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Effects of zinc phosphate binder on the immobilization properties of photocatalytic ZnO nanopowders synthesized by a solution combustion method

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Three different inorganic materials; commercial sodiumsilicate, commercial potassiumsilicate and zinc phosphate synthesized, were tried as a binder to immobilize the photocatalyst nanopowders. These binders were used to immobilize ZnO and TiO_2 nanopowders on the glass substrates. The ZnO nanopowder was synthesized by the solution combustion method (SCM) which was developed by the authors. After immobilization, the scratch and ultrasonic vibration test were carried out to examine the adhesion properties of the binders. The zinc phosphate exhibited the best overall adhesion characteristics. It immobilized the SCM ZnO nanopowder twice more than other combinations of the binders and photocatalysts. Furthermore, it showed the highest photocatalytic efficiency. The efficiency reached to about 80% of the powder type photocatalytic reaction. These excellent results seem to be attributed to an interfacial binding layer between the SCM ZnO powders and the zinc phosphate binder.

Keywords: Photocatalytic nanopowder, Immobilization, Inorganic binder, Zinc phosphate.

Introduction

As an environmental pollution becomes a serious problem, tighter pollution control is required. Photocatalysis is one of most viable choices since it can remove pollutants to even ppb (part per billion) level. Especially, for water-treatment, the photocatalyst powders are usually suspended in water. The use of suspended photocatalyst powders is efficient due to the large surface area available for photocatalytic reaction. When the photocatalyst powders are completely mixed, there is no segregation of phases, and when the photocatalyst powders are small enough (such as nanopowders), their entire external surface can be irradiated during the reaction time. However, in the large-scale application, the use of suspended photocatalyst powders requires the separation of the photocatalyst powders from the treated wastewater prior to the discharge which can be a time-consuming and expensive process. This problem can be avoided by the immobilization of photocatalyst over suitable supports. Thus, the immobilization of photocatalyst becomes important in wastewater treatment area [1-6].

There are two approaches to immobilize the photocatalysts; one is a binding method and the others is a direct formation of photocatalyst films. Since the direct formation method usually results in poorer crystalline quality of photocatalyst materials compared with the binding method, the binding method is more desirable to keep the crystalline properties of photocatalysts. The selection of proper binding materials is the most important factor for the binding method. Even though the organic binders have superior adhesion properties, they could be decomposed by the photocatalytic reaction. On the contrary, the inorganic binders are not decomposed, but they have poor adhesion properties. This is a kind of dilemma. Ideally, the binders should be inorganic materials with good adhesion properties. In this paper, several inorganic binding materials were studied systematically to obtain the best inorganic binders with good adhesion properties.

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Experimental

ZnO nanopowders were prepared by the solution-combustion method. The zinc hydroxide ($Zn(OH)_2$, Junsei Chemicals Ltd. Japan) and the fuel, glycine (H_2NCH_2COOH, Yakuri Pure Chemicals Co. Ltd. Japan), were used as precursor materials. The zinc hydroxide powders were dissolved in nitric acid (Aldrich, USA) in order to obtain a zinc nitrate solution which acts as an oxidant. Glycine was added to the zinc nitrate solution in the proportion of 0.8 (fuel/oxidant). The solution mixture was then heated on a hot plate with stirring. As the water was evaporated, the solution became viscous with a large number of air bubbles. At this point, the oxidant reacted with the intense heat generated by the fuel. This intense heat

resulted in the instantaneous high pressure, leading to explosion. This high temperature and pressure helped to form the ZnO nanopowders. A large number of explosions occurred simultaneously, with each explosion occurring in very small space. The explosive power was similar to popping corn. Due to the explosive nature of the reaction the experiment was performed inside a stainless steel chamber. The resulting ZnO nanopowders were collected and annealed at 400 °C for 1 hour to remove adsorbed gases and other organic species.

The synthesized SCM ZnO nanopowder and commercial TiO_2 (P25, Degussa) were immobilized by various inorganic binders. Sodiumsilicate (Shinheung silicate), potassiumsilicate (Shinheung silicate) and zinc phosphate were used as the inorganic binders. The sodiumsilicate and potassiumsilicate were purchased. The zinc phosphate was synthesized by the reaction of commercial ZnO powder (Junsei) and phosphoric acid. The binders were screen-printed on the glass substrates, and their average thickness was about 30 μm. Then, the photocatalyst powders were spray-coated on the binder surface. The spray solution consists of water (80 wt%) and photocatalyst powder (20 wt%).

After immobilization, scratch test (CSEM Revetest, CSEM Instrument, Spectral range: 380-1050 nm) and ultrasonic vibration test were carried out to examine the adhesion properties of the binders. X-ray diffraction analysis (XRD, Shimadzu D-1, Japan) of the coated photocatalyst nanopowders was also performed to confirm the relative amount of immobilized photocatalyst nanopowders. Scanning electron microscope (SEM, Jeol ABT DX-130S, Japan) was used to examine the immobilized photocatalyst surfaces. Photocatalytic activity of the immobilized photocatalyst nanopowders was then confirmed by removing the Ag ions from the waste photo-development solution that contained Ag ions. The removal rate of Ag ions was measured as photocatalytic efficiency. Here water was used as a solvent for waste photo-development solution. The UV lamp (6 W, maximum energy at 365 nm) was used as the light source for the photocatalytic reaction. The concentration of remained Ag ion was measured by an atomic absorption spectrophotometer (Model 5100 PC, Perkin-Elmer).

Results and discussion

Scratch test was performed to evaluate the adhesion properties of binders for the immobilization of photocatalyst powders. Although the scratch test does not provide a direct measure of adhesion, it gives the value of a critical load which is representative of the coating adhesion. The results of the scratch test were summarized in Table 1. There are two failure types; one is cohesive type and the other one is adhesive type. The cohesive type failure occurs between the photocatalyst powders and the binder, indicating the displacement of the photocatalyst powders from the binder. The evidence

Table 1. Results of scratch test for various inorganic binders, the unit of CF (force for cohesive type failure) and AF (force for adhesive type failure) is kg (vertical force or normal force).

Binders	CF		AF	
	SCM ZnO	TiO_2(P-25)	SCM ZnO	TiO_2 (P-25)
Sodiumsilicate	0.15	0.25	1.80	0.20
Potassiumsilicate	0.21	0.15	0.35	0.60
Zinc phosphate	0.65	0.37	7.50	1.70

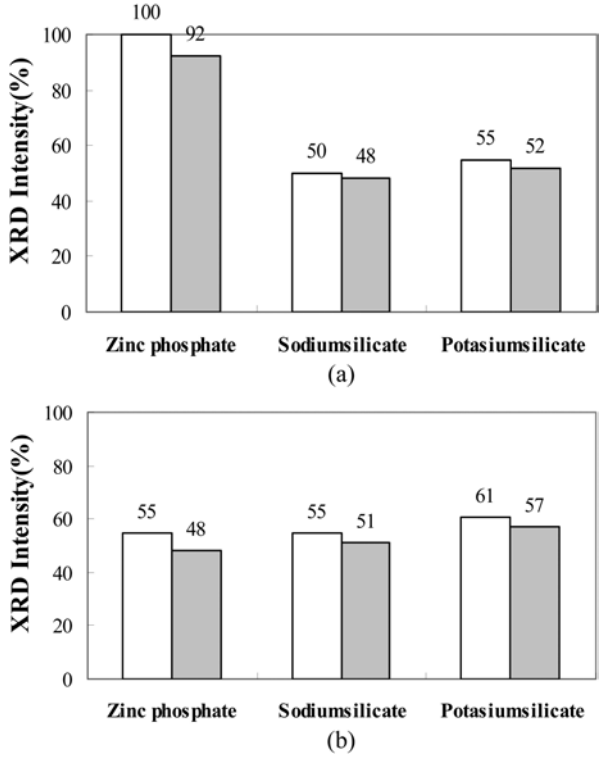

Fig. 1. Result of ultrasonic test: XRD intensity from (a) SCM ZnO nanopowder and (b) TiO_2 (P-25, Degussa) nanopowder immobilized by zinc phosphate, sodiumsilicate and potassiumsilicate before (white column) and after (grey column) ultrasonic vibration of 10 minutes.

of cohesive type failure was detected by the first change in slope from the friction coefficient vs. normal force plot. On the other hand, the adhesive type failure occurs between the substrate and the binder. The onset of this failure was detected by acoustic emission. Cracking phenomena in materials are associated with the generation of high frequency vibrations in both the binder and substrate, and each failure mode has a characteristic acoustic emission signal.

The critical loads for adhesive failure (AF) in Table 1 indicate the failure of the binders. The zinc phosphate which immobilized the SCM ZnO nanopowder showed the highest cohesive force with the SCM ZnO nanopowder which is 1.7 ~ 4.3 times higher than others, and highest adhesive force with the glass substrate which is 4.1 ~ 37.5 times higher than others. The zinc phosphate represented abnormally high cohesive and adhesive forces. This could be due to the chemical

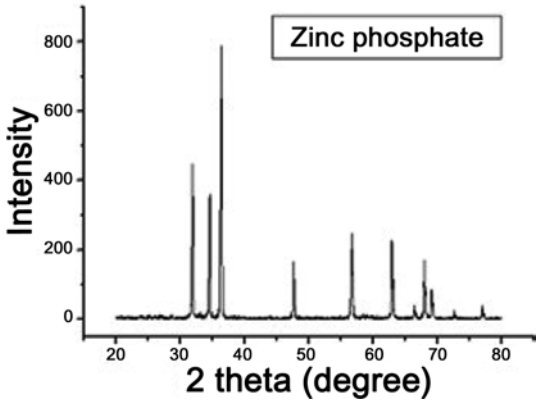

Fig. 2. XRD pattern of SCM ZnO nanopowder immobilized by zinc phosphate. (after ultrasonic vibration of 10 minutes)

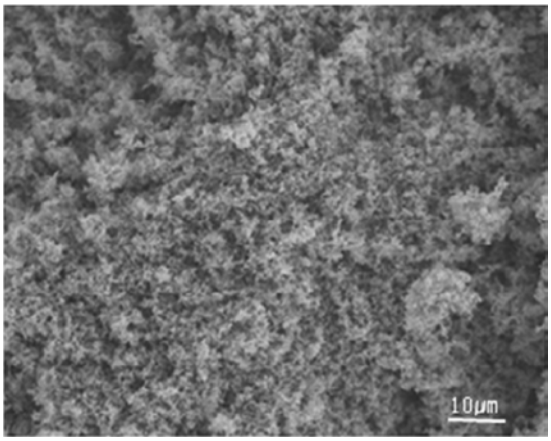

Fig. 3. SEM micrograph showing the surface of the immobilized SCM ZnO nanopowder after ultrasonic vibration of 10 minutes.

reaction rather than physical binding between the zinc phosphate and the SCM ZnO nanopowder. The water and the photocatalyst powders were mixed for the spray-coating. During spray-coating, the water dissolved phosphoric acid reacted with the SCM ZnO nanopowder to form an interface binding layer. Zn from the SCM ZnO particle surface seemed to be reacted with the remained phosphoric acid during binder forming reaction (some part of phosphoric acid is still remained if the binder forming reaction is not completed). This resulted in an interface binding layer (another zinc phosphate layer).

For the commercial TiO_2 nanopowder, cohesive force was not much different based on the binders, but adhesive force showed a little difference with binders (The zinc phosphate showed 2.8 ~ 8.5 times higher value than other binders). However, from the viewpoint of application, the absolute value of the adhesive force is not so high compared to the case of SCM ZnO nanopowder.

To investigate the mechanical stability of binders, the ultrasonic vibration was applied to the immobilized photocatalyst powders in water for 10 minutes. Fig. 1 shows the XRD intensity change of immobilized photocatalyst powders after the ultrasonic vibration.

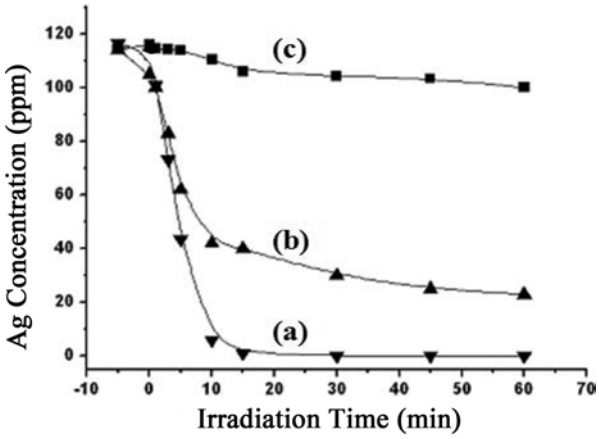

Fig. 4. Photocatalytic removal of Ag ions from wastewater with SCM ZnO nanopowder immobilized with (a) no binder (powder type), (b) zinc phosphate and (c) potassiumsilicate.

The intensity was modulated based on the white column intensity (before ultrasonic vibration) of the SCM ZnO nanopowder using zinc phosphate (100%). The intensity depends on the amount of immobilized photocatalyst powders. The SCM ZnO nanopowder immobilized by the zinc phosphate showed highest XRD intensity before and after the ultrasonic vibration. It made 92% of SCM ZnO nanopowder remained after the ultrasonic vibration. Compared to this case, sodiumsilicate and potassiumsilicate immobilized just half of the photocatalyst powders. However, most of the immobilized photocatalyst powders were still remained after the ultrasonic vibration.

Fig. 2 shows the XRD intensity of the SCM ZnO nanopowder immobilized by the zinc phosphate after the ultrasonic vibration. It still shows very sharp peaks and high intensity. Fig. 3 is an SEM micrograph representing the surface of the immobilized SCM ZnO nanopowder after ultrasonic vibration. The surface is completely covered by the photocatalyst powders. The immobilized photocatalyst surface is rough so that it provides more surface area for photocatalytic reaction.

Fig. 4 represents the variation of Ag ion concentration with a function of UV irradiation time. The zinc phosphate and potassiumsilicate were selected to investigate photocatalytic efficiency since they immobilized the largest and second largest amount of photocatalyst, respectively. The SCM ZnO nanopowder without binder was also tested for the reference. The SCM ZnO nanopowder immobilized by the zinc phosphate showed about 6 times higher photocatalytic efficiency than that by the potassiumsilicate. Furthermore, its Ag ion removal rate reached to about 80% of powder type photocatalyst.

Conclusions

The ZnO nanopowder was synthesized by the solution combustion method (SCM) which was developed by the authors. This SCM ZnO nanopowder

was immobilized by three inorganic binders such as commercial sodiumsilicate, commercial potassiumsilicate and synthesized zinc phosphate. The zinc phosphate showed best overall adhesion properties such as high cohesive force with the SCM ZnO nanopowder and high adhesive force with the glass substrate. The zinc phosphate also immobilized the SCM ZnO nanopowder twice more than other combinations of the binders and photocatalysts. It made 92% of SCM ZnO nanopowder remained after ultrasonic vibration of 10 minutes. Furthermore, it resulted in the highest photocatalytic efficiency among the inorganic binders. The SCM ZnO nanopowder immobilized by the zinc phosphate showed about six times higher photocatalytic efficiency than that by the other inorganic binders. This big difference by binding materials might be attributed to the binding type such as physical binding or chemical binding. For the zinc phosphate, interfacial chemical reaction between SCM ZnO nanopowder and the zinc phosphate provided this amazing adhesion property. The surface roughness of the immobilized SCM ZnO nanopowder seemed to provide another advantage for the photocatalytic efficiency.

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