



Effects of acidic and basic hydrolysis catalysts on the photocatalytic activity of TiO₂

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ABSTRACT

In this paper, the effects of catalysts' properties on the photocatalytic activity behavior of TiO₂ were studied. In this regards; Titania nano particles with high photocatalytic activity were prepared from titanium alkoxide dissolved in alcohol and water under acidic conditions. The properties of the powders were investigated by powder XRD, Brunauer-Emmett-Teller (BET) method and Zeta sizer. The photocatalytic activities of the TiO₂ nano particles were assessed by the degradation of Methylene blue (MB) in aqueous solution. The X-ray diffraction results showed that the product had anatase crystal structure with crystallite size below 10nm. According to the obtained results, the kinetics of photocatalytic reaction followed pseudo-first-order model. Particle size analysis showed that the mean particle size were 15 and 128nm. The chemical mechanism was discussed in relation to the sol-gel transition, which provides a possible theoretic explanation to the photocatalytic activity of TiO₂ nano particles. The results showed that the photocatalytic activity TiO₂ nano particles strongly depended on the type of stabilizer and presence of Methylcellulose (MC).

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KEYWORDS

Titanium isopropoxide;
Hydrolysis;
HNO₃;
CH₃COOH;
Photocatalytic activity.

INTRODUCTION

A great deal of effort has been devoted in recent years to developing oxide semiconductor photocatalysts with high activities for environmental protection procedures such as air purification, water disinfection, hazardous waste remediation, and water purification. Heterogeneous photocatalysis seems to be an attractive method because it can be employed for the degradation of various families of organic pollutant^[1-5]. The reason for the increased interest in such photocatalysis is that the process may use atmospheric oxygen as oxidant and can be carried out in water at room tempera-

ture and normal pressure. Among the photocatalysts, TiO₂ (in anatase phase) has been most widely used because it's easily available, inexpensive, non-toxic, and shows relative high chemical stability^[6,7]. Sol-gel processing is one of the most common methods to produce photocatalyst TiO₂ in both forms of coatings and powder because this techniques offer some advantages such as ease and versatility of processing, homogeneity at a molecular level, as well as mild and ambient atmosphere reaction conditions^[8].

Good catalytic property is governed by two major opposing physical properties: Crystallinity and surface area of photocatalyst. The high crystallinity helps to prolong

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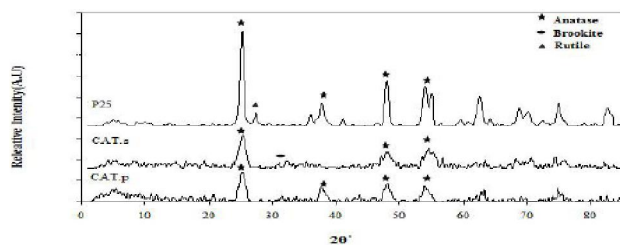


Figure 1 : XRD patterns of prepared TiO₂ nano particles and P25

the recombination rate of the photoexcited electron and positive hole, hence, strong reducing and oxidizing power of the photocatalyst. The high surface area would enhance adsorption of the target molecules on to the surface of the catalyst, as higher numbers of molecules are adsorbed the faster the rate of reaction^[9]. The photocatalytic activity in the aqueous system is usually evaluated by measuring the degradation rate of an organic molecule in the solution. Usually MB has been used as such a dye. The reasons for the choice of this particular dye are: (i) it is relatively stable against UV irradiation without any photocatalyst, (ii) its stable under environmental conditions^[10].

In this study, highly photocatalytically active nanometersized TiO₂ photocatalysts with different phase compositions have been prepared by sol-gel process. The effects of the type of stabilizer such as HNO₃ and CH₃COOH catalysts and presence of methylcellulose were investigated on the microstructures and photocatalytic activity. In this paper, P25 was studied for comparison with prepared samples.

EXPERIMENTAL

The materials for preparation of two samples (CAT.s and CAT.p) were as follows

Titanium tetra iso propoxide (TTIP) (98%, Merck) and Iso-Propanol (99.5%, Merck) were used as precursor and solvent respectively (Ti, H₂O: 0.005: mol ratio; Ti, Alcohol: 1.57: mol ratio). HNO₃ (65%, Merck) and CH₃COOH (95%, Merck) were used respectively in CAT.s and CAT.p as stabilizer. The applied stabilizer was 0.0068 molar. Methylcellulose (MC) was used as a dispersant in preparation of CAT.p. CAT.s was prepared without MC. Two samples were prepared with hydrothermal treatment.

The procedure for preparation of two sols was as follows

Titanium tetra iso propoxide was slowly added to

TABLE 1 : Properties of TiO₂ nano particles prepared under various conditions

Sample No.	Surface area(m ² g ⁻¹)	Crystallite size ^a (nm)	Crystallinity ^b (%)	Mean particle size ^c (nm)
CAT.p	180	7.1	89	128
CAT.s	165	7.4	77	15

^aCalculated from XRD data using Eq.(2), ^bCalculated from XRD data using Eq.(3a) for anatase phase, ^cCalculated from Zeta sizer

alcohol and then, the mixture of titanium tetra iso propoxide & alcohol was placed in the oil-bath. The solution was then added to the acidic solution and refluxed under vigorous stirring (800 rpm) at 90°C for 8 h. In the case of using MC, in separate container, methylcellulose solution (2wt% in distilled water) was prepared and then these two solutions (Titania sol and MC solution) were mixed and stirred for 1 hour at 90°C. Two samples were dried at room temperature and were finally calcined at 350C with a ramp rate of 2°C min⁻¹ for 1 hour.

The photocatalytic activity of the samples was estimated by decomposition of 20 ppm Methylene blue by using 50 ppm of photocatalyst. The photoreactor consisted of cylindrical glass reactor that a light source from 400 w high-pressure mercury lamp located in front of vessel. A magnetic stirrer was used to produce homogeneous reaction mixture, before and during illumination. Degradation was monitored by taking aliquots at different time intervals. The UV-vis absorption spectra of the samples were recorded with a UV-vis spectrophotometer (UV/vis-Beckman Du series-500) after and before illumination at different times at $\lambda_{max} = 665\text{nm}$. The degradation of Methylene blue was calculated by using the following formula:

$$\% \text{Degradation} = [(C_0 - C)/C_0] \times 100 \quad (4)$$

Where C₀ and C are initial concentration and the reaction concentration of MB, respectively. Photocatalytic reactions are considered as pseudo-first-order reaction^[11,12]. So, for kinetic study we can use the following expression:

$$\text{Ln}(C_0/C) = Kt \quad (5)$$

Where K is the apparent reaction rate constant and C₀ and C are initial concentration and the reaction concentration of MB, respectively^[13-15].

The particle sizes of prepared sols were analyzed using a Malvern particle sizer after 24h the preparation. The samples had to be diluted in water and they were

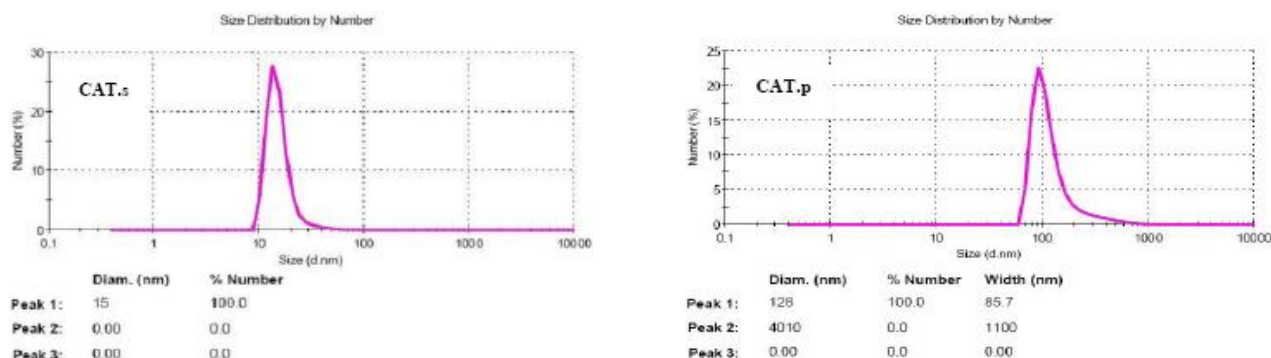


Figure 2 : Mean particle size for two samples

also sonicated for 2 min.

X-Ray diffraction measurements were made with a Philips PW 1840 automated X-ray diffractometer using graphite monochromatized $\text{CuK}\alpha$ radiation in step-by-step mode. Preferred orientations were determined by comparing their relative intensities with those reported in the JCPDS cards^[16]. The mean crystallite size D was determined from the broadening β of the most intense line, for each polymorph, in the X-ray diffraction pattern, based on the Scherer equation:

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (2)$$

Where λ is the radiation wavelength (0.15406 nm for copper lamp), $K = 0.89$ and θ the Bragg angle^[17,18].

The phase content of the samples can be calculated from the integrated intensities of anatase (101), rutile (110) and brookite (121) peaks. If a sample contains anatase, rutile and brookite, similar relations can be derived^[19];

$$W_A = \frac{K_A A_A}{K_A A_A + A_R + K_B A_B} \quad (3a)$$

$$W_R = \frac{A_R}{K_A A_A + A_R + K_B A_B} \quad (3b)$$

$$W_B = \frac{K_B A_B}{K_A A_A + A_R + K_B A_B} \quad (3c)$$

Where W_A , W_B and W_R represent the mass fractions of anatase, brookite and rutile, respectively. A_A , A_B , A_R , is the integrated intensity of the anatase (101), brookite (121) and rutile (110) peaks, and K_A and K_B are two coefficients and their values are 0.886 and 2.721, respectively. With Eq. (3), the phase contents in any TiO_2 samples can be calculated^[19].

BET surface of the samples was performed through

nitrogen adsorption at -196°C using a Quantasorb BET surface area analyzer.

RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of TiO_2 particles for all prepared samples along with the XRD of P25 sample. When the width was broader, the crystallites exhibited smaller size. In other words, sharper XRD peak indicates a larger particle size or more well-ordered crystallites as it was reported earlier by other research group^[20].

As shown in TABLE 1, for two samples; CAT.p has a high percent of anatase phase and specific surface area which was more than this amount in CAT.s. TABLE 1 shows the comparison of the mean particle of two samples. Figure 2 shows the mean particle size of CAT.s which is less than that of CAT.p. The difference in the mean particle size between powders prepared with HNO_3 and CH_3COOH as stabilizers can be explained by the influence of the peptization step on the dispersion of primary particles in the sol^[17]. For the powders prepared under excess HNO_3 , protons (H^+) from HNO_3 are adsorbed on the surface of the primary particles. As most particles carry a positive charge, they repel each other to form a stable sol with a minimum degree of aggregation; thus Titania sol that was prepared as CAT.s was more stable than that of CAT.p.

The specific surface area and crystallite size of P25 sample were determined to be about $50(\text{m}^2\text{g}^{-1})$ and $30(\text{nm})$, respectively. The degradation results of MB after 60 min for two samples are presented in figure 3, which shows that photocatalytic activity for CAT.p was more than that of CAT.s. The results showed that the addition of acid acetic and presence

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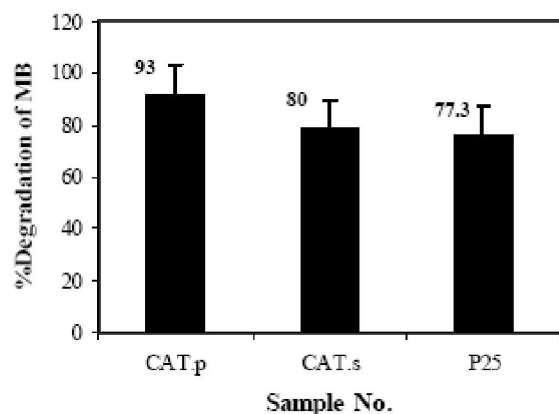


Figure 3 : Degradation of MB after 60 min for prepared samples and P25

of MC caused phase separation in the precursor solution and photocatalytic activity was increased. The increasing surface area of TiO₂ powder enhanced the photoactivity of the catalyst by increasing the percent of anatase phase. It seems to us When CH₃COOH was used as a stabilizer, the phase transformation of the TiO₂ powders from amorphous to anatase was enhanced then this in turn, enhanced the photoactivity of catalyst; because it is generally accepted that anatase is more active than two other phases of TiO₂. Therefore, by introducing MC, which results in a porous body after calcination, one could enhance percent of degradation of MB.

The photoactivity of P25, CAT.p and CAT.s samples are shown in figure 4, in terms of MB removal rate as a function of pollutant concentration and catalyst material. The oxidation of MB followed first order kinetics for all photocatalyst samples. It could be seen that CAT.p, showed high photocatalytic activity with a rate constant of $4.33 \times 10^{-2} \text{ min}^{-1}$. Its photocatalytic activity was higher than that of P25 (2.19×10^{-2}), which is well known to give a high photocatalytic activity^[21]. Figure 4 demonstrates that the rate constant for the TiO₂ powders with MC is greater than that of the TiO₂ powders without MC, showing a considerably higher efficiency as photocatalyst. It is possible to assume that the increased activity of the MC can cause more photodegradation of Methylene Blue dye, due to its greater porosity, nanostructure. Higher photoefficiency might be due to the greater accessible surface area in the system. According to TABLE 1, figure 3 and figure 4, the photoefficiency of CAT.p was highest among the samples, mainly because of its high surface area ($180 \text{ m}^2/$

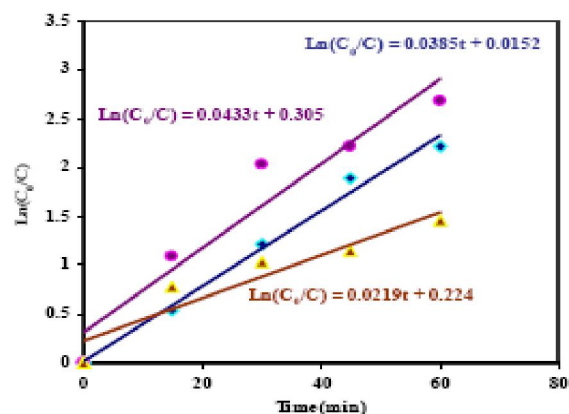


Figure 4 : Dependence of the apparent rate constant (k, min^{-1}) for CAT.p, CAT.s and P25

g) and the polymorphous structure of these materials. It has been reported that a combination of different polymorphs of TiO₂, including the amorphous phase, in some cases, exhibits a relatively higher photoefficiency than pure anatase^[22,23]. Larger particle size ($\sim 30 \text{ nm}$) of the powder, and the resulting lower surface area ($50 \text{ m}^2/\text{g}$), are considered as the main reasons for the low photoefficiency of P25 in comparison with CAT.p and CAT.s.

CONCLUSION

A nanoparticles with high photocatalytic efficiency were developed through a novel method using nanoparticles TiO₂, sol-gel process and organic dispersant. The photocatalyst is designated for used in degradation of a model dye pollutant in water. The photocatalytic activity of Titania powders prepared by hydrolysis of titanium tetra isopropoxide under ultrasonic irradiation is strongly influenced by the presence of methylcellulose (MC) as a dispersant and type of stabilizer. When CH₃COOH was used as a stabilizer caused phase separation in the precursor solution and photocatalytic activity was increased. When HNO₃ is used as a stabilizer, particles carry a positive charge and they repel each other to form a stable sol with a minimum degree of aggregation. Increasing positive charge (protons from H⁺) of sols enhanced the stability of sols. The photocatalytic activity of the TiO₂ powders prepared according to sample CAT.p was higher than that of CAT.s. When CH₃COOH and MC are used as a stabilizer and dispersant; respectively; the photocatalytic activity of the TiO₂ powders was enhanced.

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