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Effect of Various Fuels on Structure and Photo-Catalytic Activity of Nano-Crystalline TiO₂ Prepared by Microwave-Assisted Combustion Method

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ABSTRACT

ano-crystalline TiO_2 powders were synthesized by combustion method using metal nitrate solution and urea, glycine and citric acid fuels. Microwave irradiation was used as the heating source. X-ray diffraction, Scanning Electron Microscopy, Fourier Transform Infrared Spectroscopy and Brunauer-Emmett-Teller surface area analysis were performed to characterize the prepared samples. X-ray diffraction patterns revealed that in the case of citric acid, calcination step is needed to obtain the desired phase. Moreover, the ratio of rutile/anatase phases varied from 25/75 to 0/100 as the fuel type was changed from urea to glycine and citric acid. The crystallite size of the synthesized samples was calculated by Scherrer's formula which was revealed to be 8-15 nm. The highest surface area was observed when glycine fuel had been used. By Scanning Microscopy images, thick and thin flaky particles were detected in the case of citric acid and urea samples while a porous spongy morphology was seen when using glycine sample. The sample synthesized using urea is a better candidate for photo-catalytic functions due to a well-crystallized mixed crystalline structure (75% anatase - 25% rutile) which results in the synergistic effects of mixed anatase and rutile phases. Prog. Color Colorants Coat. 4(2011), 85-94. Institute for Color Science and Technology.

1. Introduction

Titanium dioxide (TiO_2) is a well-known material because of the stability of its chemical structure, biocompatibility, physical, optical and electrical properties [1]. It exists in three mineral forms; anatase,

rutile and brookite. Anatase-type TiO_2 has a crystalline structure that corresponds to the tetragonal system (with dipyramidal habit) and is used mainly as a photo-catalyst under UV irradiation. Rutile-type TiO_2 also has a tetragonal crystalline structure (with prismatic habit) and is mainly used as white pigment in paint industries.

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Brookite-type TiO_2 has an orthorhombic crystalline structure.

Titanium dioxide has a wide range of applications and has been widely used as pigment in paints with rutile phase [2], and as photo-catalyst with anatase phase [3]. TiO_2 is the most frequently used photo-catalyst because of its good performances, low cost and low toxicity. As TiO_2 is investigated by UV-Vis Spectroscopy, the photons excite valence band electrons across the band gap into the conduction band, leaving behind holes in the valence band. The holes in TiO_2 will react with water molecules or hydroxide ions (OH⁻) and then produce hydroxyl radicals (OH⁻). Oxygen is usually supplied as an electron acceptor to prolong the recombination of electron-hole pairs during photo-catalytic oxidation.

Many chemical methods have been used for preparation of nano-crystalline TiO₂ including sol-gel method [4] and hydrothermal processing [5]. Solution combustion synthesis (SCS) has emerged as an important technique for synthesis and processing of advanced ceramics (structural and functional), catalysts. composites, alloys, intermetallics and nanomaterials [6-9]. In SCS, the exothermic nature of the redox (reduction-oxidation or electron transfer) chemical reactions is used to produce the desired materials [10]. The process is based on gelation and further heating of a gel precursor to precede combustion reaction in a heating source such as furnace or microwave oven. Microwave heating can be more advantageous than furnace because of its shorter processing time and volumetric heating. Microwaves are electromagnetic waves that have a frequency range of 0.3 to 300 GHz and corresponding wavelengths ranging from 1 m to 1 mm. The frequency of 2.45 GHz is typical for material processing. It has long been established that dielectric materials such as many types of ceramics can be heated with energy in the form of microwave [11]. One of the important keys to obtain powders with enhanced properties in combustion synthesis is the fuel type. Glycine, urea and citric acid are common choices of the fuel in combustion synthesis of metal oxides [12].

In this paper, combustion synthesis of nanocrystalline TiO_2 is reported. Microwave irradiation is used as the heating source and three different fuels including urea, glycine and citric acid are used. The effects of various fuels on structure and photo-catalytic activities of the samples are investigated. X-ray Diffraction (XRD), scanning and transmission electron microscopy (SEM and TEM), specific surface area

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analysis (Brunauer-Emmett-Teller (BET)) and Fourier transform infrared spectroscopy (FT-IR) are applied to characterize the obtained samples.

2. Experimental

Nano-crystalline TiO₂ was prepared by the solution combustion method using precursor titanyl nitrate [TiO (NO₃)₂] and fuel. The titanyl nitrate was synthesized by the reaction of titanyl hydroxide [TiO (OH)₂] obtained by the hydrolysis of tetra-n-butylorthotitanat (TBT) with nitric acid. The fuels are urea [CO (NH₂)₂], glycine [C₂H₅O₂N] and citric acid [C₆H₈O₇]. Assuming that the titanyl nitrate and fuel undergo complete reaction, the formation of TiO₂ can be described by equations 1-5:

$$TiO(i - OC_4H_9)_4 + 3H_2O \rightarrow TiO(OH)_2 + 4C_4H_9OH$$
(1)

$$TiO(OH)_2 + 2HNO_3 \rightarrow TiO(NO_3)_2 + 2H_2O$$
(2)

$$6\text{TiO}(\text{NO}_{3})_{2} + 10\text{CO}(\text{NH}_{2})_{2} \rightarrow 6\text{TiO}_{2} + 16\text{N}_{2} + 10\text{CO}_{2} + 20\text{H}_{2}\text{O}$$
(3)

$$9\text{TiO}(\text{NO}_3)_2 + 10\text{C}_2\text{H}_5\text{O}_2\text{N} \rightarrow 9\text{TiO}_2 +$$

 $14\text{N}_2 + 250\text{CO}_2 + 25\text{H}_2\text{O}$ (4)

$$\frac{9}{5} \operatorname{TiO}(\mathrm{NO}_{3})_{2} + \mathrm{C}_{6}\mathrm{H}_{8}\mathrm{O}_{7} \rightarrow \frac{9}{5} \operatorname{TiO}_{2} + \frac{9}{5} \mathrm{N}_{2} + 6\mathrm{CO}_{2} + 4\mathrm{H}_{2}\mathrm{O}$$
(5)

In a typical combustion synthesis, a Pyrex dish (400 cm³) containing an aqueous redox mixture consists of stoichiometric amounts of titanyl nitrate and fuel in 20 ml of water is heated up to 50 °C while magnetic stirring is continuously applied. Under constant temperature and stirring, water is evaporated and a viscous gel is obtained. Then, the gel is exposed to microwave irradiation (900 W) for 30s.

A D-500 (Siemens, Karlsruhe, Germany) Diffractometer was used for XRD analysis. Morphology and the grain size of the samples were analyzed using LEO 1455VP (Oxford, UK) Scanning Electron Microscope (SEM) and Zeiss EM900 Transmission Electron Microscope (TEM). The IR spectra of the prepared powders were given by FTIR (Spectrum one, FTIR spectrometer, Perkin Elmer). The photo-catalytic performance was examined using a designed apparatus made from a 40 W/220 V UV lamp as illuminating source and methyl orange (MO) as reactant.

3. Results and discussion

3.1. Structural analysis

Figure 1 shows the X-ray diffraction patterns of the synthesized TiO_2 samples using three fuels. From Figure 1, it can be observed that the product synthesized in the presence of citric acid is generally amorphous and there are no distinguishable phases in its XRD pattern. Therefore, subsequent calcination was needed to obtain the desired phase. After calcination at 400 °C, pure anatase TiO_2 phase was obtained. However, in the case of urea and glycine fuels, polycrystalline TiO_2 powders were obtained initially after combustion process without any further calcination steps. According to JCPDS 01-071-1167 and 01-076-0319 cards, both anatase and rutile phases are observed in the XRD patterns of the ureabased sample.

The average crystallite size and the percentage of the anatase phase can be calculated by equations 6 and 7 [13, 14]:

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$
(6)

$$x = \frac{1}{\left[1 + 0.8 \left(\frac{I_A}{I_R}\right)\right]} \tag{7}$$

where λ is the wavelength of incident X-ray, β is the half width of the diffracted peak, θ the diffracted angle, x the weight percentage of the rutile phase, I_A and I_R are the peak intensities of the (101) and (110) planes for the anatase and rutile phases, respectively. From equations 6 and 7 and Figure 1, the average crystallite size and the percentage of the anatase phase were calculated and the results are given in Table 1. Results show that 75/25 ratio of anatase/rutile phase is obtained with urea fuel which can be explained by the nature of the fuel. In aqueous (solution) combustion synthesis, it was demonstrated that among fuels containing specific functional groups, the amino group triggers a more vigorous combustion reaction than that of the carboxylic group [15]. This is due to the fast exothermic redox reaction between nitric acid (nitric acid is released during thermal decomposition of the nitrated precursor) and the amino group. With two amino groups, urea releases more energy during combustion reaction providing the necessary energy to convert some parts of the amorphous TiO₂ to the rutile phase.



Figure 1: XRD patterns of the synthesized TiO₂ powders by various fuels.

	Percentage of the anatase phase	Crystallite size (nm)	BET surface area (m ² /g)
Sample by citric acid	100	15	17
Sample by urea	75	12	21.7
Sample by glycine	100	8	32.2

Table1: The effect of various fuels on anatase content and crystallite size of the TiO₂ powders.

Crystallite size decreases when fuel type changes from citric acid to glycine (Table 1). The higher crystallite size for citric acid is related to the calcination step which causes crystal growth. The huge amount of energy released in the combustion reaction in the presence of urea can be the main reason for the crystal growth, while the smaller crystallite size arises from rapid decomposition of glycine at lower temperatures which in turn accelerates the combustion ignition [16].

The BET results obtained from synthesized TiO_2 powders are shown in Table 1. The increase of surface area is in good correlation with crystallite size changes. The effect of fuel type on morphology of the synthesized samples is illustrated in Figure 2(a-c).

From Figure 2(a), the sample synthesized by citric acid fuel essentially consists of bulky thick flakes. In the case of urea fuel, the flakes are thin; however, for the sample synthesized by glycine a spongy and porous morphology was obtained. The observed differences between the morphology of the particles are originated from the inherent effect of the organic fuels [17]. As it was mentioned above, the sample synthesized by glycine contains the smallest crystallite size. Morphology of this sample is shown in Figure 2(c). Huge amount of exhaust gases associated with a rapid combustion reaction leads to scattering of irregular sub-nanometric particles to form loose agglomeration morphologies [18]. Sample synthesized by urea is mostly formed of thin-flake particles. Citric acid shows a different role in the formation of particles during combustion reaction (Fig. 2a) and creates complex forms with metal nitrate compounds. Moreover, because of the chelating effect citric acid plays more effective complexing role in comparison with glycine [19, 20].



Figure 2: Scanning electron microscopy images of the synthesized samples by various fuels; (a) citric acid, (b) urea, and (c) glycine.



Figure 3: Transmission electron microscopy images of the synthesized samples by various fuels; (a) citric acid, (b) urea, and (c) glycine.

Subsequently, the localization of heat on the particle boundaries during calcination step can result in bulky-thick particles.

Figure 3 (a-c) shows the TEM images for the

samples obtained by various fuels. Results demonstrate that for citric acid and urea fuels thin flaky-like structures is obtained while in the case of glycine fuel the nanometric particles with an irregular shape are observed.

According to Table 1, BET surface area of the synthesized TiO_2 powders increases when fuel type changes. The highest surface area is observed for glycine fuel as a result of the spongy and porous morphology formed.

In order to verify the chemical structure of the obtained powders, FT-IR spectral analysis was performed. Figure 4 shows that for all the samples, the vibration band of the surface OH groups is observed at 1630 cm⁻¹ and the corresponding stretching vibration peak of the OH groups is located at 3200-3600 cm⁻¹ [21]. This shows the presence of adsorbed water on the TiO₂ surface. In fact, the TiO₂–OH bonds are probably connected with chemically adsorbed H₂O and also some physically adsorbed H₂O on the surface of TiO₂ [22]. According to Jensen et al. [23] it can be assumed that the presence of surface OH groups is related to the surface area. Table 1 shows a higher value of BET surface for glycine-synthesized samples which is in good correlation with higher band intensity at 1630 cm⁻¹.

The regions from 400 to 800 cm⁻¹ in Figure 3 are dominated with weak and broad peaks identified to have the frequencies corresponding to bulk Titania skeleton [24]. The bands close to 550 cm⁻¹ correspond to O-Ti-O vibrations. The bands between 500 and 800 cm⁻¹ related to O-Ti-O was also reported by Phonthammachai *et al.* [25] when they studied the structural and rheological aspects of TiO₂ prepared by sol-gel method. The bands observed at 1200, 1370, 1380, 1610 and 1710 cm⁻¹, especially in the case of urea and citric acid fuels, can be related to C=O (carbonyl) stretching mode and unreacted residual materials.

3.2. Photo-catalytic activity

The photo-catalytic analysis was performed by a setup which was designed in our laboratory.



Figure 4: FTIR spectra of the prepared samples by various fuels.



Figure 5: Absorption spectra of MO solution on various samples after irradiation.

Figure 5 provides the UV-Vis absorption spectra of MO solution on various samples after the irradiation with a UV lamp.

Interestingly, in our photo-catalysis experiment, larger methyl orange adsorption amounts were observed in the urea fuel sample in comparison with glycine and citric acid samples. Figure 6 shows photo degradation of MO dye on the synthesized TiO₂. The concentration decrease which occurred after dispersing the samples in the MO aqueous solution and subsequent stirring in darkness reveals that some parts of the MO molecules were adsorbed on the samples' surface. Results showed that the prepared sample with urea fuel exhibits the highest photo degradation efficiency of about 80% with a MO conversion after 10 h of irradiation.



Figure 6: Photo degradation of MO solutions on various TiO₂ samples.

The surface area and particle size are also the important factors affecting the photo-catalytic effect of the TiO₂ samples; however, results demonstrated that in the case of our experiments they do not vary drastically. Therefore, the enhanced photo-catalytic effect of the urea-based sample can be otherwise explained; it is well known that the mixed structure of anatase and rutile can increase the photo-catalytic activity of TiO₂. For example, TiO₂ powder (Degussa, P25) which consists of ~ 80% anatase and ~ 20% rutile, shows high photo-catalytic activity [26]. These results can be attributed to the simultaneous effect of anatase and rutile phases [27-31]. The previous works



Anatase

shown in Figure 7.

activity [29-30].

demonstrated that anatase-dominated mixed-phase

TiO₂ nanoparticles exhibited superior photo-catalytic

coupling two different types of semiconductor photo-

catalytic materials in order to enhance electron-hole

charge separation and inhibit recombination [32-33].

In this case, heterogeneous systems of this type have

often involved in TiO2, for example, anatase/rutile

TiO₂ [27-34], TiO₂/SnO₂ [35-36], TiO₂/WO₃ [37] and

TiO₂/CdS [38]. The principle of the synergistic effect is

The synergistic effect is based on the concept of





The charge electrons (transfer) from anatase to rutile due to the slightly lower conduction band energy of rutile should be responsible for the improvement of the photocatalytic activity [27, 39]. Similar results have been reported in previous anatase/rutile heterogeneous nanostructures [27, 28]. It is demonstrated that photoexcited electrons injected into the rutile particles can migrate to the conduction band of anatase particles enhancing the photocurrent and efficiency. Interfacial electron transfer from rutile to anatase similar to that in heterogeneous photo-catalysis is proposed to account for the synergistic effect.

Following the charge transfer between anatase and rutile, the photo-generated electrons in the conduction of rutile can be scavenged by oxygen molecules to form superoxide radicals which contribute to the oxidation of methyl orange.

4. Conclusions

Microwave-assisted solution combustion was successfully applied using three different fuels in order to prepare nanocrystalline TiO₂ powders with 8-15 nm crystallite sizes. Results showed that a mixture of rutile/anatase phase was obtained with urea fuel and pure anatase phase in the case of glycine and citric acid. However, a calcination step at 400 °C was needed for citric acid sample to complete phase formation. The highest BET surface area was obtained in the case of the glycine-based sample. The morphology of the particles depends on the fuel type and varies from thick- and thinflakes to porous spongy structures. FT-IR spectral analysis confirmed O-Ti-O bonds with the bands between 500 and 800 cm⁻¹. Photo-catalytic activity of the samples also depends on the fuel type. The sample synthesized using urea is a better candidate for photocatalytic functions due to a well-crystallized mixed crystalline structure (75% anatase - 25% rutile) which results in the synergistic effect of mixed anatase and rutile phases.

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