

Effect of acid during synthesis on the agglomerated strength of TiO₂ nanoparticles

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Titanium dioxide (TiO₂ or titania) photocatalyst nanoparticle (NPs) powders were prepared. The synthesis steps were performed at room temperature. Based on X-ray diffraction evidence, it was found that only the anatase structure was formed when hydrochloric acid was added during the synthesis. With no acid, both anatase and brookite structures were formed. Transmission electron microscopy (TEM) showed that the primary particles from both the acid and no-acid routes were of approximately the same size. A particle-size analyzer equipped with an ultrasonic generator showed, however, that the aggregates of acid NPs were more difficult to break apart than those of the no-acid NPs. Gel formation was used to explain the difference in strength by which the NPs aggregated.

Key words: Nanoparticles, Titanium dioxide(TiO₂), Aggregate, Agglomerate, Acidity.

Introduction

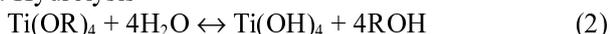
Two of the most widely used method for manufacturing TiO₂ nanoparticles (TiO₂-NPs) are the flame and the sol-gel synthesis processes. During the flame synthesis of titania NPs, titanium tetraisopropoxide (TTIP) is oxidized in a premixed methane-oxygen flame [1]. In the flame reactors, nanostructured powders are produced without control at high temperatures with extremely short process residence times (< 1 second).

Also extensively used is the sol-gel method to synthesize titanium dioxide. This method is also based on titanium alkoxides [2-5]. The total sol-gel synthesis can be described as an alcoholic permutation reaction, hydrolysis, and condensation reactions.

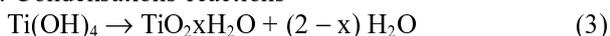
1. Alcoholic permutation



2. Hydrolysis



3. Condensations reactions



The amount of water used during gelation determines the relative contribution of each reaction. After hydrolysis and condensation, calcination is commonly used to

produce the desired crystal structure.

It has been reported that an ordered crystalline structure can be obtained when hydrolysis is completed before the beginning of the condensation reaction. In acidic conditions, the rate of the hydrolysis is accelerated through the protons that increase the partial positive charge of an OR group and at the same time defer the rate of condensation, because the positively charged surfaces of the interacting groups will cause the groups to repel each other [2]. The consequence of a fast hydrolysis (Eq. 2) and a slow condensation (Eq. 3) can result in the formation of an ordered structure directly from the solution at a low temperature without having to conduct a high temperature calcinations [6]. The synthesis of TiO₂ was then mainly focused on the use of highly acidic condition to obtain nanoparticles.

Besides an ordered crystalline structure of titania, in the use of nanoparticles, especially for photocatalysis applications where the surface area plays an important role, the ratio of surface atoms to interior atoms changes dramatically, if a macroscopic object is truly divided into smaller parts. When particles are large, the total surface energy is negligible, but becomes significant for very small particles. The high surface energy of nanoparticles causes them to aggregate. In the aggregation, many nanoparticles are associated with one another through chemical bonds and physical attraction forces at interfaces [7]. Being able to separate the nanoparticles is an important process prior to stabilizing the nanoparticles for the most effective utilization of the nanoparticles [8-9].

In this study, the effect of the use of acid (acid) and without

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the use of acid (no-acid) on the aggregated size and strength of TiO₂-NPs were investigated with a particle size analyzer equipped with an ultrasonic generator to act as an external force to separate the aggregates. Trans-mission electron micro-graphs gave evidence of the primary particle size.

Experimental

Chemical reagents

Titanium (IV) isopropoxide (Ti(OC₃H₇)₄) (TTIP) and 2-propanol ((CH₃)₂CHOH, 99.8%) were purchased from Fluka. Hydrochloric acid (HCl, 35.4%) was purchased from AnalaR. Nanopowder titanium dioxide (99.9%, surface area 20-25 m²/g) was purchased from Aldrich.

Synthesis of TiO₂

A mixture of 6 ml TTIP and 25 ml of 2-propanol was added to a premixture of 50 ml of 2-propanol and a volume of water (1 ml, 3 ml, and 10 ml: denoted as no-acid01, no-acid03, and no-acid10, respectively) and were ultrasonically treated for 2 hours. For studies with acid, an additional amount of 0.1 ml of concentrated hydrochloric acid was added to the premixture of 2-propanol and water (1 ml, 3 ml, and 10 ml: denoted as acid01, acid03, and acid10, respectively); before the addition of the TTIP mixture. Then the solution was dried at room temperature to evaporate the 2-propanol. Table 1 summarizes the appearance of TiO₂ synthesis during and after evaporation of 2-propanol. The powder or crystal obtained was manual ground for 10 minutes to obtain fine powder. The samples were then calcinated at 550°C in furnace for 2 hours [9-13].

X-ray diffraction (XRD) analysis of TiO₂

X-ray diffraction was used to confirm the crystal structure formed. The TiO₂ powders were characterized by a Bruker D8 Advance X-ray Diffractometer with a monochromatic Cu-K_α (40 kv, 30 mA) source, a step size of 0.037311°, and a step time 1 s/step. The X-ray diffraction patterns of powders before and after calcination were characterized. The crystal structure was compared to commercial TiO₂-NPs obtained from Aldrich (anatase, 75%, and rutile, 25%).

Transmission electron microscopy (TEM) analysis

TEM micrographs were taken using a Tecnai G2 Sphera operating at a voltage of 80 kV. All samples were prepared by dropping the ultrasonically treated suspensions

from the particle size analyzer onto a TEM holey carbon-coated grid and dried at room temperature. For all the samples, at least 5 TEM samples were made, and at least 10 micrographs of each of the TEM samples were investigated to analyze the ensemble average of the sample primary particle size. The micrographs shown are representative of the analysis, but it is not possible to show the average aggregation with TEM micrographs.

Aggregate segregation with an ultrasonic generator equipped on a particle size analyzer

Two hundred milligrams of TiO₂ was dispersed in 50 ml of deionized water. Aggregates of TiO₂ were dispersed by an ultrasonic homogenizer (Hydro MU, 40 kHz) that was equipped on a particle size analyzer (MASTERSIZER 2000, Malvern Instrument). The experimental setup used a homogenizer rotor speed of 2000 rpm. The ultrasonic amplitude was fixed at 20 micrometers and the treatment time was 10 minutes. The measurements were performed with the absorbance ranging from 5 to 10%. Three repeats were performed for averaging. The results from the particle size analyzer were used to compare the aggregated strength of the aggregates.

Results and Discussion

Table 1 summarizes the appearance of the synthesis TiO₂-NPs during and after the evaporation of 2-propanol. For no-acid conditions, no gel was formed. Immediately after the addition of TTIP, the solution appeared cloudy white. This indicated that after hydrolysis and condensation, either the size of TiO₂ particles formed was very large, or that immediately after the TiO₂-NPs were formed, the NPs immediately aggregated to form large agglomerates. The mole ratio of water to TTIP for 1 ml of water (no-acid01) was 2.5 : 1 ; 3 ml (no-acid03) was 8 : 1 ; and 10 ml (no-acid10) was 25 : 1. From Eq. 2, 4 moles of water is required to react with 1 mole of TTIP. Thus, no-acid01 would be considered to be a low water solution, while the no-acid03 and the no-acid10 had an excess amount of water. Under these no-acid conditions (assuming NPs were formed rather than large primary particles of TiO₂, as will be confirmed by TEM analysis), there were not enough positive charges to stabilize the surface of the TiO₂-NPs crystals as they were formed [3]. Therefore,

Table 1. Appearance summary of synthesized TiO₂ during synthesis and after evaporation of the 2-propanol

Experiment	Volume of H ₂ O	Sample	Appearance after 1 h	Appearance after 2 h	Form after evaporation
No acid	1 ml	no-Acid01	Cloudy	Cloudy	Powder
	3 ml	no-Acid03	Cloudy	Cloudy	Powder
	10 ml	no-Acid10	Cloudy	Cloudy	Powder
With acid (0.1 ml HCl)	1 ml	Acid01	Transparent	Gel	Crystal
	3 ml	Acid03	Gel	Gel	Crystal
	10 ml	Acid10	Gel	Gel	Crystal

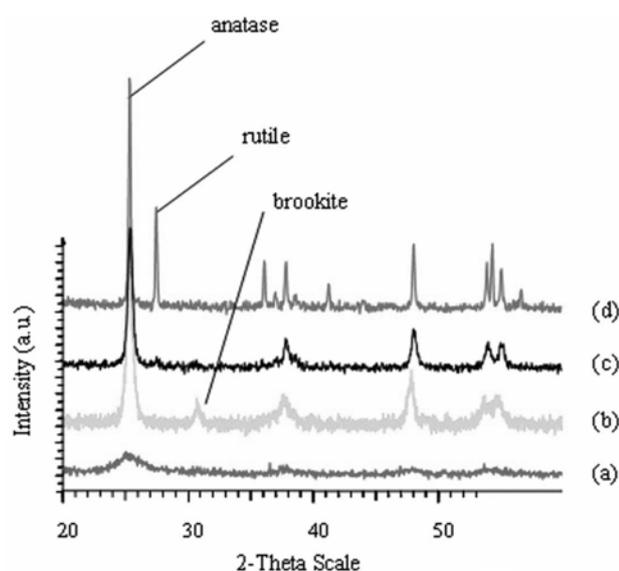


Fig. 1. XRD patterns of powders TiO₂ (a) acid01 condition before calcination, (b) no-acid01 condition after calcination, (c) acid01 condition after calcination, and (d) commercial nanoparticles from Aldrich.

the large agglomerates were then observed as a cloudy white suspension and soon precipitated.

For acid conditions, gels were formed in all three cases. With a low amount of water (acid01), it took a longer time to form a gel. This was due to the fast hydrolysis and slow condensation rate. A more stable crystalline structure, anatase, was possible with the acid syntheses because the atoms had more time to arrange themselves.

To confirm the in-house synthesis of TiO₂-NPs, X-ray powder diffractograms were obtained, Fig. 1. Fig. 1(a) showed the pattern of acid01-TiO₂ with small peaks of anatase even before calcination. The acidic condition had accelerated the rate of hydrolysis through the additional H⁺ ions. These ions increased the partial positive charge of OR group and at the same time offset the rate of condensation due to the positively charged surfaces of the interacting groups repelling each other [3]. This resulted in a crystalline structure even prior to calcination for the acid synthesis.

No crystal peak was found prior to calcination of no-acid01 in this study (not shown). However, a small amount of anatase has been reported to be formed before calcination of no-acid, if the evaporation of the 2-propanol was done at temperature > 80 °C for > 10 hours [14]. Such a temperature and time of evaporation contributed to the rearrangement of atoms that were comparable to annealing crystals.

Figs. 1(b) and (c) show the XRD patterns of the no-acid01 and the acid01 TiO₂ powders after calcination, respectively. Patterns from the no-acid01 powders showed peaks of both anatase and brookite structures. The formation of the brookite, a less stable, crystal structure under no-acid conditions resulted from the absence of stabilizing positive charges as there were less time for

atoms to order themselves [5]. Under acid conditions, only anatase structure was found (Fig. 1(c)). The formation of only anatase, a more stable, crystal structure resulted from the presence of stabilizing positive charges on the surfaces as the crystals were formed [4]. The XRD pattern of commercial TiO₂ is shown for comparison in Fig. 1(d).

Based on the TEM analysis and taking the ensemble average of particle sizes of at least 50 configurations depending on the quality of the data, the average particle size was determined. For both acid and no-acid TiO₂ NPs, the particle size was found to be in the range of 8–120 nm with an average of 15 ± 4 nm. Representative examples of different TEM configurations are shown in Figs. 2 and 3. From the TEM analysis, acid and no-acid syntheses showed insignificant differences in the size of the primary particles obtained. Relating data from Table 1 and the TEM analysis (Fig. 2), for the no-acid condition, the cloudy white suspension that was formed immediately after the addition of TTIP must be the formation of NPs that immediately aggregated into large agglomerates rather than the formation of large TiO₂ primary particles.

Although the TEM analysis showed an insignificant difference in the primary particle size, the particle size analyzer which was used to study the aggregate size and strength of TiO₂ NPs after 10 minutes of ultrasonic treatment showed that aggregates from the acid syntheses were larger than those of the no-acid syntheses, for all amounts of water (Fig. 4). It should be noted that with the particle size analyzer, one would not be able to detect the primary particle size due to the detection limit of the machine. Rather one was looking at the aggregate size that resulted from the separation by the ultrasonic treatment. For aggregates that are strongly bound to each other, it would be more difficult for the ultrasonic treatment to break the aggregates apart, therefore, larger aggregate sizes would be detected after the ultrasonic treatment. For weakly bound aggregates, the ultrasonic treatment would be able to break the aggregates and then smaller aggregates should be detected. As can be seen in Fig. 4, for the no-acid case, more of the smaller aggregates were detected after 10 minutes of ultrasonic treatment compared to the acid syntheses. This means that with the same ultrasonic power, it was possible to break the aggregates from the no-acid syntheses, but not for the acid case.

Through the gelation process from the acid syntheses, titania NPs were bound to each other more tightly than those of the no-acid titania NPs. Even though, in the no-acid syntheses, aggregates were formed immediately after the addition of TTIP, the nanoparticles were more loosely bound to each other than those from the acid syntheses conditions. In the gel formation of acid syntheses, where the particles were formed in the gel structure, crystals were more tightly packed after calcination than those without gel formation (no-acid).

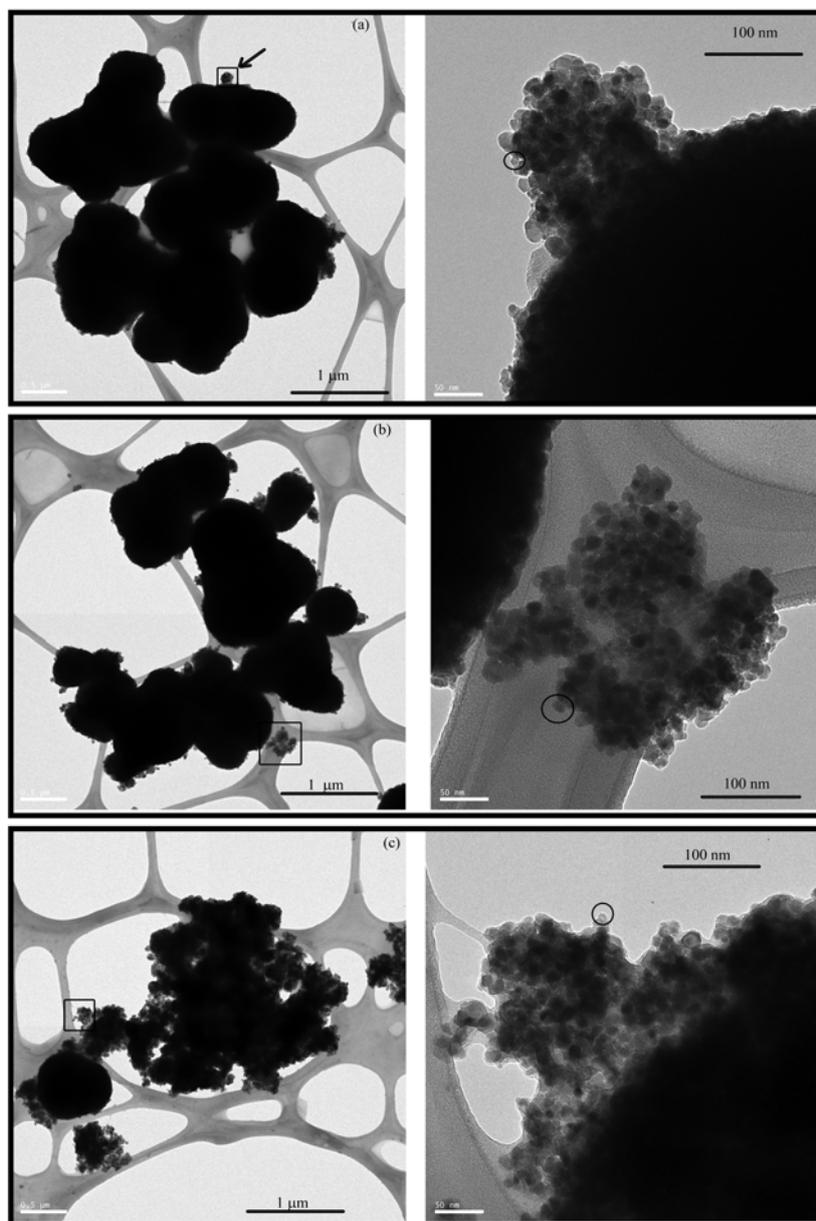


Fig. 2. TEM micrographs of TiO_2 nanoparticles aggregates from synthesis in the no-acid condition. The various amounts of water are (a) 1 ml, (b) 3 ml, and (c) 10 ml. Squares representing the area being zoomed to image on the right. Circles indicate primary particles.

Conclusions

Crystalline titania had been prepared by a sol-gel alkoxide method. It was found that with or without the use of acid, there was an insignificant difference in the size of the primary nanoparticles formed. With acid, only the anatase structure was found. Anatase is the more stable form of titania crystals compared to the brookite structure. For the no-acid conditions, anatase and brookite structures were formed. The formation of either anatase or brookite structure was due to the H^+ stabilization that allows time for atoms to rearrange themselves into different crystal structures.

The average aggregate size distribution after an ultrasonic treatment of the acid titania NPs was found to be larger

than those of the no-acid titania NPs, even though, the size of primary particles was of the same order. The aggregates from acid titania NPs were bound to each other more tightly than those of the no-acid titania NPs due to their formation during the gelation process.

In summary, acid stabilization yielded a more ordered and stable crystal structure, of anatase, but at the same time increased the strength of aggregation making it more difficult to separate with ordinary ultrasonic treatment. Acid stabilization, however, did not reduce the size of the primary particles compared to the no-acid case. Therefore, in a choice of synthesizing titania NPs that could be separated by an ordinary ultrasonic treatment, it would be better to choose the no-acid synthesis, since NPs of

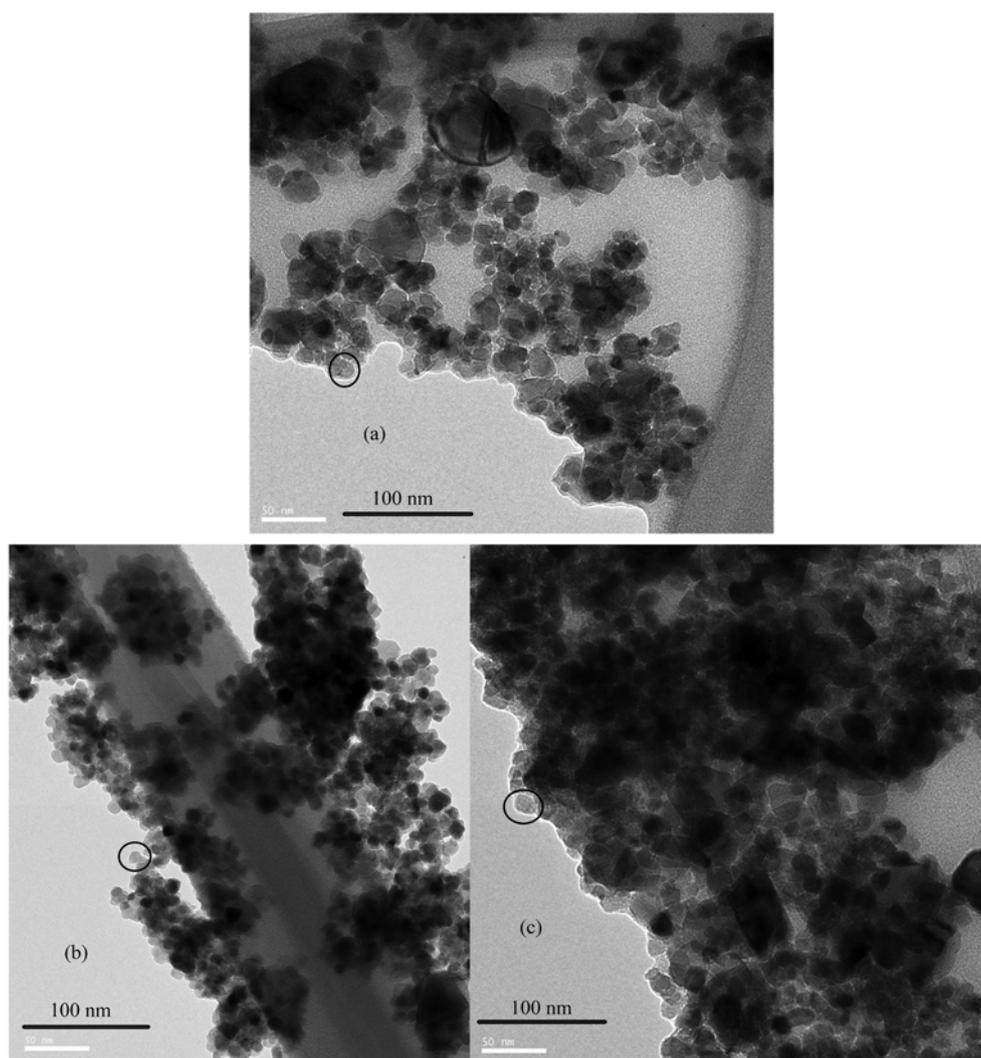


Fig. 3. TEM micrographs of TiO₂ nanoparticles aggregates from synthesis in the acid condition. The various amounts of water are (a) 1 ml, (b) 3 ml, and (c) 10 ml. Circles indicate primary particles.

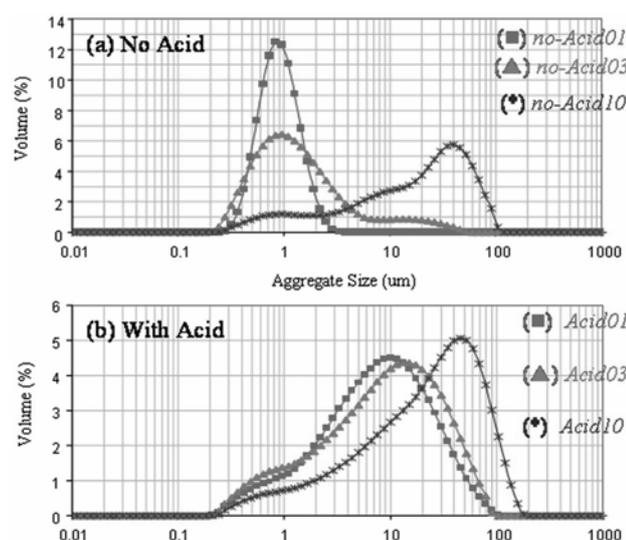


Fig. 4. Aggregate size analysis with the use of a particle size analyzer (a) without the use of acid and (b) with the use of acid for 3 different amounts of water added.

comparable size could be obtained and separated for future stabilization with a surfactant to utilize the large increase in surface area of the NPs. As for the crystal structure, if anatase is the desired phase, the crystal structure could be transformed with a longer calcination time.

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