Microwave plasma synthesis of nano titanium dioxide powder and its characterization

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Abstract :- This work describes the application of microwave plasma synthesis technology to prepare TiO₂ nano powder using oxygen as plasma forming gas as well as carrier gas. The powder thus produced is characterized by means of (1) SEM (scanning electron microscopy) (2) XRD (3) BET surface area test. The average particle size is determined to be around 60-70 nm quite compatible with the commercially available titania powder (P-25). The prepared powder has 67 % Anatas and 33 % Rutile phase in it. Using this process a photocatalytically active TiO₂ powder is synthesized which is tested using methylene blue for decolourisation effect.

Key-Words : Photocatalysis, Microwave plasma (MWP), Tube fraction, Bag fraction, ultrasonifier
Methylene blue, XRD (X-Ray diffraction), BET (Brunauer, Emmett and Teller).

1. Introduction

Nanopowders have a combination of small particle size, narrow size distribution and high surface area to volume ratio. The physical and chemical properties of these nano particles often deviate from their bulk materials when the particle size decreases to a specific regime. The powder shows a dramatic increase in photocatalytic action and increases strength, hardness and cutting efficiency as particles become nano sized.

Titanium dioxide occurs in nature as well as in known mineral forms such as rutile, anatase and brookite. Most common form is rutile, which is also the most stable form. Anatase and brookite both convert to rutile upon heating. Rutile, anatase and brookite all contain six coordinated titanium. Titanium dioxide powder is commonly referred to as Titania.

2. Experimental set up: The experimental set-up used in this work is represented schematically in Fig. 1.

2.1 Specification of MWP unit:
- Maximum output of the microwave generator ----- 5kw.
- Frequency of microwave generator 2450MHz

2.2 Components of MWP

Magnetron: It is the unit that produces the micro waves that are to be introduced into the plasma. It basically contains one cathode and multiple anodes each carrying a current 1.4 Amp. The output of this unit is upto 5 kw. This system unlike others have separate cooling systems such as fans. The magnetron is followed up by a isolator which performs the function of directing waves only in one particular direction to avoid reflected waves which would otherwise generate more heat which is not desirable. Wave guides are also provided which more or less perform the same function of aligning the waves in one direction.

Plasmatron: Super high frequency plasmatron is designed for heating of stationary gas flow of oxygen to 1500-3000 k due to absorption by ionized gas of microwave irradiation delivered from magnetron via wave guides. Gas is introduced into plasmatron first passes through twisting chamber. Primary gas ionization, which is necessary for initiating stationary gas micro wave discharge, is performed by a short term insertion of stainless steel wire into the discharge zone. Plasmatron provides stable “burning”of discharge in the range of gas flow of 1.8-4.0 m³/hr, and input power of 2- 5kw. Plasmatron housing is supplied with cooling water to absorb the heat generated [5].
2.2.1 Technological Equipment

**Reactor:** It is a water cooled tube consisting of two separate sections high temperature plasma jet and chemicals participating in the reaction are fed to the upper part of the reactor. They interact in the reactor and form condensed products as ultra-dispersed powder.

**Injector:** It is for introduction of reagents and is placed between plasmatron and the upper part of the reactor, and it is used for feeding the starting material participating in plasma chemical process. The case of the injector is supplied with water cooling.

**Heat Exchanger:** It is assigned for reduction of temperature of exiting dust-gas flow before it is fed into the filter. It consists of two co axially located water cooled cylinders, with axis perpendicular to the axis of running high temperature flow.

**Filter:** It is assigned for isolation of ultra dispersed powder from cooled dust-gas flow and its accumulation during the technological process. Filtration of dust-gas flow is performed when the flow passes through a bag filter made of thermostable phenylon tissue.

**Dosing Device:** This is connected to the injector for reagents and is assigned for controlled feeding of the stock into plasma chemical reactor. Performance of dosing device for a large scale production of powder is based on the entrainment of the liquid chloride vapours by carrier gas from thermostating space of the dosing device.

3. SYNTHESIS OF TiO$_2$:

**Precursor:** The input substance which is used to prepare the required product is called precursor. Here the precursor used is TiCl$_4$ which is in liquid state. It is very sensitive to moisture and has high vapour pressure. It is feed into the plasma at rate of $107 \times 10^{-6}$ m$^3$/hr.

**Carrier gas:** It is used to carry the vapours of the precursor into the reaction chamber. The carrier gas used here is oxygen and is feed at rate of 0.3 m$^3$/hr.

**Plasma forming gas:** Oxygen is used as plasma forming gas here at a rate of 2.2 m$^3$/hr.

The precursor TiCl$_4$ reacts with the oxygen which is sent inside as the plasma forming gas as well as the carrier gas according to the following reaction:

$$\text{TiCl}_4(l) + O_2(g) \rightarrow \text{TiO}_2(s) + 2\text{Cl}_2(g) \uparrow \quad (1)$$

The powders were quenched at the wall of the heat exchanger and then separated from the gas by the filter bag. Powder deposited directly in the bag provided is designated in this work as bag fraction and the residual powder stuck along the walls of the output tube is designated as tube fraction.
4. CHARACTERIZATION AND RESULTS:

4.1 Photocatalytic activity:

We took the nano titania powder in two separate beakers and mixed it with Methylene blue to form a concentrated homogenous solution.

Tube fraction: 0.0252 gm

Bag fraction: 0.0247 gm

P-25: 0.0258 gm

Commercially available powder is taken in another beaker and is mixed with same concentration methylene blue to form a solution. Some amount of pure methylene blue is taken for reference. The three beakers containing TiO$_2$ powder are kept in the ultrasonifier for fine dispersion of nano powder in the methylene blue solution. All the 4 beakers are introduced to direct sunlight with light intensity measuring upto 70 mW/12mm$^2$.[4]

Methylene blue: Its unique ability to remain unreacted upon action with UV rays and being a common pollutant makes it apt for this activity.

Fig 3: Reactions involved in photocatalysis

(a) BEFORE EXPOSURE TO SUNLIGHT

(b) AFTER EXPOSURE TO SUNLIGHT:

Fig 4: Bottles as they stand in order from left
(1) only methylene solution (2) commercially available powder (3) Bag fraction powder (4) Tube fraction powder

- The activity was carried out for 20 min in daylight.
- The deviation in colour in the samples containing TiO$_2$ powder from the reference solution colour justifies the photocatalytic action of TiO$_2$.
- The colour change is first observed in bag fraction.
4.2 SEM analysis

In this we kept the drop of finely dispersed TiO$_2$ powder in distilled water on a carbon tape. It is then kept under the scanning electron microscope, which has very high resolution power. Photograph of TiO$_2$ atoms in nanometer dimension are shown in Fig (7)

Fig 5: SEM images of (a) Tube fraction

(b)

Fig 6: Using the SEM photographs the average particle size of the atoms are plotted on Graphs (a): Tube fraction (b): Bag fraction

From the SEM analysis we obtained the

- The average particle size in bag fraction is 78 nm.
- The average particle size in tube fraction is 97 nm.
4.3 XRD analysis:

(a) Tube fraction XRD graph

(b) Bag fraction XRD graph

Fig 7: XRD graphs of (a) Tube fraction (b) Bag fraction

BASED ON THE ABOVE XRD RESULTS:

Average size:

Tube fraction: The average anatase crystallite size is 46.69 nm. The average rutile crystallite size is 46.67 nm.

Bag fraction: The average anatase crystallite size is 59.17 nm. The average rutile crystallite size is 51.11 nm.

%composition:

Tube fraction: Anatase is 67.77% and the Rutile is 32.23%

Bag fraction: Anatase is 67.73% and the Rutile is 32.27%

4.4 BET surface area test:

The equipment used here is manufactured by MICROMERITICS. Model is ASAP 2020 V3.00 H

Using this equipment values of the surface area of the prepared powder are obtained by sending nitrogen gas (with known surface area) into a vacuum chamber containing nano titania powder particles. The powder particles are then surrounded by nitrogen molecules and thus gives the empirical value of the surface area of the required nano powder.

Surface area of the bag fraction is 18.067 m²/gm. Surface area of tube fraction is 20.073 m²/gm.

5. CONCLUSION: A photocatalytically active nano TiO₂ powder is successfully synthesized using microwave oxygen plasma and its compatibility with commercially available power is checked using the photocatalytic activity and the size range is justified using the SEM analysis and only slight deviation is observed in tube fraction from bag fraction. Composition and phases are also analyzed using XRD analysis. So a commercially compatible powder is synthesized using MWP technique.

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