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Synthesis of Nano Phase Titanium Dioxide (Tio_2) In Diffusion Flame Reactor and It Application in Photocatalytic Reaction

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ABSTRACT
Nano phase Titanium dioxide (TiO_2) is synthesized by flame synthesis method using LPG as fuel, oxygen as oxidant. In this method Titanium Tetraisopropoxide (TTIP) is used as titanium. The synthesized Nano phase TiO_2 is characterized by SEM and XRD. In this current paper process parameters has been investigated to synthesize the Nano-phase TiO_2 in Flame reactor and its performance is studied in photocatalytic reaction. The performance of the synthesized Nano-phase TiO_2 is compared with Degussa P25 catalyst. The results conclude that Nano-phase TiO_2 shows better performance then Degussa P25.
***Keywords* -** Flame synthesis, LPG, Nano rods, Nano TiO_2, Titanium tetraisopropoxide

1 INTRODUCTION

Gas phase combustion synthesis of inorganic particles is used routinely today to make a variety of commodities like SiO_2, TiO_2, Al_2O_3 etc. Titanium dioxide (TiO_2) is a wide-band gap (3.2eV) semiconductor; it is one of many metal oxides currently under investigation. It is readily converted into different nanostructured forms, including nanotubes.TiO_2 has attracted considerable attention because it has great potential applications such as catalysis [1], Photocatalysis [2] and dye-sensitized solar cells [3] extensive research has been conducted on TiO_2 nanoparticles [4] thin film [5] and mesoporous TiO_2 [6, 7].The two mainstream methods to synthesize nano-particles are wet methods (sol-gel) and aerosol methods such as flame synthesis. Wet methods offer fine control over particle size and particle size distributions. However in wet- process the final product often includes a mixture of amorphous and crystalline particles, resulting in costly and time consuming in post process steps. Flame aerosol methods can be operated continuously allowing for greater output with minimal post processing. Recently much research has be done to obtain TiO_2 nanotubes with a large surface area and high photocatalytic activity. P. Hoyer et al synthesized

TiO_2 nano tubes with diameter of 70-100 nm with sol-gel method [8].H. Imai 1n 1996 reported anatase phase TiO_2 nanotubes with diameter of 8nm [9].anatase and rutiles phase TiO_2 nanotubes has been synthesized by S.L. Zang group in 2000 [10]. Kranthi K. Akurati [11] synthesized TiO_2 nanoparticles by Flame aerosol method using methane, Oxygen as fuel and oxidant respectively with Titanium tetraisopropoxide as precursor. Ashok Bhanwala et al [12] synthesized pure and carbon doped TiO_2 nanoparticles in flame aerosol reactor using inexpensive fuel gas LPG (liquid petroleum gas) as fuel and air/Oxygen as oxidant with titanium tetrachloride ($TiCl_4$) as precursor, reported using of oxygen instead of air increases the production of spherical particles with average diameter of particle size is 104nm. Jaturong Jitputti and his group [13] proved that TiO_2 nanotubes synthesized by hydrothermal treatment of Degussa P-25 showed higher photocatalytic activity then Degussa P-25 commercially available. These methods produce fewer byproducts, usually making them more economically viable then wet methods [14, 15].

In this current paper Nano-phase TiO_2 is synthesized by diffusion Flame reactor using LPG as fuel and oxygen as oxidant. The performance of the flame synthesized nano phase TiO_2 is compared with Degussa P25 catalyst in photocatalysis reaction to degrade the amount methylene.

2. Materials and methods

2.1. Materials

Titanium tetraisopropoxide (TTIP) are purchased from SRL Chemicals India, LPG (domestic, Bharat Gas), oxygen and Nitrogen gas is purchased from Industrial gas Aagency of Pvt. Ltd India. All Experiments carried out in a Flame reactor indigenously by JNTUH Hyderabad as shown in Fig-1.

2.2 Methodology

The flame reactor has been indigenously designed to produce nano materials. The detailed setup of the reactor has been discussed in our previous paper to synthesis of nano carbon materials. [16] The reactor operates under atmospheric pressure. The measured quantity of the LPG and the oxidant reaches the ignition chamber. During the process we have observed the dark orange flame color which is perfectly in a spindle form. Along the entire length of the flame, its temperature was recorded using a K-type thermocouple.

In this study, Nano-phase TiO_2 were synthesized in diffusion flame by using titanium tetraisoproxide (TTIP, 98% purity, spectrochem) as the titanium precursor. In this Experiment Flame is ignited in the burner with LPG and Oxygen, Nitrogen gas is bubbled through a Reagent vessel containing liquid TTIP to deliver the TTIP vapour to the burner, as shown in Fig-2.In order to prevent any condensation of the precursor, all gas line downstream the TTIP reagent vessel and the burner were wrapped with heating tapes to maintain them at 125^{o}C.The TiO_2 produced is captured on a glass fiber filter (Axiva GF/A) Fig-3, is scrapped carefully and weighed. Later heat treated at 350 ^{O}C in the presence of air for 60 minutes to remove any traces of amorphous carbon impurities then the samples were characterized by SEM and XRD.

3.0 Characterization

3.1 X-ray Diffraction Analysis

The XRD (7000 Schimazu) analysis was carried out using Cu Kα1 type of radiation with a wavelength (λ) of 1.54060 A^{o}. XRD graph of TiO_2 nano materials produced using LPG-Oxygen at flow rates of 0.2Slpm and 0.7 Slpm is shown in Fig-4. The step size was 0.02 degree/step and step time was 0.2 sec/step. The working range was 2□ = 20-100, the average crystal size TiO_2 is calculated according the equation (1) is commonly known as scherer's equation [17] by selecting particle peak (suryanarayana and Norton, 1998).

$$L = \frac{k\lambda}{\beta \cos \theta} \qquad (1)$$

Where L is the length of the crystal in the direction of the d spacing, K is the constant of 0.9, □ is the wavelength of X-Ray,β is the full width at half-maximum (FWHM) of the selected peak and □ is the Bragg's angle of the diffraction of the peak. The mass fraction of the Anatase and Rutile phase content is calculated by intensities of the XRD spectra according to spurr's equation [18] shown in equation (2)

$$F_r = \frac{1}{1+1.26\left[I_A(101)/I_R(110)\right]} \qquad (2)$$

Where F_r is the percentage content of rutile, IA (101) and IR (110) are the integral intensities of (101) of Anatase and (110) of Rutile, respectively.

3.2 Scanning Electron Microscope (SEM) Analysis

The samples were analyzed using Phillips XL 30 series Scanning Electron Microscope (SEM) in Osmania University college of Technology, Hyderabad. From the Fig-6 we can see a dense growth of TiO_2 particles synthesized by using diffusion reactor using LPG and Oxygen at a Flow rate of 0.2 Slpm and 0.7 Slpm respectively. Where as in Fig-7 we can observe SEM image of Degussa P25 TiO_2 catalyst similarly equal to our flame synthesized Nano phase TiO2.

4.0 Results and Discussion

Nano phase Titanium Dioxide is successfully synthesized by using a pilot Scale Diffusion Flame reactor, using inexpensive fuel, LPG as fuel and Oxygen as oxidant.Fig-4 and Fig-6 is the XRD pattern and SEM image of the TiO_2 material synthesized at flowrate of 0.2 and 0.7 Slpm of LPG and Oxygen. Using PCPDFWIN –XRD database the peaks were identified for their lattice structure of the orientation. The strongest peaks of TiO_2 (Fig-4) corresponds at 2□ = 25.323 is Anatase (101) and at 2□ = 27.421 is Rutile (110).The average particle diameter (equation-1) is calculated from scherer's at 2□ of 25.32 is 26 nm. Anatase and Rutile content is calculated from equation-2 is 65% Anatase and 28% Rutile. Fig-5 and Fig-7 are the XRD pattern and SEM images of the Degussa P25 catalyst anatase phase of P25 is 80% and rutile phase is 20%. As compared to Degussa P25 catalyst flame synthesized nano catalyst contain less amount of anatase phase but average particle diameter of P25 is 43nm which is higher then flame synthesized catalyst.

4.1 Photocatalytic performance of catalysts

Performance of the combustion method synthesized TiO_2 (C-TiO_2) has been tested in a UV photocatalytic reaction to degrade the methylene blue compound for about 3 hours duration at neutral pH (7.0) condition. The results reveal that P25 has degraded the MB from 20 to 8 ppm whereas C-TiO_2 is from 20 to 2.2ppm with in 3hours time the degradation graph as shown in Fig-8. C-TiO_2 is 15% more efficient then P25.Even though the p25 has more anatase phase (Anatase content 80%) then C-TiO_2 (Anatase content 65%) calculated from Equation – (2). Synthesized C-TiO2 showed more efficient then P25.

5.0 Conclusion

A pilot scale Diffusion flame reactor experiments has been carried out to synthesis the

Nano C- TiO_2 materials, with inexpensive LPG as fuel gas, Oxygen as oxidant in flame reactor. In this experiment TTIP is used as Precursor for TiO_2 material and nitrogen as carrier gas. C-TiO_2 is synthesized with LPG flowrate of 0.2 slpm and 0.7slpm of oxygen contain 65% of anatase and 28 % of rutile phase showed better performance than p25 even though it had 80% anatase content. The synthesized C-TiO_2 has average particle diameter of 26nm, calculated from XRD data scherer equation where as P25 has 46nm.Hence in this paper one step synthesis method of Nano phase TiO_2 method is described using LPG as fuel and oxygen as Oxidant in flame reactor. This one step synthesis method is very useful compared to sol-Gel method where requires numbers of synthesis steps like filteration, purification and calcination in sol-gel method.

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Figure Citations:

Figure 1 – Flame Reactor setup, with flow meters front view (Rotameters).
Figure 2 – Flow chart diagram of flame reactor unit.
Figure 3 –Sample collector with glass fiber filter paper holder.
Figure 4 – XRD Pattern of Flame synthesized TiO_2 at 0.2 Slpm.
Figure 5- XRD Pattern of Flame synthesized P25
Figure 6- SEM image of the Flame synthesizes TiO_2
Figure 7- SEM image of P25
Figure 8- Photocatalytic acitivity of the P25 and C-TiO_2

Figures

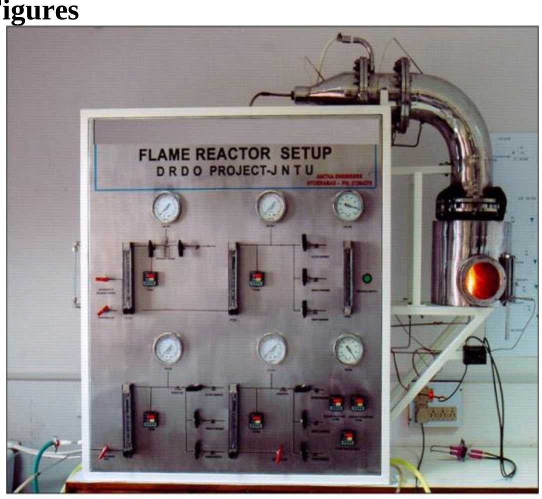

Fig. 1

Figure 1 – Flame Reactor setup, with flow meters front view (Rotameters).

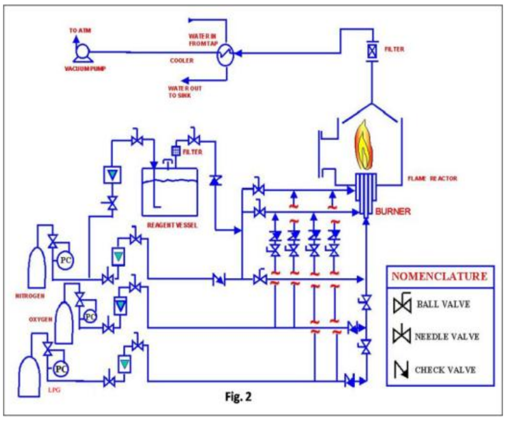

Figure 2 – Flow chart diagram of flame reactor unit

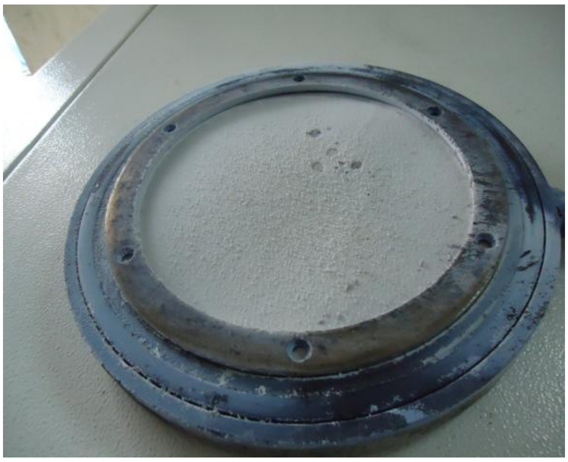
Figure 3 –Sample collector with glass fiber filter paper holder.

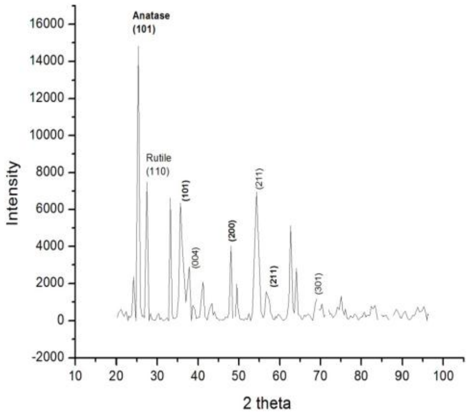

Figure 4 – XRD Pattern of Flame synthesized TiO_2 at 0.2 Slpm.

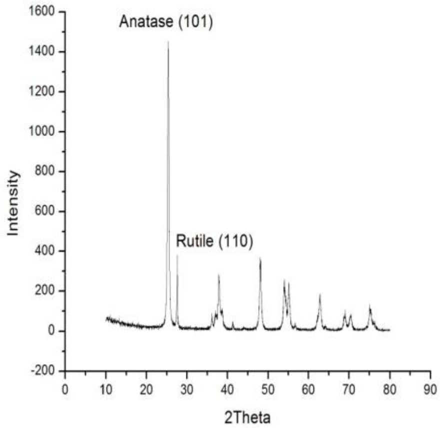

Figure 5- XRD Pattern of Flame synthesized P25

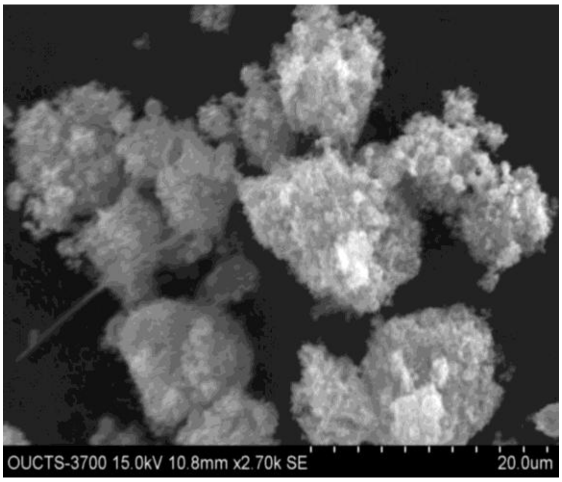

Figure 6- SEM image of the Flame synthesizes TiO_2

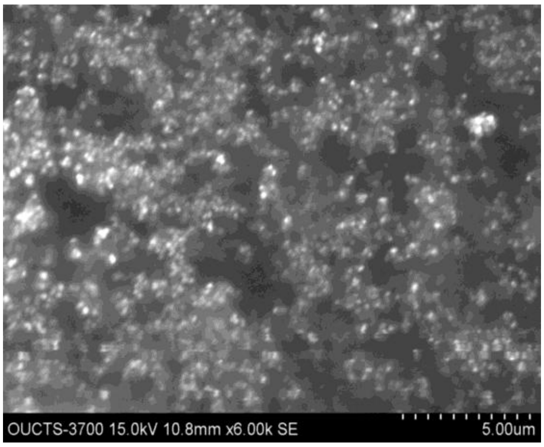

Figure 7- SEM image of P25

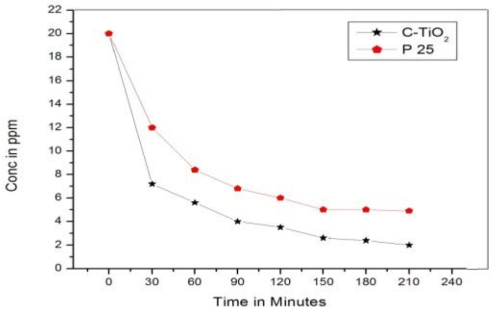

Figure 8- Photocatalytic acitivity of the P25 and C-TiO_2