text{Planck's constant}; \) and \( c = \text{speed of light}.

### 2.3 Results and discussion

The X-ray diffraction spectra (XRD) of the prepared samples calcined at different calcination temperatures are depicted in Figure 2.3. The high intensity peaks of the spectra show high crystallinity of the sample. On careful study of the phase transition of the samples (T60 – T85), it is found that the samples calcined at low temperatures (T< 600 °C) resulted in pure anatase phase. The phase transition began at 650 °C and was followed by a series of mixed phases at high temperatures. The peaks in the spectra of T60 to T85 are in good agreement with the JCPDS file no: 894921 and 894202 of tetragonal systems for pure anatase phase and pure rutile phase, respectively. The samples T65 to T80 show mixed phase with a consistent increase of intensity of rutile phase. The complete phase transformation occurred for T85 at 850 °C which is in good agreement with the earlier reports [11, 21]. The assumption of T65 and T85 to be pristine phases is limited by the resolution of XRD spectra and hence any deviation in the results in the literature may be attributed to the
presence of other phases as well. The average crystallite size of each TiO\textsubscript{2} sample (given in Table 2.1) is estimated from the broadening of XRD peak (101) for anatase, (110) for rutile and both (101), (110) for mixed samples using Scherrer formula (equation 2.1). The crystallite size is found to be in nanoscale and a consistent increase in the size is observed in accordance with calcination temperature in both anatase and rutile phase. Each of the anatase and rutile phase mass fraction and anatase-to-rutile ratio (A/R) of the samples are calculated using Spurr’s equation (equation 2.2 to 2.4). The values of anatase and rutile fraction as well as A/R ratio are depicted in Table 2.1.

Table 2.1: Crystallite size, phase composition and band gap details for titania catalysts calcined at different temperature

<table>
<thead>
<tr>
<th>Sl. No</th>
<th>Calcination Temperature (°C)</th>
<th>Crystallite Size (nm)</th>
<th>Fraction (%)</th>
<th>A/R Ratio</th>
<th>Band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Anatase</td>
<td>Rutile</td>
<td>Anatase</td>
<td>Rutile</td>
</tr>
<tr>
<td>1.</td>
<td>600</td>
<td>33.66</td>
<td>-</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>2.</td>
<td>650</td>
<td>38.38</td>
<td>51.38</td>
<td>91.93</td>
<td>8.07</td>
</tr>
<tr>
<td>3.</td>
<td>675</td>
<td>41.60</td>
<td>45.20</td>
<td>87.52</td>
<td>12.48</td>
</tr>
<tr>
<td>4.</td>
<td>700</td>
<td>40.65</td>
<td>51.76</td>
<td>37.84</td>
<td>62.16</td>
</tr>
<tr>
<td>5.</td>
<td>750</td>
<td>47.27</td>
<td>60.60</td>
<td>23.60</td>
<td>76.40</td>
</tr>
<tr>
<td>6.</td>
<td>800</td>
<td>51.48</td>
<td>51.87</td>
<td>8.53</td>
<td>91.47</td>
</tr>
<tr>
<td>7.</td>
<td>850</td>
<td>-</td>
<td>55.32</td>
<td>0</td>
<td>100</td>
</tr>
</tbody>
</table>

The SEM micrographs of prepared catalytic materials were obtained to investigate the powder morphology and microstructures of the samples (Figure 2.4). The particles size of the developed materials in the micrographs shows a homogeneous distribution of the crystalline material. The SEM micrograph of the sample T60 (pure anatase) shows spherical morphology with an agglomerate size of ~100 nm. Sample T70 and T75 show a size distribution with mixed morphology clearly depicting a phase transition. The two dissimilar size distributions in the mixed phase could be ascribed to the different phases as estimated from XRD spectra. The sample calcined at 850 °C (pure rutile) shows a uniform agglomerate size distribution of ~200 nm. The crystallite sizes increased with the calcination temperature and are comparable with the XRD data. The highly agglomerated large crystallite size in Figure 2.4(d) indicates that the particle growth occurs with temperature and pristine rutile phase has large crystal size.
The elemental compositions of the synthesized TiO₂ nanoparticles were analyzed by EDAX spectrum Figure 2.4 (inset). The EDAX spectra confirm the presence of titanium and oxygen on the surface.

The optical response of the samples were analyzed using UV-DRS and are shown in Figure 2.5. The samples calcined at higher temperature shows a red shift in the absorption in accordance with the temperature. The sample T60 (pure anatase) and T65 show absorption edge around 380 nm. The absorption edge is at 400 nm for samples T67 and T70. The samples calcined at higher temperature (T75 to T85) show a red-shifted absorption edge at about 420 nm. The band gap of the material was calculated by plotting $hv$ vs. $(a(hv))^2$ using Tauc’s equation (equation 2.5) as shown in Figure 2.6, and depicted in Table 2.1. The sample T60 (pure anatase) and T85 (pure rutile) showed a band gap of 3.25 and 3.0 eV respectively which agree well with the earlier reports [6, 12] as well as the XRD data. The band gaps of the
mixed phase samples (T65 to T80) lie between 3.00 to 3.25 eV and are in good agreement with the literature [6, 12] and the XRD data. The significant shift in the optical band gap observed in the Tauc’s plot (Figure 2.6) suggests a change in the electronic structure of the titania catalysts with increasing temperature.

Figure 2.5: Diffuse reflectance spectra of titania catalysts calcined at different temperature.

Figure 2.6: Tauc’s plot showing optical band gap.
absorption profiles to lower energies with the rise in calcination temperature may be linked to the increase in the rutile fraction and growth of titania particles.

The photoluminescence responses of the samples were studied using PL spectra as shown in Figure 2.7. The excitation wave length of 340 nm was employed in all the cases. All the samples showed an emission peak corresponding to the band edge corresponding to direct transition as discussed in UV-DRS. The emission peaks of the samples may be attributed to corresponding phases. The small emission peak of the samples T65 to T80 can be attributed to the polymorphic nature of titania as discussed in the above characterizations. These trap levels were identified in the PL spectra between 475 nm to 550 nm and are attributed to the oxygen vacancy levels [28]. The trap levels play a positive role in reducing the recombination. The change in the PL intensities can be related to presence of oxygen vacancies and the recombination rate [10]. Low PL intensity is ascribed to the reduced recombination which plays a positive role in the photocatalytic activity.

FTIR analyses were carried out to study the surface chemistry of the samples calcined at different temperature. Figure 2.8. represents FTIR spectra of the samples.
T60 to T85. The bands around 3400 cm\(^{-1}\) and 1640 cm\(^{-1}\) correspond to the surface absorbed water and hydroxyl groups [3]. The spectra of the samples showed a decrease in the intensity of the band around 3400 cm\(^{-1}\) with the calcination temperature. It can be attributed to the decrease of surface absorbed water and hydroxyl groups. The band around 2400 cm\(^{-1}\) is because of the surface adsorbed CO\(_2\) from the air[3]. It can be observed that with the increase in the calcination temperature the amount of CO\(_2\) is decreasing. The band observed at 550 cm\(^{-1}\) in the samples’ spectra is ascribed to pure anatase phase and the bands between 530-640 cm\(^{-1}\) to the rutile phase [29]. The bands around 400-700 cm\(^{-1}\) are due to the Ti-O stretching and Ti-O-Ti bridging stretching modes in the sample [29]. It is observed that the band at 400 cm\(^{-1}\) is extending slowly up to 700 cm\(^{-1}\) with the increase in calcination temperature and the maximum broadening is observed in the sample with pure rutile phase. The bands around 3635, 3645, 3680 cm\(^{-1}\) are due to tetrahedral coordinated vacancies (\(\delta\text{Ti}^{4+}-\text{OH}\)) and the bands around 3750-3850 cm\(^{-1}\) are due to the octahedral vacancies (\(\delta\text{Ti}^{3+}-\text{OH}\)) [30]. The number of bands due to tetrahedral coordinated vacancies (\(\delta\text{Ti}^{4+}-\text{OH}\)) is more in the case of mixed phase. The number of bands for octahedral vacancies (\(\delta\text{Ti}^{3+}-\text{OH}\)) is more in the case of pure anatase as well.
as pure rutile phase. But the intensity of tetrahedral co-ordinated vacancies (\(\text{Ti}^{4+}\)-OH) is high in the case of pure rutile samples which could be playing a positive role in the reduction of recombination [31]. The bands around 3563, 3172, 1600 cm\(^{-1}\) are the corresponding peaks for Ti-OH. It is found to be increasing with the calcination temperature and can be directly correlated to the active sites and the photoactivity.

2.3.1 Kinetic study for degradation of phenol

Photocatalytic performances of the samples were tested for degradation of phenol under UV and visible light (Figure 2.9. and Figure 2.10). The degradation data is found to fit pseudo-first-order kinetics as shown in Figure 2.11 and 2.12. The rate constants, calculated by plotting \(\ln \frac{C}{C_0}\) vs. time, are shown in Table 2.2. The results of experiments conducted under UV irradiation facilitates its direct comparison with the results of Bickley et al. [5].

![Figure 2.9: The degradation curve of the phenol under UV exposure](image)

The results of visible light irradiation may be compared with the results of Hurum et al. [4]. Under both irradiation conditions the mixed phase samples showed higher activity compared to pristine phases with the optimum corresponding to different A/R ratio respectively [Table 2.1]. Under UV radiation the samples T65 and T67 showed
gradually increasing photoactivity. These samples have high (> 1) A/R ratio of 11 and 7, respectively, corresponding to anatase content of 92 and 88%. These results corroborate the high activity of Degussa P-25 which has the A/R ratio of 3.3 with anatase content of 77%. Further decrease in the A/R ratio results in inferior performance under UV radiation. On the other hand under visible radiation the samples T70 and T75 show better activity. Both the samples have low (<1) A/R ratio of 0.3 and 0.6 respectively corresponding to anatase content of 24 and 38%, respectively.

![Figure 2.10: The degradation curve of the phenol under visible light exposure](image)

It leads us to conclude that for the photocatalysts to have high activity under visible radiation the A/R ratio should be low and in a narrow range within 0.6 to 0.3 [Figure 2.13]. Figure 2.13. clearly shows that the optimum values for high photoactivity under UV and visible radiation are about 5.0 and 0.5, respectively. It leads us to believe that mixed phases are superior to pristine phases under both UV and visible irradiation conditions. The sample T85 (rutile) showed a rise in the activity under UV as well as visible radiation. It may be assigned to higher absorption of T85 sample in the visible region coupled with reduced recombination as indicated in FTIR analysis. However it needs further investigation. It is well-known that the pair of polymorphs
in mixed-phase photocatalysts can effectively reduce the recombination of photo-generated electrons and holes to enhance the photocatalytic activity.

![Figure 2.1: $-\ln (C/C_0)$ vs. time plot for determination of rate constants of degradation of phenol under UV irradiation](image1)

Figure 2.11: $-\ln (C/C_0)$ vs. time plot for determination of rate constants of degradation of phenol under UV irradiation

![Figure 2.12: $-\ln C/C_0$ vs. time plot for determination of rate constants of degradation of phenol under visible light irradiation](image2)

Figure 2.12: $-\ln C/C_0$ vs. time plot for determination of rate constants of degradation of phenol under visible light irradiation
Once irradiated, the electrons would be excited from the valance band into the conduction band and move down from one phase to another depending on the availability of favorable energy states, thus, avoiding recombination[4,24]. This synergistic effect may increase the photocatalytic activity of the mixed-phase nanocrystals to some degree. According to Li et al. [22], such an interfacial structure between the two TiO$_2$ polymorphs would include large amounts of tetrahedral Ti$^{4+}$ sites. These tetrahedral Ti$^{4+}$ sites could serve as hot spots for photocatalytic activity and thus make the mixed-phase nanocrystals into an effective photocatalytic relay for solar energy utilization. Such interfacial benefits have been observed mainly between anatase and rutile. The activity of the photocatalysts is directly correlated with particle size and specific surface area. It has been shown recently that A/R phase ratio has more influence on photoactivity than these parameters[13].

Table 2.2: Degradation rate constants and photonic efficiency of the catalysts for phenol degradation under UV and visible light irradiation

<table>
<thead>
<tr>
<th>Sl. No</th>
<th>Catalyst samples</th>
<th>Under UV Light Irradiation</th>
<th>Under Visible Light Irradiation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rate Constant (hr$^{-1}$)</td>
<td>Photonic efficiency (%)</td>
<td>Rate Constant (hr$^{-1}$)</td>
</tr>
<tr>
<td>1.</td>
<td>T600</td>
<td>0.094</td>
<td>0.314</td>
</tr>
<tr>
<td>2.</td>
<td>T650</td>
<td>0.165</td>
<td>0.544</td>
</tr>
<tr>
<td>3.</td>
<td>T675</td>
<td>0.208</td>
<td>0.518</td>
</tr>
<tr>
<td>4.</td>
<td>T700</td>
<td>0.070</td>
<td>0.243</td>
</tr>
<tr>
<td>5.</td>
<td>T750</td>
<td>0.076</td>
<td>0.266</td>
</tr>
<tr>
<td>6.</td>
<td>T800</td>
<td>0.037</td>
<td>0.156</td>
</tr>
<tr>
<td>7.</td>
<td>T850</td>
<td>0.055</td>
<td>0.207</td>
</tr>
</tbody>
</table>

For the comparative analysis of the performance of heterogeneous photocatalysts with respect to the radiation intensity and the irradiation spectrum, the photonic efficiency appears to be a reasonably appropriate parameter which is measurable. The photonic efficiency were calculated using the equation 2.6 and 2.7 and shown in Table 2.2 and are identical to the earlier report [32]. The photonic efficiencies of all the mixed phases are high compared to pristine phases across the irradiation wavelength range. Among them the samples T65(A/R ratio =11) and T70(A/R ratio=0.61) showed the highest photonic efficiency under UV and visible
light respectively. It is in accordance with the conclusion drawn from the results of kinetic studies. However it may be noted that photonic efficiency is dependent on

![Graph showing variation in rate constants of degradation of phenol with increase in rutile content (%)](image)

Figure 2.13: Variation in rate constants of degradation of phenol with increase in rutile content (%) under UV and visible light irradiation

the type and design of the reactor as well. So only the relative values of photonic efficiency are significant

2.3. 2 Proposed model

In the proposed model, rutile and anatase phases are visualized to be in intimate contact in a nanocrystallite. According to band theory of energy states the band bending at the interface of the crystallite will occur in accordance with the work function, carrier type, carrier density and band gap of the nanocrystallite materials. In fact in the region of band-bending an intrinsic barrier potential will be created. The titania phases are basically n-type [33] and the work function for anatase has been reported to be greater than rutile [34]. Under equilibrium the band structure of the interface region will be as shown in Figure. 2.14(a). Li et al. [22], based on the results of Leytner and Hupp[20], have explained the existence of a barrier potential of 0.2 Volt between the anatase and rutile phases in the band bending region. In the
nanocrystallite the band bending region is expected to be large and may be of the same order as that of the crystallite size. From a very conservative estimate the intrinsic field in the region would be of the order of $10^7$ V/m. The band bending region will become narrower under illumination due to increase in photo-generated carrier concentration. The figure shows the band bending in the interfacial region

![Band bending diagram](image)

Figure 2.14: Proposed interface band model a). under equilibrium, b). under irradiation $\lambda \leq 380$ nm, c). under irradiation $\lambda > 380$ nm

of two n-type region of titania phases in contact under equilibrium in dark. To understand the band bending region of titania phases under illumination, we consider the two conditions of irradiation of the sample - Condition- A: irradiation with $\lambda \leq 380$ nm (photons having energy corresponding to the band gap of anatase phase) and Condition-B: irradiation with $\lambda > 380$ nm (photons with energy less than the band gap of anatase). Under condition- A there is an equal probability of excitation of electrons to the conduction band in the interfacial region of two phases under UV irradiation. Hence the band structure remains almost same although Fermi level will show an upward shift (Figure 2.14b). The barrier field in the interfacial region will draw the electrons towards rutile conduction band. This conforms to the model propounded by Bickley et al.[5]. It must be noted that this is corroborated by a recent
observation by Scotti et al.[7] based on EPR measurements wherein the presence of a large number of electrons have been reported in the rutile side of the interface. In both the reports UV irradiation source was used. Under condition-B the radiation will be absorbed by rutile phase only resulting in excitation of electrons in its conduction band. Consequently the energy band profile under illumination will identical be as shown in Figure 2.14c. The barrier potential at the interface will favor the electrons’ movement towards an intermediate lower energy level below anatase conduction band. This is supported by another observation made by Hurum et al.[4] based on EPR measurements under illumination covering visible range (λ > 400 nm). The results reported in the present work also support this explanation. Crystallite size in the mixed phase has extremely important role to play. The present mechanism also supports the dependence of photoactivity on crystallite size of mixed phase catalyst. Under visible light illumination rutile side of the barrier potential region (band bending region) will generate photo exited electrons and holes which under the influence of the barrier potential will move in opposite directions. As stated earlier the barrier potential region may be of the order of the crystallite size. Now if the crystallite is very small carriers will reach the surface to take part in the photoactivity. In large nanocrystallites the separated charge carriers will undergo trapping or recombination outside the barrier region depending on the physico-chemical environment. Hence the probability of recombination is high. This is reflected in the photoactivity of the samples as well. The radiation absorbed outside the barrier region acts in the manner similar to pure anatase and rutile phases unaffected by the interfacial effects. Thus the “interface model” presented here is able to support the observation made by both Bickley et al. and Hurum et al.

2.4. Conclusion:

Photoactivity of the mixed phase titania for the degradation of phenol under UV and visible light has been studied with a view to explain the behavior of the mixed phase. The results suggest that mixed phases are more active than pristine phases. These results also suggest that the optimum range of A/R ratio under UV and visible light are different. This study may help in further development of photocatalyst with high activity across the wavelength range. The suggested model
explains the mechanism of mixed phase photoactivity and supports both "rutile sink" and "rutile antenna" model. Here the proposed model, called "interface model", is based on the experimental investigations and the analysis of results after considering interfacial band bending and resulting movement of electrons in different directions under irradiation with \(\lambda \leq 380\, \text{nm}\) and \(\lambda > 380\, \text{nm}\).

For the development of highly active photoactive photocatalyst the absorption of titania has to be shifted to visible range as the major solar spectra is in visible region.
References


