

Novel immobilization of titanium dioxide (TiO₂) on the fluidizing carrier and its application to the degradation of azo-dye

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Abstract

A photocatalyst was prepared by attaching TiO₂ powder (diameter, 50 nm) in the sol state to fluidizing spherical ceramic carriers using a silicon binder. A high initial photocatalytic activity and strong attachment was obtained at a sintering temperature of 500 °C. An azo-dye (Orange-G) was used as the test contaminant to examine the photocatalytic effect of the new photocatalyst. The initial pseudo-first order degradation rate constant for Orange-G was 0.11 min⁻¹. However, the photocatalytic activity doubled when boric acid was added to the silicon binder at a B to Si ratio of 106.5%. When sodium ethoxide was added to the silicon binder at a sodium ion to Si ratio of 15.0%, as much as 80% of the initial photocatalytic activity was maintained after the photocatalyst had been agitated at 180 rpm for 300 min. Adding both boric acid at a B/Si ratio of 106.5% and sodium ethoxide at a Na/Si ratio of 15% increased the photocatalytic activity and stability by three and four times, respectively.

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1. Introduction

Organic pollutants are a major problem in cities, and regulations of organic pollutants have tightened. Therefore, many technologies for removing various pollutants have been developed. Conventional technologies have many disadvantages such as a low treatment speed and the requirement of expensive facilities. In particular, a general biological treatment with microorganisms cannot completely degrade all the pollutants. This suggests that conventional technology cannot comply with the more restrictive environment regulations, which is why advanced treatment technologies are needed [1–3].

Advanced technologies using OH radicals, which have more oxidative activity than commercial oxidants, can degrade var-

ious organic pollutants in water to carbon dioxide, water or innocuous hydrogen chloride. Ozonization, UV radiation and treatment with titanium dioxide are the frequently reported methods. However, ozonization generates a low level of OH radicals and reacts with the organic pollutants slowly. Moreover, since ozone gas is toxic, it can be a significant pollutant when discharged from a facility. In the UV system, the ferrous catalyst has a tendency to form scale deposits and an additional facility is required to remove the sludge. The catalyst also reacts with hydrogen peroxide to form additional hydroxide sludge.

A water treatment system using titanium dioxide (TiO₂) has been studied over the last 10 years and it is widely accepted as an alternative novel technology [1–3]. Photocatalytic oxidation, oxidizing pollutants by irradiating TiO₂ with UV, is non-toxic to humans and is generally considered to be a clean technology. Moreover, the degradation rates of organic pollutants using this method are much faster than with other methods and it can degrade most of the organic pollutants completely. It is

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inexpensive and produces a high efficiency of sterilization and removal of toxins, and the operation is quite stable. It also shows excellent performance in both liquid and gas phases and the commercialization of the technology has been attempted in many countries.

Although the reaction mechanism responsible for photocatalytic oxidation is unclear, the following mechanism is generally accepted. When TiO_2 is irradiated with light (UV with a wavelength smaller than 380 nm) with energy higher than the peculiar band gap of TiO_2 (approximately, 3.2 eV), electrons in the valence band are excited to the conduction band resulting in the production of holes (h^+) in the valence band. The electrons move to the TiO_2 surface. These holes and electrons are quite mobile; the electrons participate in reduction reactions and the holes participate in oxidation reactions. The released electrons react with the dissolved oxygen acting, which as an electron acceptor to form a high oxidative radical (superoxide radical, $\bullet\text{O}_2^-$), and the radical reacts with water molecules to form a high reactive peroxide radical ($\bullet\text{OOH}$). In addition, water molecule or dissolved peroxide ions either react with the hole on the surface of the titanium dioxide to form highly reactive peroxide radicals, or reacts with the organic compounds to be degraded. Therefore, both the released electrons and the holes generate peroxide radicals, which act as strong oxidizing agents to degrade organic compounds.

Both TiO_2 powder and immobilized TiO_2 on a carrier are being used in real wastewater treatment processes. Titanium dioxide powder has a high treatment efficiency [4,5] but is rarely recovered and recycled on account of its small particle size (ca. 0.1 μm) [3]. In addition, since the powder absorbs light, it is difficult to irradiate the catalyst uniformly on the photoreactor. Although the immobilization of TiO_2 is strongly recommended [6], the low stability of the immobilized photocatalyst due to the weak attachment of TiO_2 to a carrier has been a fatal problem. When applying titanium dioxide to wastewater treatment, organic pollutants are degraded either by irradiating the surface of reactor coated with TiO_2 with UV light [7] or by being contacted with a rotating disc coated with TiO_2 [8]. However, the feasibility of the two processes is poor because they have a low reaction efficiency, and that it is difficult to scale up the processes.

In this study, TiO_2 nano-scale particles were immobilized on fluidizing carriers to allow for easy recovery and continuous operation. The immobilized titanium dioxide on the carriers showed comparable removal efficiency with the most efficient powder type TiO_2 ever reported. In addition, a novel immobilization method, adding additives to the binder, was suggested in this study. The TiO_2 was strongly attached to the carriers and could be reused with a high photocatalytic activity and operational stability.

2. Materials and methods

2.1. Preparation of the photocatalyst

Anatase, which has the highest photocatalytic activity of the TiO_2 phases, was used in this study [9]. Nano-sized (circa.,

Table 1

The physical and chemical properties of the porous ceramic carrier

Technical details	Physical properties
Form	Free flowing white powder
Average particle size	500 μm
Colour	White
Relative density	0.6–0.8 g/ml
Bulk density	0.4 g/ml
Shell thickness	10% of diameter
Melting point	1600–1800 °C
Compressive strength	45 MPa
Chemical properties	Typical (by weight)
Silica SiO_2	55–60%
Alumina Al_2O_3	36–40%
Iron oxide Fe_2O_3	0.4–0.5%

40 nm in diameter) TiO_2 (anatase-type P-25) suspended in methanol (Enpion) was chosen because a smaller particle has a wider surface area and higher photocatalytic activity [10]. A spherical porous organic ceramic (nanosolution) in the range of 300–500 μm in diameter was used as the carrier for immobilization [3] and its characteristics are shown in Table 1. The density of the carrier was lower than that of water. Because TiO_2 particles have a high melting temperature, heat treatment at temperatures up to 800 °C are needed to attach the TiO_2 particles on ceramic support. This high temperature usually results in an anatase to rutile phase transition [10]. Since a binder can facilitate the attachment of TiO_2 to the supporting media even at relatively low temperatures, an alumina silica sol ($\text{SiO}_2/\text{Al}_2\text{O}_3$ sol, 10%, nanosolution) was used to bind the TiO_2 to the carrier. Boric acid (H_3BO_3 , Aldrich) and/or sodium ethoxide ($\text{C}_2\text{H}_5\text{ONa}$, Aldrich) at various concentrations was added to the binder to increase the stability of the photocatalyst, immobilized TiO_2 on the carrier. The additives affected the binder material only. However, sodium diffused to TiO_2 has a detrimental effect because it can act as photoelectron consumer [11], and may alter the crystal structure of anatase. The immobilization procedure used in this study is as follows. First, 20 g of 15% TiO_2 in a sol and 1 g of an alumina silica sol as a binder were mixed with 25 g of methanol. Various concentrations of boric acid and/or sodium ethoxide were added to the solution. The solution was agitated at 500 rpm for 15 min to be dispersed homogeneously. Twenty grams of the porous ceramic carrier was then placed into the solution. The solution was agitated at 250 rpm for 1 h in a shaking mixer to coat the carrier completely. After coating, the carrier was put in a hot-wind dryer at 100 °C to remove the solvent and water. As a final step, the porous ceramic carrier was heated at 400 °C for 4 h to bind the TiO_2 strongly to the carrier particles.

2.2. Experimental apparatus

Fig. 1 and Table 2 shows a schematic of the homemade experimental apparatus and its specifications, respectively. The working volume of the cylindrical photoreactor was 1 L. A black light blue UV lamp (Sankyo Denki, Japan) installed in an immersion tube made from quartz with a transmission over 95% was

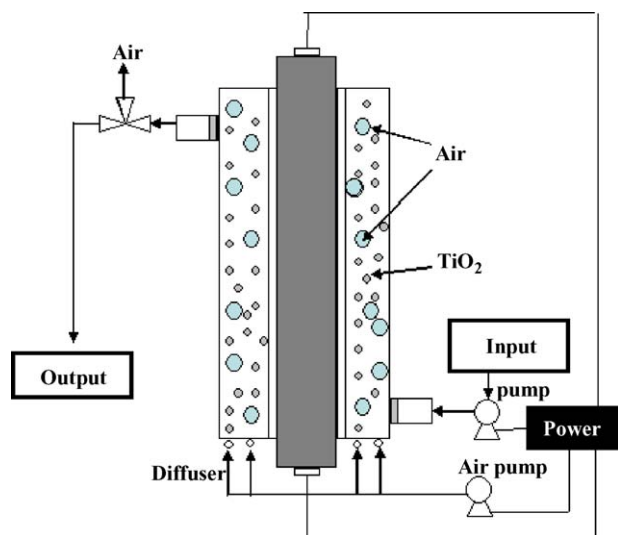


Fig. 1. Schematic diagram of the photocatalytic reactor.

placed in the middle of the reactor. The photocatalyst was fluidized in the reactor in order to produce uniform UV irradiation. An air diffuser was installed at the bottom of the reactor to supply oxygen at 1 L/min, which reacted with the electrons released from the TiO₂.

2.3. Experimental procedure

Orange-G (chemical structure shown in Fig. 2) was chosen as a model pollutant because it is a well-known azo-containing dye and is hazardous to humans and the environment [12,13]. A 20 mg/L of Orange-G (Aldrich) was used as the synthetic wastewater in this study. Batch experiments with the photoreactor were performed to investigate the effect of boric acid and/or sodium ethoxide on the photocatalytic activity. The data was measured three times and averaged values are shown in the tables and figures. The concentration of the dye was measured using a spectrophotometer (UV-160A, Shimadzu, Japan) at 480 nm where Orange-G has the highest absorbance. Since the degradation of azo-dyes by a photocatalyst was reported to follow pseudo-first order kinetics [3,13] and the degradation profile in this study can be fitted with a first-order degradation model, as

Table 2
Specification of the photocatalytic reactor

Items	Value
Reactor length (cm)	50
Reactor diameter (cm)	5.5
Reactor volume (cm ³)	800
Quartz diameter (cm)	4
UV lamp	
Length (cm)	58
Diameter (cm)	3
Wattage (W)	20
Wave length (nm)	340
Air flow rate (L/min)	1

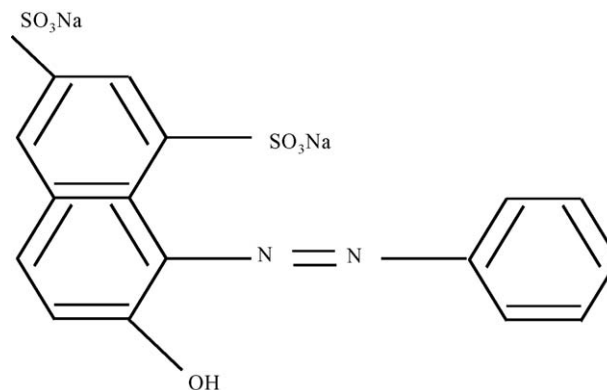


Fig. 2. Chemical structure of Orange-G.

shown in Fig. 3, the first-order degradation rate constant, which was defined as the photocatalytic activity, K , was determined for the various photocatalysts. Throughout the batch experiments, a fixed level of the photocatalyst (20 g/L) was maintained in the reactor. Experiments investigating the immobilization stability of the TiO₂ particles were also performed. The stability was defined as the ratio of photocatalytic activity of a photocatalyst after agitation at 180 rpm for 400 min to that before agitation. In order to determine the photocatalytic activity after agitation, 20 g of the photocatalyst was taken from the reactor after 1 h of operation and mixed with water to make a total volume of 100 mL in a 500 mL beaker. A shear force was applied to the photocatalyst by agitating at 180 rpm for 50 min with a shaking mixer. The photocatalyst was then placed in the reactor again for further degradation and the rate constant was calculated. Scanning electron microscopy (SEM, JEOL JSM-840A, USA) was used to observe the coating condition of TiO₂ on the carrier. X-ray diffraction (XRD, Rigaku D/MAX-IIIB, Japan) was used to determine the type of the TiO₂ on the surface of the carrier. The surface area, pore volume and average pore size of the immobilized TiO₂ on the ceramic supports were measured using a BET system (ASAP 2400, Micromeritics, USA).

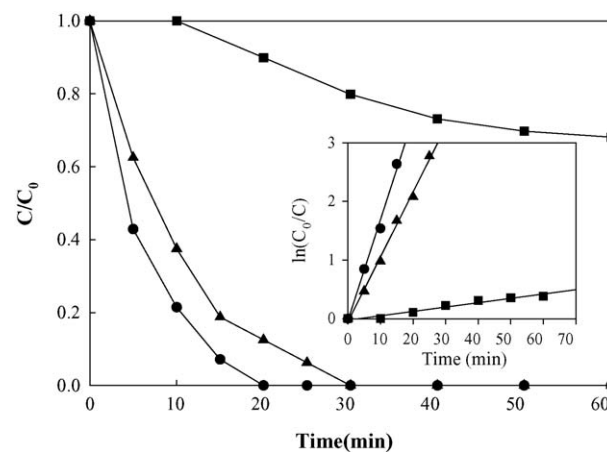


Fig. 3. The first-order degradation kinetics of Orange-G by ozone or TiO₂. C₀ represents initial Orange-G concentration. (●) Suspended TiO₂, (▲) immobilized TiO₂, (■) ozone.

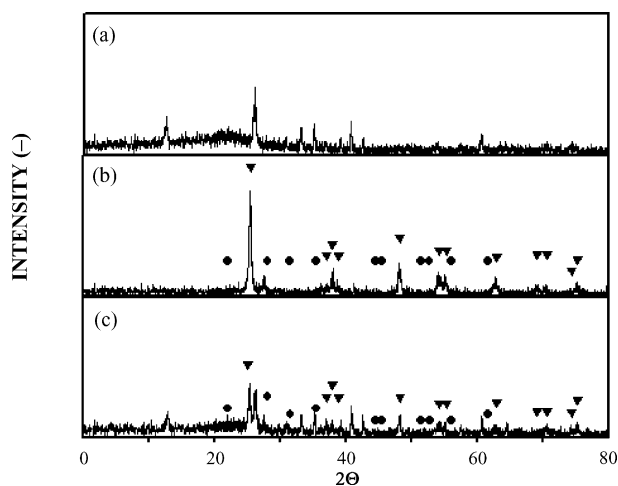


Fig. 4. XRD patterns for (a) carrier, (b) anatase-type P-25 TiO₂ powder, (c) immobilized TiO₂ on the carrier. (●) Rutile peak, (▼) anatase peak.

3. Results and discussion

3.1. Characterization of the photocatalyst

The most commonly used phases of TiO₂ are rutile and anatase. Anatase is more useful as a photocatalyst than rutile owing to its higher photoactivity [8]. The crystal structure of the TiO₂ on the photocatalyst, as determined by XRD (Fig. 4(c)), was compared with the XRD pattern of the original starting powder, as shown in Fig. 4(b). The structure shown in Fig. 4(c) was

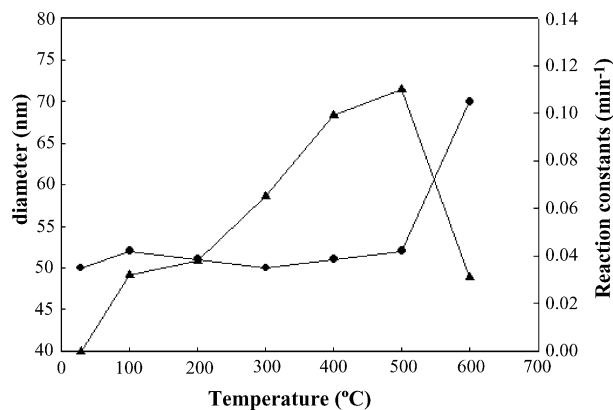


Fig. 6. Effect of the sintering temperature on the size of TiO₂ and the reaction rate constant. (●) Size of the TiO₂ granule, (▼) reaction rate constant.

mainly anatase. In addition, anatase did not transform to rutile regardless of the sintering temperatures used. Fig. 5 shows that the size of the TiO₂ particles at different sintering temperatures ranged from 15 to 30 nm. The surface area, pore volume and pore average size of the TiO₂ immobilized on the ceramic support was 5.542 ± 0.04 m²/g, 0.0240 cm³/g and 173.4 Å, respectively. The effect of size on the reaction rate constant, *K*, was examined by measuring the Orange-G concentration in the effluent, as shown in Fig. 6. The size did not change up to 500 °C while it suddenly increased at 600 °C because the TiO₂ coagulated noticeably [14]. The coagulation decreased the surface area of the TiO₂, which lowered the activity of the photocatalyst. The reaction between an organic pollutant and a photocatalyst is

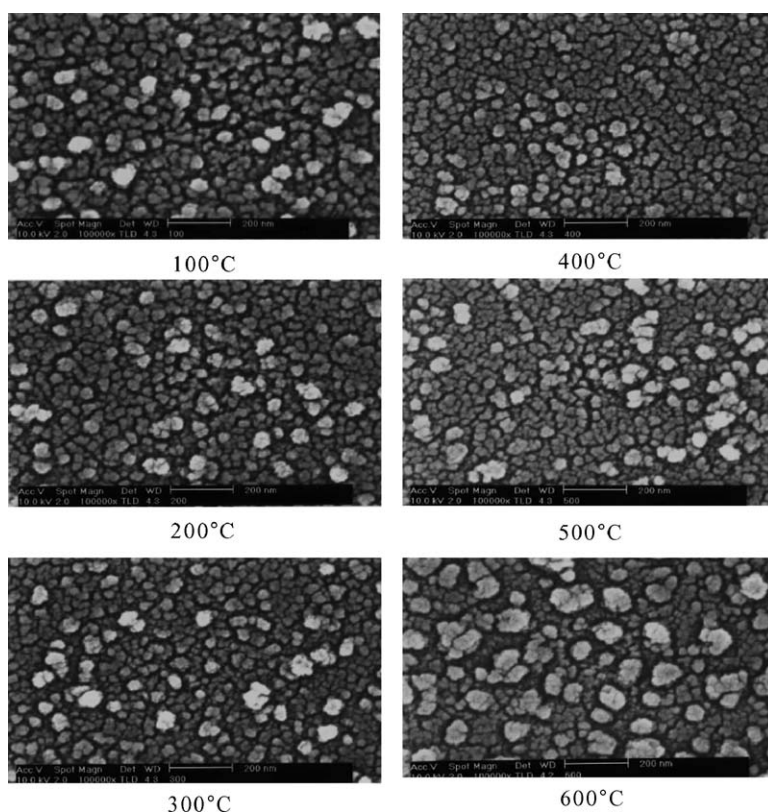


Fig. 5. The effect of the sintering temperature on the size of the immobilized TiO₂. The scale bars in the figures represent 200 nm.

known to occur on the TiO₂ surface. If the UV intensity and the concentration of the target pollutant is constant, the rate of photocatalytic degradation will depend on how fast the targeting pollutant is adsorbed and how wide the UV is irradiated on the surface. These parameters are directly related to the surface area of TiO₂ and a smaller specific surface can lead to a lower photocatalytic activity. The deactivation of TiO₂ might be another cause of the decrease in the photocatalytic activity. However, the inactivation of TiO₂ may be negligible with a relatively short experiment time [13]. Interestingly, after coating the TiO₂ on the carriers, the K value (pseudo-first order degradation rate constant, min⁻¹) increased up to 500 °C while there was no decrease in the specific surface area. This is believed to be due to the higher sintering temperature, which led to a stronger attachment of TiO₂ onto the surface of the carriers, which increased the stability of immobilization. Therefore, the sintering temperature used to prepare the photocatalyst was fixed to 500 °C in further experiments.

3.2. The effect of additives on the attachment of TiO₂ on the carrier

It is generally accepted that the addition of boric acid and sodium ethoxide has a positive effect on the glass-making process [15]. The addition of boric acid lowers the thermal expansion coefficient of Si [15]. Therefore, boric acid was added to the mixture of TiO₂, binder and methanol to prevent the separation of TiO₂ from the carriers as a result of thermal expansion and contraction during the thermal treatment. The photocatalysts were prepared with various B to Si molar ratios in the binder, 106.5, 319.5 and 852.2%, and their photocatalytic activities were compared with the one coated with only 1 g of the pure binder without boric acid, as shown in Fig. 7. The effect of boric acid on the attachment of TiO₂ to the carriers was examined by measuring the photocatalytic activity after the photocatalyst had been agitated in a shaking mixer at 180 rpm for 400 min. In addition, the Ti to Si ratio on the surface of the photocatalyst after degradation was analyzed by energy dispersive X-ray spectroscopy (EDX), which was attached to the SEM. The K -value after 400 min of agitation was increased until the B/Si ratio

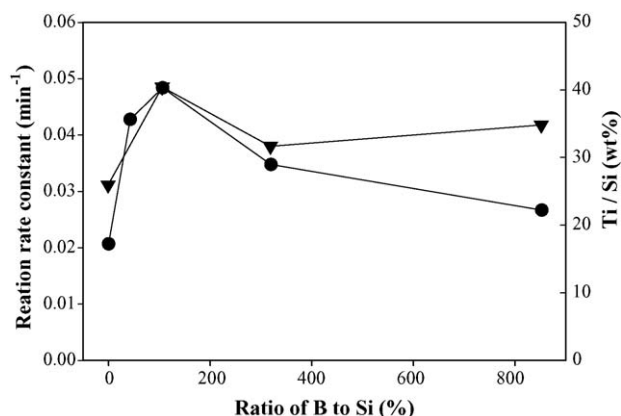


Fig. 7. The effect of boric acid on the photocatalytic activity. (●) Reaction rate constant, (▼) weight ratio of Ti to Si on the surface of photocatalyst.

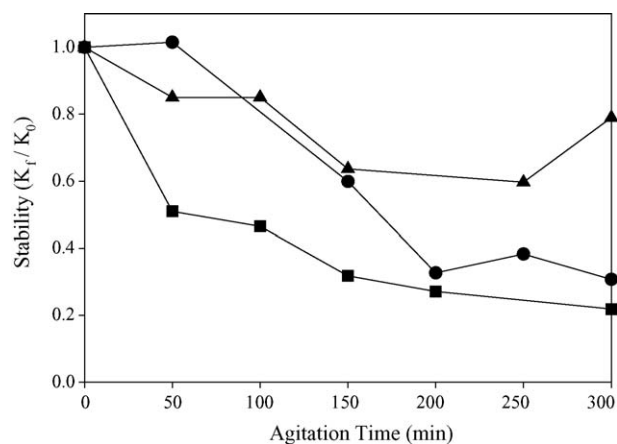


Fig. 8. The effect of sodium ethoxide on the stability of the photocatalyst as a function of the agitation time. (■) 0% Na/Si, (●) 5% Na/Si, (▲) 15% Na/Si.

reached 106.5%. The Ti to Si ratio on the surface of the photocatalyst showed a similar trend. Therefore, it is believed that the addition of boric acid strengthened the attachment of active TiO₂ on the surface of the carriers, which increased the photocatalytic activity. However, the photocatalytic activity decreased when the B to Si ratio was above 106.5%. This suggests that the highest photocatalytic activity could be obtained at B to Si ratio of 106.5%. The value is consistent with the theoretical concentration reported in the conventional glass-making industry [15].

Sodium ethoxide was also used as an additive in the glass-making process. The addition of sodium ethoxide is known to decrease the melting point of silicon dioxide (SiO₂) by breaking the Si–O bonds [15]. Although the melting temperature of pure silica is as high as 1500–1700 °C, network breakers such as sodium and potassium can dramatically decrease the melting point [16]. The added sodium ethoxide is believed to liberate sodium ions, which act as a network breaker. Therefore, it was expected that the addition of sodium ethoxide would lower the melting point of the binder, resulting in the strong attachment to the carrier.

Sodium ethoxide was added to the binder at a sodium ion to Si ratio of 5 and 15%. The activities of the photocatalyst harboring sodium ethoxide were compared with that without sodium ethoxide, as shown in Fig. 8. The azo-dye degradation

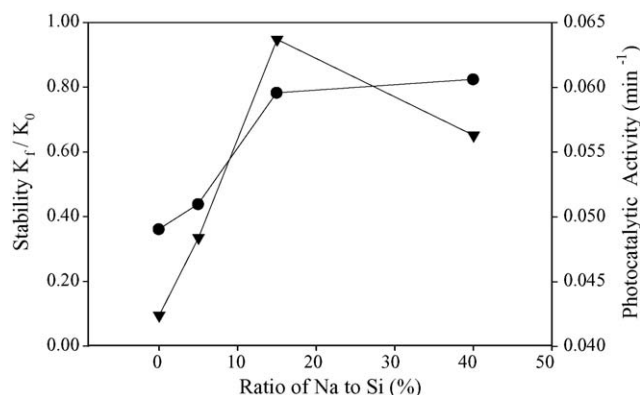


Fig. 9. Effect of sodium ethoxide on the activity and stability of photocatalyst harboring boric acid with 106.5 B/Si ratio. (●) Stability, (▼) activity.

Table 3

The effect of adding boric acid and sodium ethoxide on the activity and stability of the photocatalyst

	Binder composition	Initial activity (K_0 , min^{-1})	Stability (K_f/K_0 , %)	Weight ratio of Ti to Si on the surface of photocatalyst (–)
Control method	Only 1 g alumina silica	0.021	18.12	25.92
Novel method	1 g alumina silica with boric acid (106.5% B/Si ratio) and sodium ethoxide (15% Na/Si ratio)	0.064	78.25	33.67

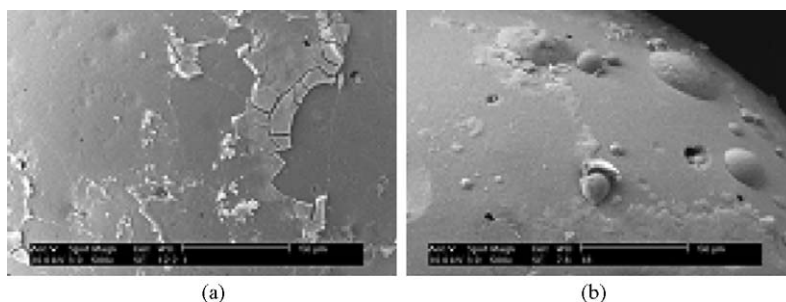


Fig. 10. The addition effect of boric acid and sodium ethoxide on the coating condition of TiO_2 on the carrier (a) only 1 g binder; (b) 1 g binder with boric acid (106.5% B/Si ratio) and sodium ethoxide (15% Na/Si ratio).

experiments by the photocatalyst were carried out repeatedly after agitating the photocatalyst with the shaking mixer. The effects of the agitation time on the stability of the photocatalyst were investigated. The results are shown in Fig. 8. K_0 and K_f represent the photocatalytic activity before and after agitation, respectively. The initial photocatalytic activities, K_0 , were 0.1142, 0.0528 and 0.0673 min^{-1} for the photocatalyst containing 0, 5 and 10% of Na/Si ratio, respectively. The results showed that the addition of sodium ethoxide decreased photocatalytic activity by approximately 50%. However, when the Na^+ to Si ratio was 15%, the photocatalyst maintained as much as 80% of the initial activity after 300 min of agitation. An increase in stability was observed when the agitation time was extended from 250 to 300 min. The increase in stability at an agitation time of 300 min might be due to the breakage of the ceramic carriers, which can increase the surface area resulting in a slight increase in stability. However, it is believed that this is a temporal phenomenon and its stability will decrease again.

It should be noted that the boric acid increased the initial activity but decreased the stability of the photocatalyst while sodium ethoxide increased the stability but decreased the initial activity. Therefore, the combination of sodium ethoxide and boric acid was expected to improve the quality of photocatalyst noticeably by lowering the thermal expansion coefficient of the binder and enhancing the stability by lowering the melting point. With a B/Si ratio of 106.5% at which the highest photocatalytic activity was obtained, sodium ethoxide was added to the photocatalyst at a 5, 15 or 40% of Na/Si ratio in the binder. Their activities are shown in Fig. 9. Both the stability and activity of photocatalyst was noticeably increased as the sodium ethoxide concentration was increased to 15%. The activity was highest at a Na/Si ratio of 15% but decreased above this concentration possibly due to the effect of sodium ions, which can be integrated into the TiO_2 lattice by diffusion. This integration can deteriorate the catalytic activity. The stability was almost constant above a

Na/Si ratio of 15%. Therefore, the highest activity and stability of the photocatalyst is expected at a B/Si ratio of 106.5% and a Na/Si ratio of 15%. The novel photocatalyst prepared using the suggested optimal conditions showed a three times higher photocatalytic activity after agitation (K_f) than the photocatalyst prepared without the two additives, and the stability (K_f/K_0) was more than four times higher, as shown in Table 3.

SEM revealed a crack on the surface of the photocatalyst after 400 min of agitation at 180 rpm in the shaking mixer. As shown in Fig. 10, many cracks were observed on the surface of the photocatalyst without additives while only a few were observed on the novel photocatalyst. When a crack on the surface progresses, small collisions between the photocatalysts might separate the TiO_2 from the carriers, which would mean that the photocatalyst would have to be replaced. Therefore, a novel photocatalyst showing a high activity and stability can reduce the fixed and operation cost of wastewater treatment. The principles suggested in this study can be applied to other immobilization strategies used in the chemical industry and in various environmental processes.

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