CHAPTER 4B

EVALUATING THE POTENTIAL OF A NEW TITANIA PRECURSOR FOR THE SYNTHESIS OF MESOPOROUS Fe-DOPED TITANIA WITH ENHANCED PHOTOCATALYTIC ACTIVITY

4B.1 INTRODUCTION:

Amongst the metal ions, special attention is paid on iron doped nanosized TiO$_2$ for several reasons [1]. They are – (a) the charge carrier recombination time is largely influenced by the presence of iron cations (b) presence of iron induces a batho-chromic effect and (c) iron doped photocatalyst is efficient in several important photocatalytic reduction and oxidation reactions.

In this chapter we have reported the potential of a new titania precursor namely potassium hexafluorotitanate which is extremely stable, water soluble, non-corrosive, not eco-toxic and above all the product itself and its products of degradation are not toxic and non-inflammable. Although titanium alkoxides are widely utilized as raw materials in the so-called sol–gel process, they are very unstable with respect to hydrolysis in water and produce water-insoluble precipitates and thus they cannot be regarded as suitable titanium reagents for an aqueous solution process. Potassium hexafluorotitanate is soluble in water with a solubility of 1.28 g per 100 g of water at 293 K. The aqueous solution produces a precipitate when treated with ammonia. The novelty of the precursor and the reported process is that-

(i) Water is used as a processing solvent which is less costly, environment friendly and can be regarded as a green solvent.

(ii) A “gel”-like matter rather than a simple precipitate is formed.

(iii) A chelate-type ligand is used as a stabilizer for the constituent metal ions.

(iv) The precursor material, obtained after a thermal decomposition of the “gel”-like matter, is found to be amorphous from XRD analysis, ensuring in most cases the compositional homogeneity of the target oxide material.
In this chapter we have reported the synthesis of mesoporous Fe-doped TiO$_2$ from K$_2$TiF$_6$ with block polymer as template and studied the photodegradation of bromocresol green in aqueous media and then compared its activity with Fe-doped titania prepared from titanium isopropoxide and also with undoped as well as commercial titania.

4B.2 Experimental:

4B.2.1 Photocatalyst preparation

Preparation of Fe (III) doped TiO$_2$ from ferrous sulphate hexahydrate and potassium hexafluorotitanate:

K$_2$TiF$_6$ was dissolved in 125 ml distilled water and hydrolyzed by slow addition of NH$_4$OH solution under constant stirring at room temperature, in a Teflon beaker, until the reaction mixture had attained a pH of 7.5. The precipitate thus obtained was filtered, washed free from F ions with distilled water. The precipitate was further dispersed in 250 ml of hot distilled water and peptized by the addition of 10% HNO$_3$ solution. Required amount of FeSO$_4$.7H$_2$O was added to the solution, which immediately oxidized to Fe (III) ions. The solution was then added into surfactant triblock copolymer poly (ethylene glycol) –block –poly (propylene glycol) –block poly (ethylene glycol) EO$_{20}$PO$_{20}$EO$_{20}$ solution under stirring. The molar ratio of K$_2$TiF$_6$: FeSO$_4$: Surfactant P123:H$_2$O is 0.9: 0.1: 0.12:100. After stirring the mixture for 30min, the resulting mixture was aged at room temperature for 12hrs and then transferred into a Teflon lined stainless steel autoclave at 373 K for hydrothermal treatment. After 72 hrs, the resulting mixture was cooled to room temperature, separated by centrifugation, washed with water and ethanol, and then dried at 393 K overnight. The organic materials were removed by stirring the titania powders with a water and ethanol solution (molar ratio 1:1) of 0.4 gm NaCl at 313 K for 5 hrs. The resultant solids were washed with water and ethanol and then dried at 393 K overnight. The as-synthesized sample was divided into two parts. One part was calcined in air at 873 K for 6 hrs with a heating rate of 2 degree per minute and is marked F1 and the other part is labeled as-synthesized sample.
4B.2.2. Preparation of Fe (III) doped TiO$_2$ from ferric nitrate hexahydrate and titanium isopropoxide:

One molar solution of Ti (OCH (CH$_3$)$_2$)$_4$ in absolute ethanol (5 ml) was drop-wise added to 47 ml of distilled water under vigorous stirring. The final pH was adjusted to 1.77 with nitric acid. The TiO$_2$ sol was drop wise added to an aqueous 0.1 molar solution of Fe (NO$_3$)$_3$ ·9H$_2$O/ in a water bath at 323K with continuous stirring. The final mixture was stirred for 2 h until it became a transparent yellowish clear solution. The mixture was subjected to a hydrothermal treatment for 3 days at 423 K and was further calcined at 673 K for 5 h in an electric furnace to obtain crystalline powders of Fe doped TiO$_2$. The powder as obtained is marked as F2. For the purpose of comparison, undoped TiO$_2$ (T) was prepared by the same method without the use of ferric nitrate nonahydrate.

4B.3. RESULT AND DISCUSSION:

The XRD patterns of the as synthesized and calcined catalysts are shown in figure 4B.1 and compared with the XRD pattern of pure anatase phase (JCPDS No. 84-1286). The XRD peak of Fe$_2$O$_3$ normally appears at two theta value 35° (110). Absence of this peak indicates that probably some Fe$^{3+}$ ions replaced Ti$^{4+}$ ions in the crystal framework of TiO$_2$ because the radius of Fe$^{3+}$ is similar to that of Ti$^{4+}$[2]. Average crystal sizes calculated from the broadening of the (101) peak of anatase phase were ca.8.6 nm and ca.13.7 nm for as synthesized F1 and F2, while for undoped TiO$_2$ (T), it is ca. 17.23 nm. The average crystal sizes of F1, F2 and T increase after calcinations to ca. 14.79, 16.23 and 26 nm respectively because of the growth of the quantum sized grains [3]. Data in Table 4B.1 showed that the particle size and surface area of the samples were dependent on method of preparation. Chemical composition of TiO$_2$ pigments depends on the production method, the raw material used, and on the purpose for which the photocatalyst was synthesized.
It was reported that polymorphous transformation occurs at a wide range of temperatures 673-1373 K, though normally it takes place at about 1073—1123 K. XRD of our products reveals that no such transformation to rutile phase took place when calcined up to 773 K.

Figure 4B.2- SEM image of mesoporous Fe-doped TiO$_2$ (F1)
The surface morphology of Fe doped photocatalysts was studied by scanning electron microscopy and the micrographs is presented in figure 4B.2. SEM image showed that F1 samples consist of uniform porous structure. EDX analysis of Fe doped titania samples F1 (figure 4B.3) and F2 (figure 4B.4) showed the presence of Fe in the mesostructure.

Figure 4B.3- EDX of Fe_doped titania F1

Figure 4B.4 EDX of Fe_doped titania F2
The diffuse reflectance UV–VIS spectra of the calcined samples T, F1 and F2 are reported in Fig. 4B.5. All the samples have in common an intense UV absorption band with a maximum in the range 220–320 nm due to charge transfer from oxygen to titanium (IV) [4-6]. The position of this band is affected by the coordination geometry around the titanium atom and by the presence of adsorbents. More precisely, the bands in the region 210–240 nm are attributed to charge transfer from oxygen to tetrahedral Ti (IV) [7], whereas the bands at higher wavelength ($\lambda > 240$ nm) are due to octahedral Ti (IV) sites [8-10]. The position of the band maximum of UV-VIS spectra shifts towards higher wavelengths in the order T < F2 < F1 (Fig 5). In T the tetrahedral component of Ti (IV) was prevalent, whereas in the F1 and F2 a remarkable amount of the titanium sites was in the octahedral coordination. It can be clearly seen that the band gap energy values decrease with the presence of Fe dopant. TiO$_2$ nanomaterials show band-to-band absorption at 380 nm (curve T).

Figure 4B.5 UV visible absorption spectra of T, F1, and F2

In comparison to TiO$_2$, the absorption edge of F1 and F2 was broader and shifted to higher wavelengths. The band gap values for F1, F2 and T were ca. 2.08 eV, ca. 2.76 eV and ca. 3.1 eV respectively. Both F1 and F2 showed shoulder peaks in the
wavelength range of 400-700nm which is absent in T. It was reported that Fe (III) ions shows strong absorption bands in the UV region [11]. Therefore shoulder peaks are probably due to the absorption induced by iron.

The pore size distributions and N\textsubscript{2} adsorption-desorption isotherms of calcined F1 and F2 were shown in figure 4B.6. The BET surface area for T, F1, and F2 were presented in Table 4B.1. All the isotherms are type IV, which is characteristic of mesoporous materials.

![Figure 4B.6 BET isotherm of F1, F2 (calcined) Figure 4B.7 BJH pore diameter](image)

In both F1 and F2, the pore size distributions are narrower than that of undoped titania. BJH pore size distribution plot (figure 4B.7) showed the particle size distribution in the range 12-17 nm which was also consistent with the XRD data. The surface area of the as synthesized T, F1 and F2 were 44, 184 and 133 m\textsuperscript{2}/g and on calcinations the surface area decreased to 36, 118, 64 m\textsuperscript{2}/g, respectively. These results confirm that the frameworks of Fe –doped mesoporous TiO\textsubscript{2} have relative higher thermal stabilities and higher surface area than commercial TiO\textsubscript{2}. In case of F1 use of block polymer as a template resulted a large increase in surface area compared to undoped titania and F2 where no such template forming agent was used. However on calcinations at higher temperatures at 873K, resulted in breakdown of the mesoporous wall of F1 and as a consequence (the calcined F1 has) surface area decreases to 118(m\textsuperscript{2}/g) compared to 184 (m\textsuperscript{2}/g) in the as synthesized sample.
Figure 4B.8 and 4B.9 display the HRTEM image of F1. As shown in figure 5a, Fe-doped titania F1 exhibits uniform spherical particle and the images are consistent with the formation of inter particulates pores. It seems from figure 4B.9 that well crystallized anatase is dispersed in an amorphous Fe-containing titania nanoparticles, and the figure clearly displayed well-resolved crystal lattice and fused crystal boundaries. The grain boundary might inhibit the crystal growth of TiO$_2$ anatase and amorphous Fe-containing nanoparticles in size, as well as degradation of mesostructure during calcinations.

**TABLE 4B.1: Physical properties of synthesized photocatalysts**

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<th>COMPOUND</th>
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<th>hkl</th>
<th>FWHM</th>
<th>Crystalline Size nm</th>
<th>BET surface area m$^2$/g calcined</th>
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The infrared spectra of undoped TiO$_2$ (T), iron-doped TiO$_2$ (F1) calcined at 873K and 673K were shown in figure 4B.10, 4B.11, 4B.12 and they show a broad band in the region from 3600-2600 cm$^{-1}$ (OH stretching mode vibration) [12]. For T the peak at 3424 cm$^{-1}$ is assigned to stretching vibration mode of the OH group and for F1 and F2 the respective peaks are at 3389 and 3440 cm$^{-1}$. This was accompanied by a small band at 1625-1629 cm$^{-1}$ (H-O-H bending mode vibration), indicating that these samples contain heterogeneously distributed loosely adsorbed water molecules [13]. Figure 4B.11 and 4B.12 shows the infrared spectra for iron doped titania samples calcined at 873K and 673K temperatures in the region from 1200-400 cm$^{-1}$. All iron doped samples spectra showed peaks of Fe$_2$O$_3$ at 415, 454, 491,502, 583, 605 cm$^{-1}$[14]. This may be due to Ti-O-Fe bond vibrations. It was reported that vibration bends of $\alpha$-Fe$_2$O$_3$ appeared in the range 450-460 cm$^{-1}$ [15].
As expected, these peaks were absent in undoped titania which contains only peak at 639 cm\(^{-1}\) which is the characteristic band of Ti-O bond. The F1 sample calcined at 873 K, exhibits band at 502 and 605 cm\(^{-1}\), which may be due to Ti-O bending vibrations. In F1 absence of band at 1389 cm\(^{-1}\) (C-H bending vibrations) confirms the total removal of organic residual groups in the calcined samples [16].

As we know, XRD usually reveals the long-range order of materials and gives average structural information within several unit cells whereas Raman spectroscopy is a highly specific analytical method which is sensitive to crystallinity and microstructures of the materials. Fe doping leads to reduction of particle size irrespective of their synthetic routes and Ti source. The average crystal sizes of F1, F2 and T after calcinations are ca.
14.79, 16.23 and 26 nm respectively. As shown in figure 4B.13, the Raman spectrum shows principal peaks at ca 144 (E\textsubscript{g}(1)), 199 (E\textsubscript{g}(2)), 396 (B\textsubscript{1g}(1)), 519 (A\textsubscript{1g}, B\textsubscript{1g}(2)) and 639 cm\textsuperscript{-1}(E\textsubscript{g}(3)). However, the most intense anatase peak at \approx 144 cm\textsuperscript{-1} showed significant differences amongst the different samples. The Raman peaks usually display smaller line widths (FWHM) for larger crystallites due to an increase in the correlation length of the vibrations; with increasing intensity indicating greater concentrations of anatase phase.

The FWHM of the undoped titania is smaller compared to that of F1 and F2. More importantly, the Raman peak intensity of T reduced to half compared to that of F1 and F2, indicating low crystallinity. Lottici et al [17] explained this effect as the size-induced pressure effect on the vibration modes, with smaller the crystallite size, the higher the pressure and Raman frequencies.

In order to analyze chemical composition of the prepared Fe-doped photocatalyst F1 and to identify the chemical status of Fe element in the samples, the samples were characterized by XPS.
Fig. 4B.14 presents the XPS survey spectrum of the F1 nanoparticles. The F1 sample contain Ti, O, C and Fe elements, with sharp photoelectron peaks appearing at binding energies of 458 (Ti 2p), 531 (O 1s) and 285 eV (C 1s) and a weak photoelectron peak at 711 eV (Fe 2p). The carbon peak is attributed to adventitious hydrocarbon from XPS instrument itself. The higher resolution XPS spectrum (figure 4B.15) of the Fe 2p3/2 region of corresponding sample indicates that the peak at 712.2 eV is symmetrical and can be ascribed to Fe$^{3+}$ ions. Thus, the Fe element in the samples exists mainly in the +3 oxidation state (Fe$^{3+}$). Since the radius of Fe$^{3+}$ and Ti$^{4+}$ is similar, the Fe$^{3+}$ could be incorporated into the lattice of TiO$_2$ to form Ti–O–Fe bonds in the Fe-TiO$_2$ nanoparticles by calcinations in air [18]. This is further confirmed by the chemical binding energy at 712.2 eV of Fe$^{3+}$, which is different from that of Fe$^{3+}$ in Fe$_2$O$_3$ (at 911 eV) or in Fe (OH) O (at 711.3 eV). Variations in the elemental binding energies (the chemical shifts) (1.2 eV) arise from the difference in the chemical potential and polarizability of F1 photocatalysts and Fe$_2$O$_3$ [19]. The exact amount of surface Fe elements in F1 is further characterized by XPS and their surface atomic percentage is 2.2%. This atomic percentage is not in agreement with the initial nominal atomic ratio of the sample. The higher surface iron concentration indicates that during the impregnating-calcinations, a certain amount of iron is accumulated in the surface layer probably due to the transfer of iron from the inner to the surface of the Fe-doped titania [20]. No F was detected by XPS. EDX (from SEM) showed that the atomic percent of
Fe in F1 was 1.84%. For F2 the EDX analysis from SEM showed that the atomic percentage of Fe was 2.35. Since F1 was photocatalytically more active therefore the optimal doping amount of Fe in the doped samples should be 1.84 atomic percent.

The primary photocatalytic reactions of Fe- undoped titania may be summarized as follows [21]:

Charge-pair generation

\[ \text{Fe}^{+3} + h\nu \rightarrow \text{Fe}^{+4} + e^- \]
\[ \text{Fe}^{+3} + h\nu \rightarrow \text{Fe}^{+2} + h^+ \]

Charge carrier trapping:

\[ \text{Fe}^{+3} + e^- \rightarrow \text{Fe}^{+2} \]
\[ \text{Fe}^{+3} + h^+ \rightarrow \text{Fe}^{+4} \]

Charge release and migration:

\[ \text{Fe}^{+2} + \text{Ti}^{+4} \rightarrow \text{Fe}^{+3} + \text{Ti}^{+3} \]
\[ \text{Fe}^{+4} + >\text{OH}^- \rightarrow \text{Fe}^{+3} + \text{OH}^- \]

Recombination:

\[ \text{Fe}^{+2} + h^+ \rightarrow \text{Fe}^{+3} \]
\[ \text{Fe}^{+2} + \text{OH}^0 \rightarrow \text{Fe}^{+3} + \text{OH}^- \]
\[ \text{Fe}^{+4} + e^- \rightarrow \text{Fe}^{+3} \]
\[ \text{Fe}^{+4} + \text{Ti}^{+3} \rightarrow \text{Fe}^{+3} + \text{Ti}^{+4} \]

Interfacial charge transfer:

\[ e^-(\text{Fe}^{+2}) + \text{Ox} \rightarrow \text{Ox}^- \]
\[ h^+ (\text{Fe}^{+4}) + \text{Red} \rightarrow \text{Red}^+ \]

The CV data gives two peaks for +III and +IV oxidation states of titanium (figure 4B, 16). Incorporation of Fe$^{+3}$ ions in place of Ti$^{+4}$ results in a shift of oxidation peaks towards negative potential confirming the fact that Fe$^{+3}$ is more prone to reduction than Ti$^{+4}$. Incorporation of metal ions always shifts reduction potential towards more negative value. Thus it can be concluded that some Fe ions must have entered the TiO$_2$ network resulting in shift of peaks towards negative potential.
Figure 4B.16 cyclic voltammogram of undoped titania, commercial titania and Fe doped titania.

The EPR of both F1 and F2 are shown figure 4B.17.

Figure 4B.17- EPR of F1 and F2.
It can be seen from Fig. 4B.17 that the EPR spectra are composed of two signals. EPR signal I at \( g = 4.30 \) is attributed to the Fe\(^{3+}\) (Surface bound-Fe\(^{3+}\)) dispersed on the surface of the TiO\(_2\) nanoparticles, whereas EPR signal at \( g = 1.99 \) can be assigned to Fe\(^{3+}\) (Bulk-Fe\(^{3+}\)) distributed in the bulk TiO\(_2\) matrix [22]. The Fe\(^{3+}\) spin (S) is 5/2 and this gives us an idea about the local symmetry of the host TiO\(_2\). The two overlapping lines of F1 and F2 observed at \( g = 2.0 \) can be ascribed in the anatase structure. The weak line at \( g = 4.2 \) probably indicates that a very small amount of amorphous TiO\(_2\) is present, as such a signal is very common for Fe\(^{3+}\) ion in glass. For all of the F1 and F2 nano samples, it may be seen from Figure 9 that the relative EPR intensity of surface Fe\(^{3+}\) on the TiO\(_2\) surface is much lower than that of Bulk-Fe\(^{3+}\) in the TiO\(_2\) matrix indicating that most of the Fe\(^{3+}\) was incorporated to the TiO\(_2\) matrix.

### 4B.4 Photocatalytic activity of the catalysts in the aqueous phase degradation of Bromocresol Green:

For experiments under UV light, the desired bromocresol green dye solution was prepared in double distilled water.

![Figure 4B.18- Comparison of photocatalytic properties of commercial titania, T, F1 and F2.](image)
An immersion well photochemical reactor (HEBER) made of Pyrex glass was used in this study. Irradiations were carried out using a 25W, 254nm medium pressure mercury lamp. IR radiation and short wavelength UV radiation were eliminated by a water circulating Pyrex glass jacket. The bromocresol green dye solution ($10^{-5}$ M) was poured into the Pyrex vessel of the photo reactor. Aqueous dispersions of the catalyst were prepared by addition of a given weight (0.2 gm) of catalyst to about 50 ml of aqueous solution of the dye and sonicated it in a sonicator for 5 min. The dispersion is then put in to the Pyrex vessel of the photoreactor along with an additional amount of the dye solution ($10^{-5}$ M) just enough to fill the vessel. The dispersions were kept under constant air bubbling with the help of the air pump during irradiation. At intervals of 10 min, 10 ml aliquots of reaction mixture were withdrawn and were analyzed by recording variations of absorption band maximum (616 nm for bromocresol green) in a UV-Visible spectrometer. The rate of decomposition of the dye can thus be determined from the absorption vs. Time plots. There is slight photolysis of bromocresol green by UV light even in the absence of titania, but in presence of the photocatalysts, the decomposition is much more and faster as found from our experiments and shown in figure 4B.18, which is in agreement with the observations found by other workers [23-25]. Practically all Fe-doped samples expressed higher initial activities than that of pure TiO$_2$ and of commercial TiO$_2$. This result can be well explained by the presence of Fe making the amount of active sites higher in F1 and F2 due to the formation of Fe-O-Ti bonds in the TiO$_2$ crystal lattice, as well as consequent formation of defects on the catalyst surface that plays the role of a trap for preventing electron-hole recombination. Again, as is evident from the Table 4B.1, Fe doping leads to reduction of particle size irrespective of their synthetic routes and Ti source. Further the mesoporous nature of the material result in the increase of surface area. This combined effect makes the substrate adsorption stronger. Another important factor of the modification of TiO$_2$ by iron oxide doping must be the reduction of its band gap energy value. This results in easier and greater reduction of the substrate. It is clear from figure 11 that F1 with higher surface area and smaller particle size, photocatalytic activity was better. Both F1 and F2 showed higher photocatalytic activity then undoped titania.
4B.5 CONCLUSIONS:

Successful synthesis of Fe doped TiO$_2$ nanomaterials by the simple sol-gel process with K$_2$TiF$_6$ demonstrated that this is a promising technique for synthesizing cation doped TiO$_2$ nanostructures. Fe doping was favorable for organizing a mesoporous structure and maintaining the pore structure at higher temperatures. It suggests that proper Fe doping to the framework may become an effective way to improve the properties of mesoporous TiO$_2$ materials. A small amount of Fe doping showed better performance; hence, these materials may be used as a photocatalyst for the degradation of organic compounds under solar irradiation to prevent environmental pollution.
References:


