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Preparation of Nanosized TiO_2 Particles via Ultrasonic Irradiation and Their Photocatalytic Activity on the Decomposition of 4-Nitrophenol

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Abstract−TiO_2 nanoparticles were prepared by hydrolysis of TTIP (titanium tetraisopropoxide) using an ultrasonication technique coupled with a sol-gel method. The physical properties of nanosized TiO_2 were investigated. The photocatalytic degradation of 4-nitrophenol was studied by using a batch reactor in the presence of UV light. The crystallite size of the anatase phase is increased with an increase of R_{EtOH} ratio (EtOH/H_2O molar ratio). The particles' crystallite size prepared with and without ultrasonic irradiation is marginally different. Those particles prepared with ultrasonic irradiation show a higher activity on the photocatalytic decomposition of 4-nitrophenol compared to those prepared without ultrasonic irradiation. The photocatalytic activity decreases with an increase of R_{EtOH} ratio. In addition, the photocatalytic activity shows the highest value on the titania particle calcined at 500 °C.

Key words: Nanosized Titania, Ultrasonication, Sol-gel Method, Photocatalytic Degradation of 4-Nitrophenol

INTRODUCTION

Up to the present time the most widely used methods for the elimination of organic pollutants from water have been adsorbed over activated carbon, chemical oxidation, or an aerobic biological treatment. All these processes suffer from several disadvantages. Adsorption is not a destructive process so that a further step is needed for the elimination of the organic compounds, while the chemical oxidation does not generally result in the complete mineralization of the organic compound and it is economically favorable only for significant concentrations of pollutant. Biological treatment has several drawbacks, such as the low reaction rate, the difficulty of disposal of the activated sludge, and the very narrow range of pH [Suryanyana and Froes, 1992; Alivisatos, 1995]. None of these disadvantages is shared by methods based on the utilization of light, i.e., photocatalysis using semiconductors irradiated by near UV-light. The complete mineralization of the organic compound with the absence of dangerous residual intermediate compounds, and the possibility of working over wide ranges of operational conditions make the photocatalytic method preferable or, at least, competitive with the others.

Phenol and its derivatives are some of the most refractory pollutants present in industrial waste water. Their high stability and solubility in water are the main reasons why the degradation of these compounds to non-dangerous levels is a very difficult process [Augugliaro et al., 1991]--in particular, 4-nitrophenol and its derivatives, which result from the production processes of pesticides, herbicides and synthetic dyes. These pollutants have high toxicity and carcinogenic character.

Nanocrystalline powders of titania are widely used as catalysts in photocatalytic reactions, as gas sensors, and as white pigment materials [Wold, 1993]. The synthesis of nanocrystalline particles with controlled size and composition is of technological importance because they present more active sites per unit area achieving enhanced performance. Up to now, many methods have been established for the synthesis of titania [Hong et al., 2003; Lim et al., 2002]. The sol-gel technique is the most often used. Unfortunately, sol-gel derived precipitates are usually amorphous in nature, requiring further treatment to induce crystallization [Yang et al., 2001; Jung and Imaishi, 2001]. The sonochemical synthesis, which has been described elsewhere,has been employed to prepare amorphous metals and oxides [Cao et al., 1997; Awate et al., 2001]. The use of ultrasound to enhance the rate of reaction has become a routine synthetic technique for many homogeneous and heterogeneous chemical reactions [Hyeon et al., 1996].

In this paper, we prepared nanosized TiO_2 particles by hydrolysis of TTIP (titanium tetraisopropoxide) with and without ultrasonic irradiation coupled with the sol-gel method. The physical properties of prepared nanosized TiO_2 particles were investigated. We also investigated the effect of R ratios (H_2O/TTIP and EtOH/H_2O) and calcination temperature on the physical properties of nanosized TiO_2 particles, and examined the activity of TiO_2 particles as a photocatalyst for the decomposition of 4-nitrophenol.

EXPERIMENTAL

All chemicals used in this study were reagent-grade supplied from Aldrich and used as received. Millipore water was used in all experiments.

To prepare nanosized titania particles, titanium tetraisopropoxide ($Ti(OC_3H_7)_4$, 97%, Aldrich) was used as a precursor of titania. Hydrolysis was carried out at room temperature by adding slowly controlled amounts of TTIP to an ethanol-H_2O mixture under vigorous stirring. This solution was mixed for 6 h with rapid agitation (3,500 rpm) and then washed and filtered.

Sol samples formed by the hydrolysis process were treated with

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and without ultrasonic irradiation in an ultrasonic cleaning bath (Branson, USA, 115 V, 2 kW, 38 kHz) for 1 h. The produced TiO_2 particles were separated in a centrifuge at 10,000 rpm for 10 min and were then washed by distilled water. The particles were dried at 100 °C for 24 h and then calcined at 300-700 °C for 3 h.

The dried fine powder of synthesized TiO_2 was subjected to thermogravimetric-differential thermal analysis (TG, Perkin-Elmer) to determine the temperature of possible decomposition. The major phase of the obtained particles was analyzed by X-ray diffraction (Rigaku D/MAXIIC) using Cu-Kα radiation. The crystallite size of the prepared particles was determined from the broadening of the anatase main peak at 2θ=25.3° by the Schrerrer equation [Cullity, 1978]. The particle size and external morphology of the prepared particles were observed on a transmission electron microscope (TEM, JEOL, JEM-2020) using a 200 kV accelerating voltage. The BET specific surface area of the prepared particles was determined by nitrogen adsorption isotherms at liquid N_2 temperature (77 K). The particles were evacuated at 573 K prior to N_2 adsorption.

A biannular quartz glass reactor with the lamp immersed in the inner part was used for all the photocatalytic experiments. The batch reactor was filled with 500 ml of an aqueous dispersion in which the concentration of titania and of 4-nitrophenol was 67 mg/L and 100 mg/L, respectively, and magnetically stirred to maintain uniformly both concentration and temperature. A 500 W high-pressure mercury lamp (Kumkang Co.) was used. The circulation of water in the quartz glass tube between the reactor and the lamp served to cool the lamp and to warm the reactor to the desired temperature. Nitrogen was used as a carrier gas and pure oxygen was used as an oxidant. After reaction, the samples were immediately centrifuged and a quantitative determination of p-nitrophenol was performed by a UV-vis spectrophotometer (Shimazu UV-240).

RESULTS AND DISCUSSION

1. Thermal Analysis

Fig. 1 shows the TG curves of the dried titania powders prepared at different R_{EtOH} ratio using ultrasonic irradiation. These particles are dried at 100 °C without calcination. Two main zones in weight loss can be identified regardless of the R_{EtOH} ratio ratio. The first zone, from 50 to 150 °C, corresponds to the removal of physically adsorbed water and alcohol [Yu et al., 2003]. The second zone, from 150 to 400 °C, corresponds to the oxidation of residual organic compounds. However, the weight loss of titania powders prepared at R_{EtOH} ratio ratio=10 is obviously larger than that prepared without ethanol. We suggest that the former has a large amount of residual unhydrolyzed alkyl organics in the titania powders.

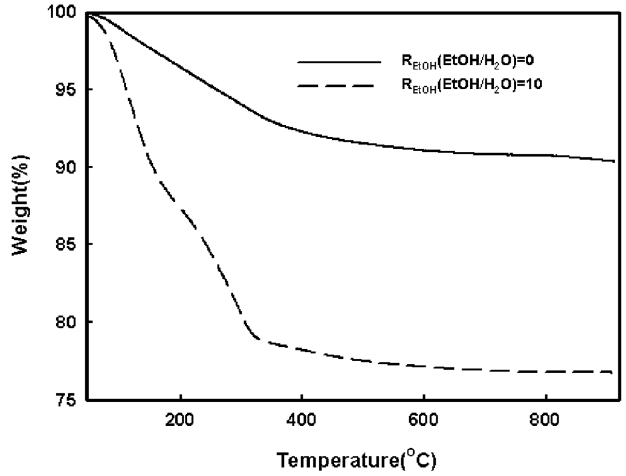

Fig. 1. TG curves of the nanosized TiO_2 powders prepared with ultrasonic irradiation at different $EtOH/H_2O$ molar ratio: dried at 100 °C, $R(H_2O/TTIP)$ ratio=75.

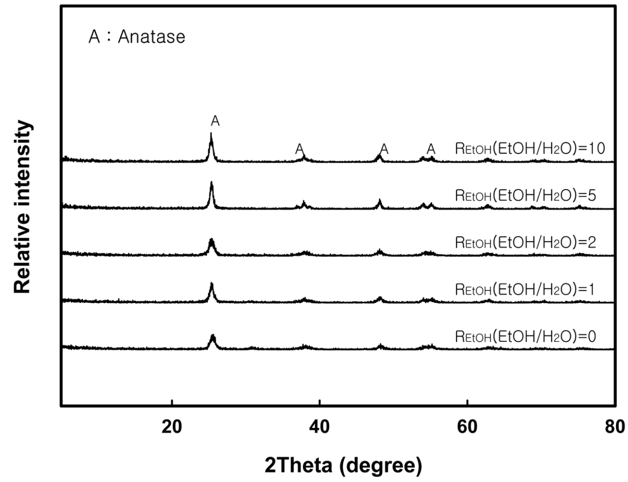

Fig. 2. XRD patterns of nanosized TiO_2 powders prepared with ultrasonic irradiation at different $EtOH/H_2O$ molar ratio; calcination temperature=500 °C, $R(H_2O/TTIP)$ ratio=75.

2. X-ray Diffraction Analysis

Fig. 2 shows the XRD patterns of the TiO_2 particles prepared at different R_{EtOH} ratio ($EtOH/H_2O$ molar ratio) using ultrasonic irradiation and calcined at different temperatures. The major phases of all the prepared particles are anatase structure; the anatase crystallinity increases with an increase of R_{EtOH} ratio.

The crystallite size of the particles can be determined by the Scherrers equation [Cullity, 1978], with the particle size of the titania particles shown in Table 1. The crystallite size of the anatase phase increases from 9.0 to 16.6 nm as the R_{EtOH} ratio increases from 0 to 10. This result indicates that the growth of anatase crystallites depends on the initial R_{EtOH} ratio. As shown in Fig. 3, the phase transforma-

Table 1. Physical properties of nanosized TiO_2 powders prepared with ultrasonic irradiation at different $EtOH/H_2O$ molar ratio and their photocatalytic activity

Catalysts $EtOH/H_2O$ ratio	XRD			Activity
	Structure	Intensity	Crystallite size (nm)[a]	k′(min^{-1})×10^{-3b}
0	anatase	166	9.0	17.0
1	anatase	220	11.2	9.8
2	anatase	230	14.2	7.3
5	anatase	295	16.4	5.7
10	anatase	315	16.6	5.0

[a] obtained by Scherrers equation.

[b] apparent first-order constants (k′) of 4-nitrophenol.

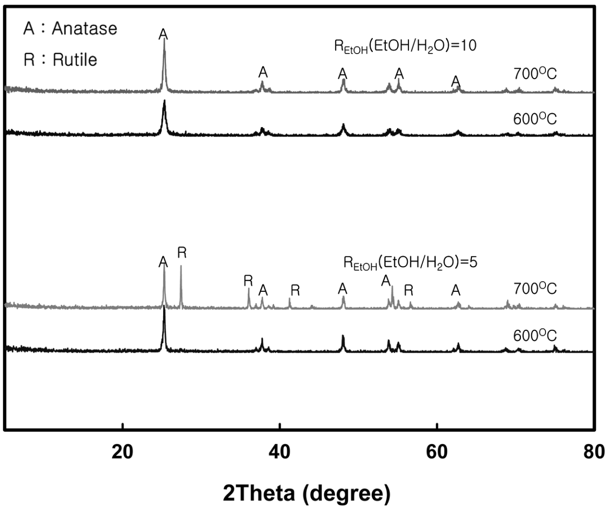

Fig. 3. XRD patterns of nanosized TiO_2 powders prepared with ultrasonic irradiation at different calcination temperature and different $EtOH/H_2O$ molar ratio: $R(H_2O/TTIP)$ ratio=75.

tion temperature increases with an increase of the initial R_{EtOH} ratio. For high R_{EtOH} ratio, the water concentration during hydrolysis reaction is small and a large amount of unhydrolyzed alkyl groups remain in the resulting powders. These alkyl groups prevent phase transformation but cause the growth of anatase crystallites by providing the heat of combustion of residual organic compounds. On the other hand, with an increase of the water concentration, a stronger nucleophilic substitution reaction between H_2O and alkoxide molecules will occur and thus, more alkoxyl groups in the alkoxide will be substituted by hydroxyl groups of H_2O, the amount of residual alkyl groups preventing the growth of anatase crystallites.

Fig. 4 shows the XRD patterns of the TiO_2 particles prepared by using ultrasonic irradiation and calcined at different temperatures. The major phases of all the prepared particles are anatase structure; however, a rutile peak is observed above 600 °C.

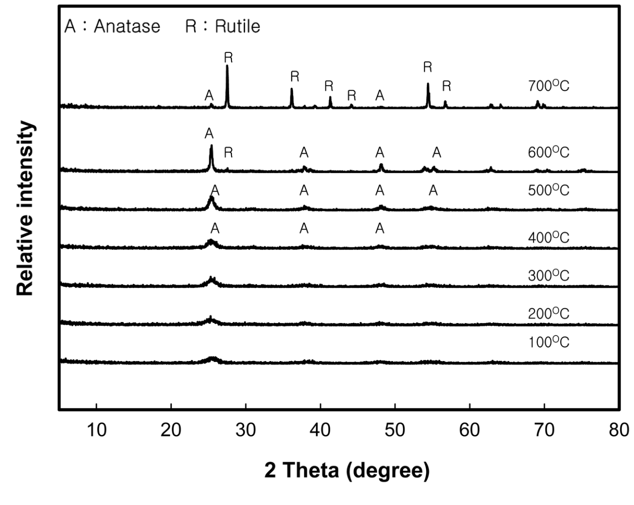

Fig. 4. XRD patterns of nanosized TiO_2 powders prepared with ultrasonic irradiation at different calcination temperature: $R(H_2O/TTIP)$ ratio=75.

Table 2. Physical properties of nanosized TiO_2 powders prepared with and without ultrasonic irradiation at different calcination temperature and their photocatalytic activity

Calcination temperature (°C)		BET	XRD	TEM	Activity
		Surface area (m^2/g)	Crystallite size (nm)[c]	Crystallite size (nm)	$k'(min^{-1})\times10^{-3}$[d]
TiO_2[a]	200	189	5.9	-	-
	300	111	6.5	-	10.2
	400	103	7.1	-	-
	500	63	11.0	22	14.1
	600	30	25.2	-	-
TiO_2[b]	200	198	5.1	-	-
	300	125	6.5	-	10.8
	400	108	7.4	-	15.1
	500	69	9.0	14	17.0
	600	25	21.6	-	11.7
	700	-	48.4[e]	-	5.0

[a] prepared without ultrasonic irradiation.
[b] prepared with ultrasonic irradiation.
[c] obtained by Scherrers equation.
[d] apparent first-order constants (k′) of 4-nitrophenol.
[e] rutile structure.

Anatase crystallinity increases with an increase in calcination temperature up to 500 °C. Upon increasing the temperature to 600 °C, the rutile peak appears. The increasing sharpness and narrowing of the X-ray peaks with increasing temperature reflect the dependence of titania crystallinity on temperature.

The crystallite size of titania particles calcined at different temperature is shown in Table 2. One can see that the crystallite size of the anatase phase increases from 5.1 to 21.6 nm as the calcination temperature increases from 300 °C to 600 °C. In addition, the crystallite size of the titania particles prepared with and without ultrasonic irradiation is marginally different.

The measured BET specific surface areas of titania particles prepared by ultrasonic irradiation and calcined at different temperatures from 200 to 600 °C are in the range of 25-198 m^2/g. These show slightly larger surface area compared to titania particles prepared without ultrasonic irradiation.

3. TEM Analysis

Fig. 5 shows the TEM micrographs of the titania nanoparticles prepared with and without ultrasonic irradiation. The particles prepared with ultrasonic irradiation are shown to have a spherical shape and have a uniform size distribution (Fig. 5(a) and (c)) compared to those prepared without ultrasonic irradiation (Fig. 5(b) and (d)). The photographs clearly reveal the role of ultrasonication, which produces less agglomeration and more homogeneity in the particles. The crystallite size were determined by counting the number of particle sizes in a given area, suggesting an average diameter of 14 nm when prepared with ultrasonic irradiation but increasing to 22 nm when prepared without ultrasonic irradiation. The particles prepared without ultrasonic irradiation are shown in Table 2 to have larger values in particle size compared to those obtained from XRD analysis. Overall, these results indicate that the preparation of titania via ultrasonification decreases the crystallite size by reducing the

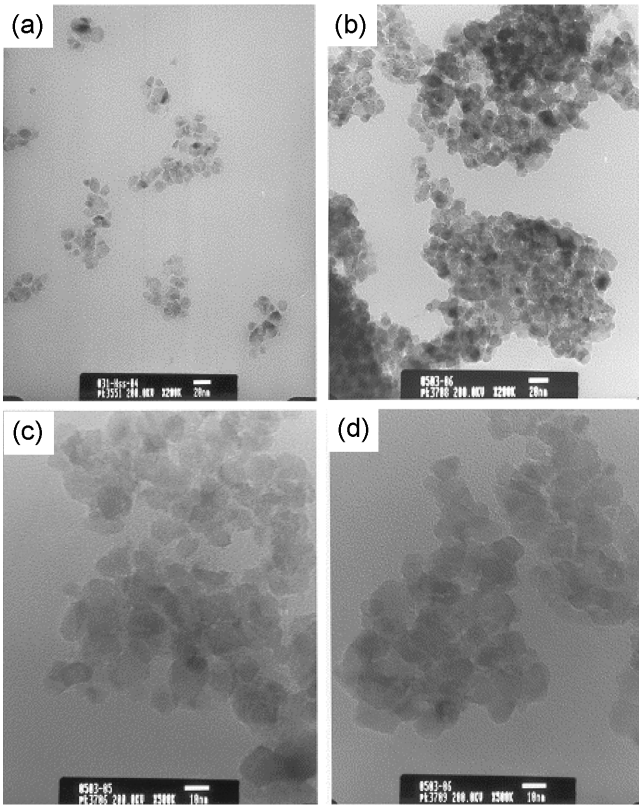

Fig. 5. TEM micrographs of nanosized TiO_2 powders prepared using different method: (a) and (c) with ultrasonic irradiation, (b) and (d) without ultrasonic irradiation.

likelihood of particle agglomeration.

4. Activity Test

It is well known that photocatalytic oxidation of organic pollutants follows Langmuir-Hinshelwood kinetics [Turchi and Ollis, 1990; Hong et al., 2001]. This kind of reaction is typically represented as:

$$-dc/dt=kC \tag{1}$$

which, on integration gives:

$$C=C_o \exp(-kt) \tag{2}$$

C_o is the initial concentration of the 4-nitrophenol and k is a rate constant related to the reaction properties of the solute, which depends on the reaction conditions, such as reaction temperature, and solution pH. The photocatalytic activity of an adsorbent is regarded as proportional to this value.

The photocatalytic activity for the decomposition of 4-nitrophenol on the titania particles prepared at different R_{EtOH} ratio was examined and the result is summarized in Table 1. The photocatalytic activity decreases with an increase of R_{EtOH} ratio; the activity shows a significantly higher value for the titania particle prepared without ethanol compared to that prepared with ethanol. This increase may be attributed to the fact that the titania particle prepared without ethanol has small crystallite size. This observation is consistent with previous results, wherein the photocatalytic activity increases with a decrease of particle size [Jung and Park, 2000]. It can be also confirmed that a small particle has a large illuminated surface area because the particles have a constant density at the same structure.

The photocatalytic activity for the decomposition of 4-nitrophenol on the titania particles calcined at different temperature was also examined, with the results summarized in Table 2. As shown in Table 2, the photocatalytic activity exhibits the highest value for the titania particles calcined at 500 °C. The titania particles prepared with ultrasonic irradiation show the higher activity in the photocatalytic decomposition of 4-nitrophenol compared to those prepared without ultrasonic irradiation. Again, this fact is attributed to the former having a larger surface area and smaller crystallite size. It is consistent with the result that the photocatalytic reaction has a small particle-size effect, wherein the photocatalytic activity increases with a decrease of particle size.

Titanium dioxide can take on any of the following three crystal structures: rutile, anatase, or brookite. Anatase-type titanium dioxide generally exhibits a higher photocatalytic activity than the other types of titanium dioxide with respect to the decomposition of organic pollutants by suppressing the electron-hole recombination [Fujishima et al., 1999]. In the case of titania particles calcined at 600 °C, the anatase and rutile phases are combined, while the amorphous phase is mixed with the anatase phase in the titania particles calcined below 300 °C. Therefore, the pure anatase titania calcined at 500 °C shows the highest activity in the photocatalytic decomposition of 4-nitrophenol.

5. Effect of R(H_2O/TTIP) Ratio

Fig. 6 represents the photocatalytic degradation of 4-nitrophenol over titania prepared by different R ratio. The photocatalytic activity, given by the slope of the concentration ratio, shows a maximum value at the R ratio=75.

In the preparation of titania by the sol-gel process, the physical properties of titania depend on the preparation conditions, such as R(water/alkoxide) ratio, calcination temperature and on the presence of acid. It is well known that water plays an important role in the nucleation and growth of crystallites, and that the nucleus can be homogeneously formed in the R=10 [Hong et al., 2001].

The metal alkoxide requires 2 mol water in the preparation of titania, as shown in the following reaction:

$$nTi(OR)_4+2nH_2O \rightarrow nTiO_2+4nROH$$

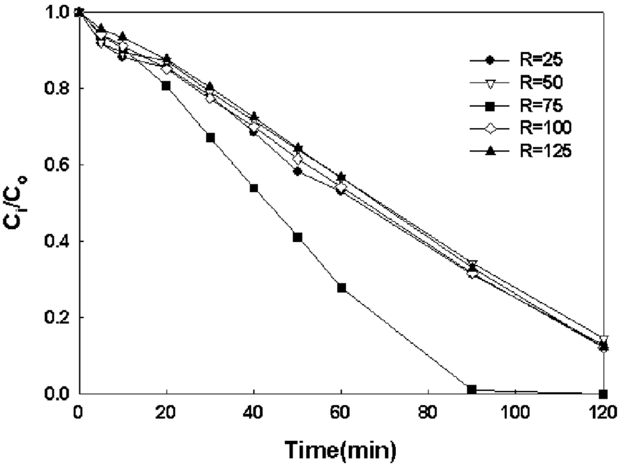

Fig. 6. Photocatalytic decomposition of p-nitrophenol over TiO_2 prepared at various R ratios: C_o=100 mg/L, W=0.067 g/L.

It is well known that nucleation occurs readily at the expense of crystallite growth as the R ratio increases and crystallite size becomes small [Ward and Ko, 1995]. In addition, the photocatalytic reaction has small-particle size effect, of which the photoactivity increases with decreasing particle size. For high R ratio, larger than 100, particle aggregation results in an increase in particle size and decrease in photocatalytic activity [Ward and Ko, 1995].

CONCLUSIONS

In the present work, we have synthesized TiO_2 nanoparticles by hydrolysis of TTIP (titanium tetraisopropoxide) using an ultrasonication technique coupled with a sol-gel method. The physical properties of nanosized TiO_2 have been investigated by TG, TEM, XRD and BET analyses. The photocatalytic degradation of 4-nitrophenol has been studied by using a batch reactor in the presence of UV light. The crystallite size of the anatase phase increases from 9.0 to 16.6 nm as the R_{EtOH} ratio increases from 0 to 10. In addition, the crystallite size of titania particles prepared with and without ultrasonic irradiation is marginally different. The particles prepared with ultrasonic irradiation have a spherical shape and have a uniform size distribution compared to those prepared without ultrasonic irradiation. The titania particles prepared with ultrasonic irradiation exhibit a higher activity for the photocatalytic decomposition of 4-nitrophenol compared to those prepared without ultrasonic irradiation, since the former has a larger surface area and smaller crystallite size. The photocatalytic activity decreases with an increase of R_{EtOH} ratio. In addition, the photocatalytic activity shows the highest value on the titania particle calcined at 500 °C.

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