A Novel Mixed Reverse Microemulsion Route for the Synthesis of Nanosized Titania Particles

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Abstract: The main objective of this work was to prepare nanosized titania (TiO_2) particles by mixed reverse microemulsion route. In this work titania was prepared by quaternary microemulsion system (water/surfactant/co-surfactant/oil-phase). Span-80, Aerosol-OT, n-Propanol, Isooctane, and Titanium tetra isopropoxide (TTIP) were used as surfactant, co-surfactant, oil-phase and titania precursor respectively. The effect of water to surfactant ratio (w_0) on the size of titania particles was studied. The X-ray diffraction pattern shows the presence of pure Anatase phase with tetragonal crystal structure. The calculation of particle size using scherrer equation shows that the particle size of titania nanoparticles increases with increasing water to surfactant ratio. The TEM image exhibited spherical morphology and narrow size distribution of the nanosized titania particles. The nanoparticles thus prepared can find applications in i.) For gas sensing. ii.) Photo-electrodes for dye-sensitized solar cells. iii.) In removing the organic chemicals which occur as pollutants in wastewater effluents.

Keywords: Mixed reverse microemulsion, nanosized, titania, pure anatase phase, spherical shape, narrow size distribution.

INTRODUCTION

Nanosized titania particles have been the subject of a great deal of research because of their unique physicochemical properties and applications in the areas of pigments, catalysts and supports, fine ceramics, cosmetics, gas sensors, inorganic membranes, environmental purification, and dielectric materials [1-9].

Much interest has been shown in photochemical reactions on nanosized titania particles due to their potential application in the conversion of solar energy into chemical energy [10-13] and electric energy [14, 15]. When titania powder is irradiated with photon energy larger than the band-gap energy, electrons (e−) and holes (h+) are generated in the conduction band and the valence band, respectively. These electrons and holes are thought to have the respective abilities to reduce and oxidize chemical species adsorbed on the surfaces of titania particles [16]. The uses and performance for a given application are, however, strongly influenced by the crystalline structure, the morphology, and the size of the particles. It is well known that titania exists in three kinds of crystal structures namely anatase, rutile and brookite. Anatase and brookite phases are thermodynamically metastable and can be transformed exothermally and irreversibly to the rutile phase at higher temperatures. The transition temperatures reported in the literature ranges from 450 to 1200 ◦C. The transformation temperature depends on the nature and structure of the precursor and the preparation conditions [17, 18]. Among the three kinds of crystal structures of titania, commercially available anatase titania fine particles are the most effective for photocatalytic degradation of organic compounds. Therefore, it is very important to develop methods for the synthesis of nanosized titania particles in which the particle size and the crystal structure of the products can be controlled.

Various synthesis methods including the CVD method [19], colloidal template [20], hydrolysis [21, 22], sol-gel [23-25], microemulsion (or reverse micelle systems) [17, 18, 26, 27] and hydrothermal synthesis [28, 29], have been used to prepare nanosized titania particles. The sol-gel method [30] requires costly organic solvents. The direct hydrolysis of titanium salts and chemical vapor deposition procedure, in which $TiCl_4$ vapor is oxidized at very high temperatures (~500 °C) can be used to prepare nanosized titania particles [31-33].

In the last few years reverse micelle method was successfully applied to synthesize nanosized titania particles in reverse micelles or water/oil (W/O) microemulsion systems using titanium alkoxides as starting materials [18-20]. Reverse micelles are small aggregates (60-800 Å) formed by surfactant molecules that surround a well defined nanometer-sized water core [34]. This unique formation of water droplets in an microemulsion may be considered as a small reactor used for the synthesis of nanoparticles. The reactants are confined within such dispersed droplets when water-soluble precursors are used. It has been shown that this structure is the most suitable for the preparation of fine inorganic colloidal particles, since the aggregates have very small size and are monodispersed. Additionally, the fact that most metal precursors are water-soluble that enhances the particle synthesis procedure, which takes place inside the water core of the reverse micelles. Even though the microemulsions

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have been considered as being stable systems, it was demonstrated by Agrell, Li and Park [35, 36] that they are dynamic systems, wherein the droplets collide continuously with each other, resulting sometimes in formation of coalesced drops that tend to break up, since as they lose their thermodynamic stability. As the particle formation takes place inside the droplet, the nature of the formed colloidal particles will be influenced by the droplet structure and its ability to exchange micellar-containing material [37]. Additionally, the size of the water droplets will determine the size of the catalyst nanoparticles. Generally, a low water to surfactant ratio (w_0) is required to form reverse micelles, depending also on the type of the surfactant, i.e. number and length of hydrophobic chains. For a given surfactants, w_0 will give aggregates of different size and shape (spherical micelles, rod-like micelles and others) [38]. The synthesis of the metal nanoparticles may be carried out in two different manners [39, 40]. The first manner includes the addition of a reducing agent, such as hydrazine directly into the microemulsion containing the metal precursor. The second manner involves the mixing of two reverse-micelle microemulsion solutions, one containing the metal precursor and the other one containing the reducing (or precipitating) agent [41].

In the present work we prepared nanosized titania particles using the single microemulsion system in which mixed reverse microemulsion of water, surfactant, and oil phase was used. Titanium Tetra Isopropoxide(TTIP) diluted by Isopropyl alcohol(IPA) was directly added to the above microemulsion system. To study the effect of water to surfactant ratio(w_0) on the size titania particles, a mixed reverse microemulsion solution containing water droplets which was precipitated by TTIP diluted in IPA. The synthesis involves hydrolysis of TTIP in a reverse micelle system leading to the formation of phase pure tetragonal nanosized titania particles at room temperature.

EXPERIMENTAL WORK

Materials

The materials used for making phase pure tetragonal nanosized titania particles included i.) Isooctane as oil phase (AR grade, Merck LTD., assay 99.5%), ii.) distilled water, iii.) span 80(sorbitan monooleate, LOBA CHEMIE, PVT. LTD., HLB=4.3; viscosity at 25 ^{0}C = 1,000 cp), iv.) AOT (Dioctyle sulfosuccinate, AR grade, HiMedia Laboratories Pvt. Ltd., assay 98.0%), v.) n-propanol as cosurfactant(AR grade, RANBAXY, assay 99.0%), vi.) IPA(Isopropyl alcohol, AR grade, CDH (P)), and vii.) TTIP(Titanium tetraisopropoxide, laboratory use, HiMedia Laboratories Pvt. Ltd.).

Synthesis of Phase Pure Tetragonal Nanosized Titania Particles

The flow chart for the preparation of nanosized titania powder in mixed reverse microemulsion is given in Fig. (**1**) and the detailed discussion of the same is as mentioned below.

For synthesis of nanosized titania particles, titanium tetra isopropoxide was used as titanium precursor.

Synthesis of Nanosized Titania Powder in Mixed Reverse Microemulsion at Water to Surfactant Ratio (w_o) 4

First of all a mixed reverse microemulsion was prepared using 150 ml isooctane , 1.5ml Water, 3.33 gms AOT, 6.5ml SPAN 80, and 20ml n-propanol and this microemulsion mix-

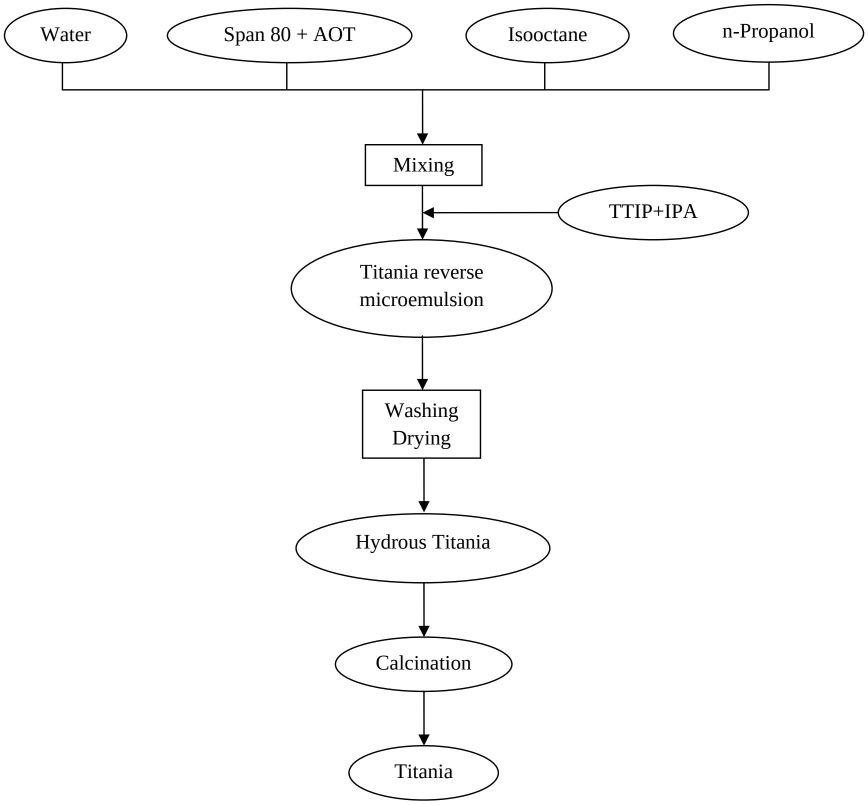

Fig. (1). Flow-Chart for nanosized titania powder preparation.

ture was stirred vigorously using a magnetic stirrer at 1500 rpm at room temperature to obtain transparent solution revealing the formation of micron size water droplets homogenously dispersed in continuous oil phase. Further a fresh solution of titanium tetra isopropoxide was prepared by taking 5 ml of titanium tetra isopropoxide and diluting it with 5 ml of isopropyl alcohol and the solution thus prepared was stored in caped measuring cylinder to avoid its hydrolysis and the solution was then taken in a burette and was added drop wise at the rate of 0.2 ml/min to the mixed reverse microemulsion system using a magnetic stirrer at 1500 rpm at room temperature till the precipitate of the titanium hydroxide was appeared. Similar experiments were performed for obtaining nanosized titania powder in mixed reverse microemulsion at water to surfactant ratio (w_o) 6 and 10.

Then the precipitate of the titanium hydroxide so obtained was filtered using whatmann 42 filter paper, and was washed repeatedly with 15 ml water deionised water in each washing cycle and followed by washing with 15 ml ethanol in each washing cycle, in order to remove the organic residues and surfactant. The washed material was then dried in an air oven at 80^0C for 10 h. The dried material was powdered with mortar and pestle and was then calcined at 500^0C for 3 h in muffle furnace.

CHARACTERIZATION STUDIES

i) Investigation of Phase Formed in the Calcined Material using XRD

The X-ray diffraction spectrum of the calcined powder was recorded using Phillips make X-ray diffraction spectrometer (model Bruker D8) using Cu $K\alpha$, radiation operated at 40 kV and 40 mA current at a scan rate of 0.008 2θ/s. The phases present were identified by comparison of intensity and d values of the possible phases in the synthesized powder with standard values given in JCPDS files [42].

ii) TEM Studies

The morphology of the nano-size materials was studied using Transmission Electron Microscope (TEM). TEM images were recorded using JEOL 3010 operating at 300 KeV. the samples were sonicated in water/acetone for 30 min followed by ambient drying and mounted on carbon coated copper grids.

RESULTS & DISCUSSION

i) X-Ray Diffraction Study

The XRD patterns of the calcined sample of nanosized titania powder prepared using 4, 6 and 10 water to surfactant ratio are given in Fig. (**2**). The presence of peaks of anatase titania at ‘d’ values 3.49, 1.88, 2.35 have been observed in all the three XRD patterns. The average crystalline sizes of nanosized titania has been calculated by applying Scherrer’s equation ($d = k\,\lambda / \beta \cos\theta$) to the anatase (1 0 1) diffraction peak and is given in Table **1** and found that the particle size (nm) increases with the increase of water to surfactant ratio i.e. 4, 6 and 10. The observed increase in size of nanosized titania particles with increase in water to surfactant ratio can be attributed to the increased hydrolysis of titanium tetra isopropoxide precursor solution and thus facilitating the availability of increased numbers of nucleai of tiatinium species [41].

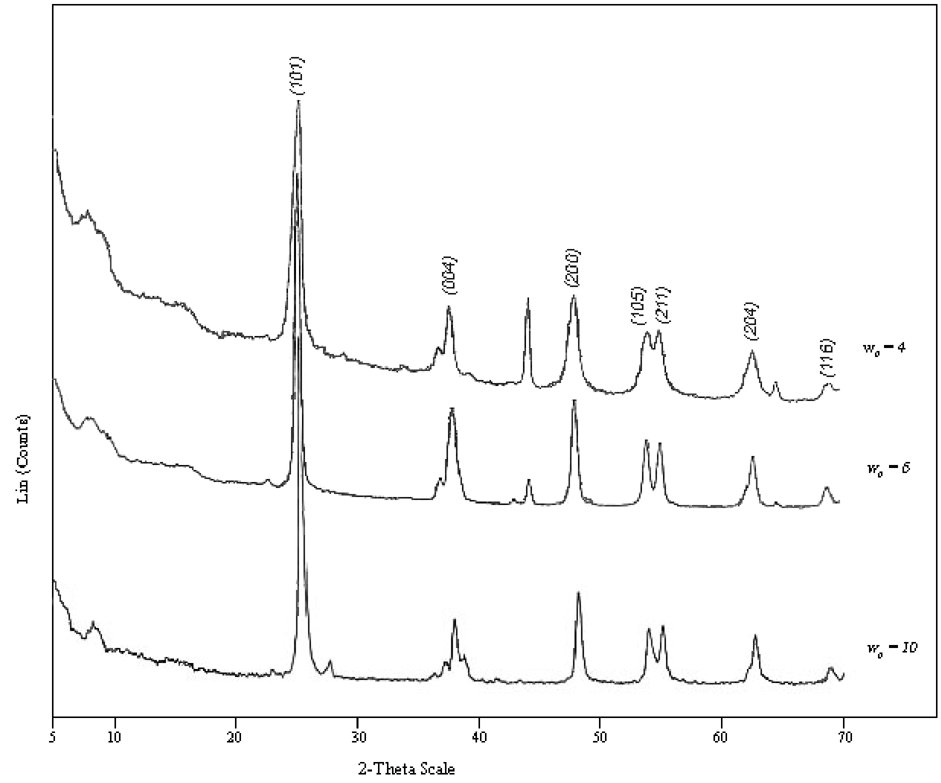

Fig. (2). XRD patterns of nanosized titania particles obtained from mixed reverse microemulsions at various water contents.

Table 1. Physical Properties of Titania Nanoparticles Prepared by Mixed Reverse Microemulsion Method

w_0	Structure	Particle Size (nm) (by Scherrer Equation)	Crystal Structure
4	Anatase	9	Tetragonal
6	Anatase	14	Tetragonal
10	Anatase	19	Tetragonal

ii) TEM Study

The typical TEM image of the calcined sample of nanosized titania powder prepared using water to surfactant ratio 4 is given in Fig. (**3**). The TEM image shows: a) the particle size obtained in the range of 20 to 25 nm. b) spherical shape and c) narrow size dispersability of the nanosized titania particle.

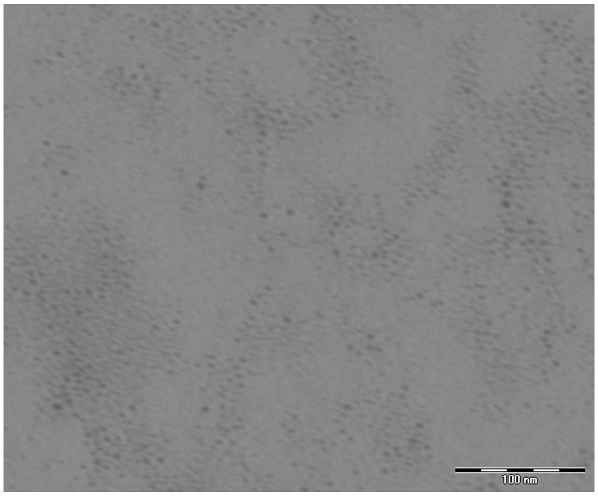

Fig. (3). TEM microphotographs of calcined sample prepared at water to surfactant ratio ($w_0 = 4$).

CONCLUSION

The following conclusions can be drawn from the results described in the present paper.

1. A novel process involving mixed reverse microemulsion route has been developed for preparing nanosized titania particles.
2. The novelty of the process lies in the fact that conventionally either catoionic or anionic or non ionic surfactants are used for the synthesis of nanoparticles of titania. Whereas in the present developed novel process preparation of nanosized titania particles has been carried out using a unique blend system consisting of SPAN -80 and AOT.
3. The X-ray diffraction pattern confirms the presence of pure Anatase phase with tetragonal crystal structure.
4. Studies performed on the effect of water to surfactant ratio shows that the particle size of nanosized titania powder increases with the increase of water to surfactant ratio.
5. The TEM image exhibits that titania particles spherical in shape, particle size varies from 20 to 25 nm and have narrow size dispersibility.

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