

Synthesis of Nanocrystalline TiO₂-Coated Coal Fly Ash for Photocatalyst

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Abstract—In order to more easily separate TiO₂ photocatalyst from treated wastewater, TiO₂ photocatalyst is immobilized on coal fly ash by precipitation method. The titanium hydroxide precipitated on coal fly ash by neutralization of titanium chloride is transformed into titanium dioxide by heat treatment in the temperature range of 300-700 °C. The crystalline structure of the titanium dioxide shows anatase type in all ranges of heat treatment temperature. The crystal size of anatase increases with increasing heat treatment temperature, with the drawback being the lower removal ability of NO gas. When the coal fly ash coated with 10 wt% of TiO₂ was calcined at 300 and 400 °C for 2 hrs, the average crystal size of anatase appeared about 9 nm, and the removal rates of NO gas were 63 and 67.5%, respectively. The major iron oxide, existing in coal fly ash as impurity, is magnetite (Fe₃O₄). Phase transformation of magnetite into hematite (Fe₂O₃) by heat treatment improves the removal rate of NO gas for TiO₂-coated coal fly ash.

Key words: Photocatalyst, Titanium Dioxide, Coal Fly Ash, Iron Oxide

INTRODUCTION

The photocatalytic detoxification of organic and inorganic compounds is very promising for the purification of polluted air and industrial wastewater, and thus has attracted extensive attention during these 20 years [Domen et al., 2001; Jung and Park, 2001; Nam and Han, 2003]. Due to its stability, non-toxicity and low cost, TiO₂ has been the most investigated photocatalyst [Park et al., 2001; You et al., 2003]. The band gap of this semiconductor is 3.2 eV, which corresponds to radiation wavelength of around 380 nm. Therefore, UV light with wavelength shorter than 380 nm is needed to excite the electrons in valence band to conduction band. Hoffmann et al. reported that the electron-hole pairs generated serve as the oxidizing and reducing agents.

A photocatalyst is generally suspended in wastewater for the degradation of pollutants, and therefore requires an additional separation step to remove the catalyst from the treated water. Removing the photocatalyst from large volumes of water is very difficult because of their small particle size. This exhibits a major hindrance to the application of the photocatalytic processes for treating wastewater. The photocatalytic activity decreased in water because of the aggregation of pure TiO₂ particles. To minimize this problem and increase the TiO₂ surface area, research has been carried out by immobilizing titania onto various porous substrates, such as active carbon, silica or zeolite [Srinivasam et al., 1994; Hashimoto et al., 2001; Hsien et al., 2000]. While this approach provides a solution to the solid-liquid separation problem, porous materials are not cheap because they are artificially synthesized. To treat the huge amount of industrial wastewater by utilizing photocatalyst, a cheaper photocatalyst should be developed.

Fly ash is generated in dry form in large quantities as a by-product of thermal power plants and thus is a major source for environ-

ment pollution. Currently, large quantities of fly ash are land-filled. Research is in progress to find the various ways to utilize this by-product to prevent any environmental problems as well as effectively use them. Fly ashes are highly dispersive powders. They consist mainly of silica-aluminate, ferriferous glass (about 60-80 wt%), quartz and unburned carbon (about 2-5 wt%). Their particle shape is spherical and their average particle size is about 20 µm. Their phase and composition is quite stable in air and water if they are not mixed with alkali materials. They are very cheap; thus, fly ash can be useful as a substrate of TiO₂ photocatalyst for purifying pollutants in air and wastewater. Fly ash does have some impurities, however, such as Fe₂O₃, CaO, Na₂O and K₂O.

In the present study, TiO₂ was supported on a coal fly ash to provide a cheaper titania-immobilized photocatalyst, and the feasibility of coal fly ash as a supporter of TiO₂ photocatalyst was investigated. The effect of iron oxide existed in a coal fly ash as an impurity on the photocatalytic activity of TiO₂ was discussed.

EXPERIMENTAL PROCEDURES

1. Preparation of TiO₂-coated Coal Fly Ash

The TiO₂ photocatalyst was coated on a coal fly ash by precipitation technique. The mixed solution of TiCl₄ (98.0%, Kanto Chemical Co.) and HCl (36.5%, Kanto Chemical Co.) was used as the coating reagent to prevent from forming orthotitanic acid, Ti(OH)₄, generated when TiCl₄ was diluted in water. The mole ratio of TiCl₄ to HCl was 1 : 2.5. To prepare the coal fly ash coated with 10 wt% of TiO₂, the coal fly ash of 36 g was suspended in the 0.2 M TiCl₄ aqueous solution of 250 ml, and then 163 ml of 2 M NH₄HCO₃ aqueous solution was added drop-wise as a precipitant to the TiCl₄ solution under vigorous stirring. In this neutralization reaction, Ti(OH)₄ was deposited on the surface of coal fly ash. The product was then washed several times with distilled water, and then filtered off and vacuum dried. The final product was calcined in the temperature range of 300-700 °C for 2 hrs to dehydrate Ti(OH)₄. The coal fly

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Table 1. Chemical compositions of coal fly ash (wt%)

SiO ₂	Al ₂ O ₃	Fe ₃ O ₄	CaO	MgO	K ₂ O	Na ₂ O	TiO ₂	MnO ₂	P ₂ O ₅	Ig. Loss
66.71	19.08	8.49	2.00	0.39	0.73	0.01	0.99	0.06	0.25	3.6

ash was used without any pre-treatment in this experiment and its average particle size was 20 μm . The chemical content of coal fly ash is shown in Table 1.

2. Elimination of Iron Oxide

The effect of iron oxide in coal fly ash on the photocatalytic activity of TiO₂ was investigated. The portion of coal fly ash with high iron oxide content was removed by electromagnetic separator. The separated coal fly ash was leached in 1 M HCl solution at 70 °C for 2 hrs to eliminate a partial iron oxide left on the surface of coal fly ash. With this process, the content of iron oxide in coal fly ash was reduced from 8.5 wt% to 4.6 wt%.

3. Characterization of Products

The morphology of TiO₂-coated coal fly ash was observed by scanning electron microscope (SEM, JEOL 5410). The chemical composition of coal fly ash was analyzed by inductively coupled plasma (ICP, OTSUTA Electronics ELS-8000). X-ray powder diffraction patterns of the samples were obtained by using a Phillips diffractometer and monochromated high intensity CuK α_1 radiation ($\lambda=1.5405$ Å). The crystallite size of TiO₂-coated on coal fly ash was calculated from the peak width by using the Scherrer equation, $D=k\lambda/(\beta\cos\theta)$, where D is the crystallite size, k is a shape factor (a value of 0.9 was used in this study), λ is the X-ray radiation wavelength (1.5405 Å for CuK α_1), and β was determined from the experimental integral width by applying standard corrections for the effects of K α_1 -K α_2 separation and instrumental broadening.

4. Measurement of Photocatalytic Activity

For the photocatalytic degradation experiment, the removal rate of NO gas was evaluated. This method using gas phase reaction for the test of photocatalytic activity is very simple and has a good reproducibility as compared with the test method of liquid phase reaction. The reactor for the removal rate test of NO gas was used as shown in Fig. 1, in which an 8 W UV lamp (Vilber Lourmat, VL-4LC, 254 nm) was positioned upon the quartz glass (denoted

as i) of the reactor. The 10 wt% TiO₂-coated coal fly ash of 0.1 g was spread on the filter paper (ID 65 mm) in which was covered upon metal filter (denoted as d). The standard gas of NO was inserted into the reactor from a three way valve (denoted as h), and then air was filled until the two rubber bag for sampling gas was full. The initial concentration of NO gas in the reactor was controlled at 4-5 ppm. Prior to photoreaction, the mixed gas was circulated in a dark condition for 2 hrs by the diaphragm air pump (denoted as e) to establish an adsorption/desorption equilibrium condition and the homogeneous mixing of NO gas in the reactor. After irradiating UV to the TiO₂-coated coal fly ash for photoreaction, the content of NO gas was analyzed by the gas detector tube (GASTEC, NO. 11 L) of nitrogen oxides (NO+NO₂) at 7 minute intervals. Nitrogen oxide is easily oxidized to nitrogen dioxide. Nitrogen dioxide reacts with diphenylamineto in the detector tube, and then produces p-nitroso-diphenylamine which color is yellowish orange. The detector tube indicates the total content of NO and NO₂ with color change. The measuring range of the detector tube is 0.04-16.5 ppm and the detecting limit is 0.01 ppm.

RESULTS AND DISCUSSION

1. Preparation of TiO₂-coated Coal Fly Ash

The SEM image of TiO₂-coated coal fly ash is illustrated in Fig. 2. From this, the small and big spheres are coal fly ashes, and TiO₂ is found on the surface of these spheres. The coating layer of TiO₂ was not uniform as can be seen in the photograph. The amount of TiO₂ found at a, b and c spots was much more than at the d spot.

Fig. 3 is the XRD patterns of TiO₂-supported coal fly ash according to different temperatures of heat treatment. The crystalline structure of TiO₂ coated on coal fly ash shows a typical anatase, and is well retained in the temperature range of 300-700 °C. Many studies have reported that pure anatase converted to rutile above about

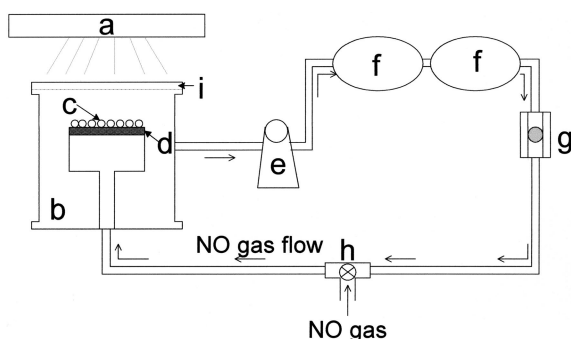


Fig. 1. Schematic diagram of the apparatus for testing NO removal rate.

- | | |
|--|--------------------|
| a: UV lamp | f: Rubber bag |
| b: Reaction vessel | g: Flow meter |
| c: TiO ₂ -coated coal fly ash | h: Gas inlet valve |
| d: Metal filter | i: Quartz plate |
| e: Circulation pump | |

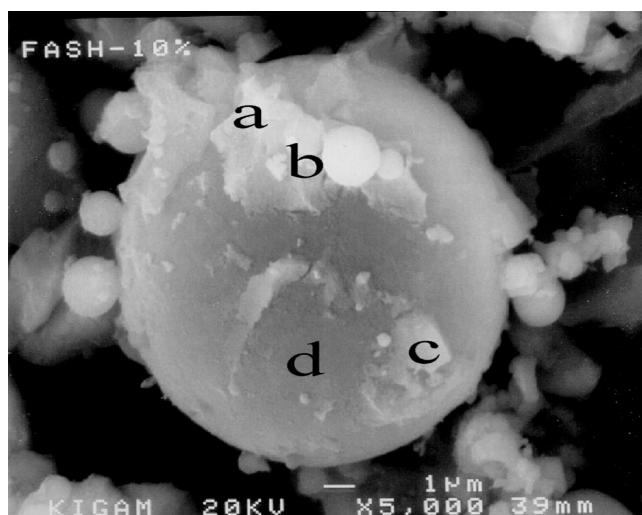


Fig. 2. SEM photograph of TiO₂-coated coal fly ash.

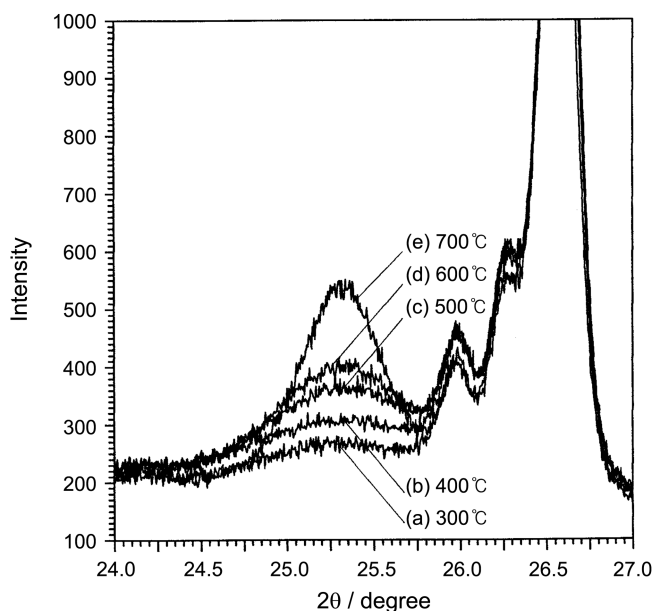


Fig. 3. X-ray diffraction patterns of TiO_2 -coated coal fly ash as a function of heat treatment temperature.

500 °C at a slow rate. In general, anatase-based material transformed to rutile depending on the temperature and time. However, the presence of different dopants may strongly affect the kinetics of this process. Bregani et al. have reported that additives such as CuO , MnO , CoO , NiO and Sb_2O_3 accelerate the transformation of anatase to rutile, and Cr_2O_3 , WO_3 and rare-earth oxides stabilize the anatase. Fly ash has many impurities. Thus, it is thought that the reason why titania still remained as anatase at the temperatures above 500 °C is ascribed to impurities in fly ash. However, further study is needed to understand what element retards the anatase transformation to rutile in fly ash system.

The peak corresponding to the 101 plane of anatase TiO_2 appeared

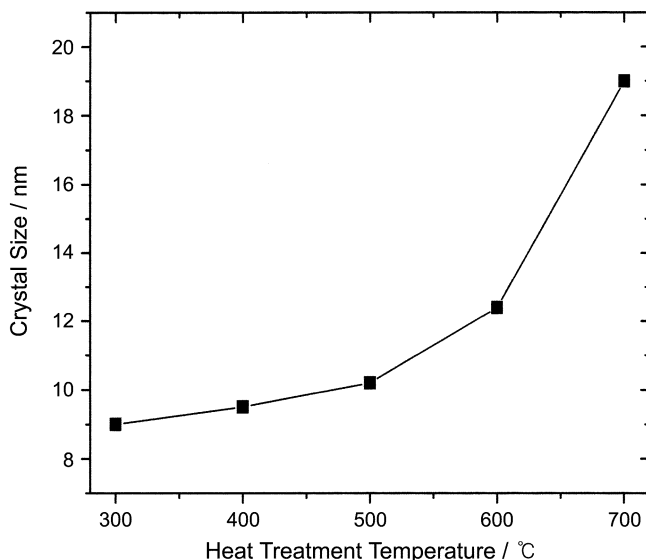


Fig. 4. The change of crystallite size of TiO_2 on coal fly ash as a function of heat treatment temperature.

at $2\theta=25.4^\circ$, and the peaks of mullite of coal fly ash appeared at $2\theta=26^\circ$ and 26.5° . The peak of anatase was broader at the lower temperature of heat treatment, and this intensity grew with increasing the temperature of heat treatment. This result implies that the crystallinity and the crystallite size of the anatase TiO_2 supported on fly ash increase as the temperature of heat treatment rises. The crystallite sizes of anatase calculated from Scherrer's equation are plotted in Fig. 4 as a function of heat treatment temperature. The crystallite size of TiO_2 showed about 9 nm in the temperature range of 300–400 °C, and started to grow rapidly at 600 °C.

The photocatalytic activity of TiO_2 -coated coal fly ash was evaluated by the removal ability of NO gas. Fig. 5 shows the change of NO gas removal efficiency as a function of UV irradiation time at various temperatures of heat treatment. The removal of NO gas increased with decreasing heat treatment temperature. This is probably due to the higher surface area and smaller crystallite size of the TiO_2 coated on fly ash. The maximum removal efficiency was achieved

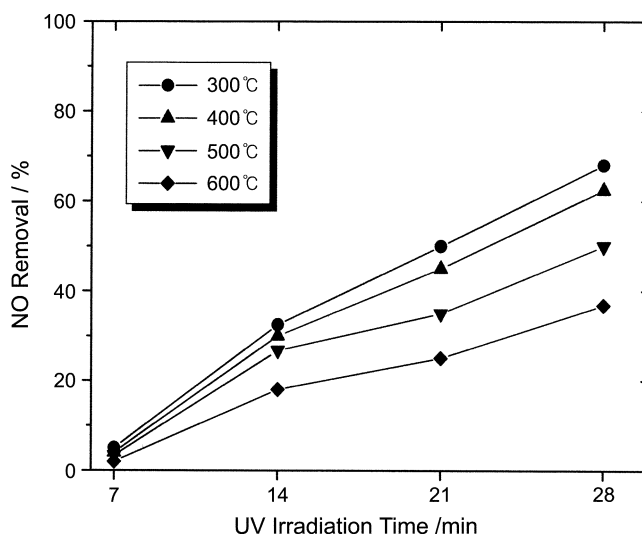


Fig. 5. The NO gas removal by TiO_2 -coated coal fly ash photocatalysts that were heat-treated at various temperatures.

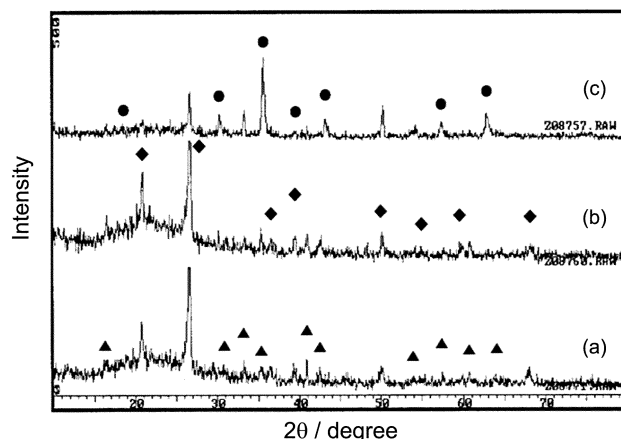


Fig. 6. X-ray diffraction patterns of raw coal fly ash (a), refined coal fly ash (b) and coal fly ash with high iron oxide content (c).

▲; Mullite, ◆; Quartz, ●; Fe_3O_4

67.5% after 28 min UV irradiation with the photocatalyst sample heat-treated at 600 °C.

2. Effect of Iron Oxide on Photocatalytic Activity

In order to investigate the effect of iron oxide in fly ash on the photocatalytic activity of TiO₂ supported on coal fly ash, the refined coal fly ash that iron oxide was partially eliminated by electromagnet and HCl leaching was used as a supporter of TiO₂ photocatalyst. Fig. 6 shows the X-ray diffraction patterns of a raw coal fly ash (with 8.5 wt% Fe₃O₄), a refined coal fly ash (with 4.6 wt% Fe₃O₄) and an eliminated coal fly ash (rich with Fe₃O₄). The crystallite structure of the raw coal fly ash is mainly composed of quartz and mullite. The X-ray diffraction pattern of the refined coal fly ash is not much different when compared to that of the raw coal fly ash. This is due to the iron oxide left in coal fly ash. The X-ray diffraction pattern of the eliminated coal fly ash composed of the peaks of coal fly ash and iron oxide of magnetite phase. This result indicates that the crystallite structure of iron oxide is mainly a magnetite. The refined coal fly ash was coated with 10 wt% TiO₂ and calcined at 300 °C for 2 hrs, and the photocatalytic activity was estimated. However, the photocatalytic activity was not improved as compared with before reducing the amount of iron oxide in coal fly ash.

To improve the photocatalytic activity of TiO₂ coated on coal fly ash, heat treatment was attempted before coating TiO₂ to transform magnetite in the refined coal fly ash to hematite. The pre-heating treatment of coal fly ash was performed in the temperature range of 400–700 °C, and the samples were heated for 2 hrs at each 100 °C temperature range. The results of the X-ray diffraction patterns over the samples are shown in Fig. 7. The diffraction peaks of magnetite and hematite are doubled with those of mullite in coal fly ash except a few peaks. The independent peaks of magnetite appear at $2\theta=24^\circ$ and 64° , and the independent peaks of hematite reveal at $2\theta=30.5^\circ$ and 57.2° . The peaks corresponding to hematite slightly appeared in the X-ray diffraction profile of the sample calcined at 400 °C. The intensity of these peaks grew with increasing temperature, whereas the peak intensity of magnetite retracted with increasing temperature. However, the magnetite was not perfectly transformed to the hematite although the temperature of heat treatment increased up to 700 °C.

The coal fly ashes calcined at various temperatures were coated

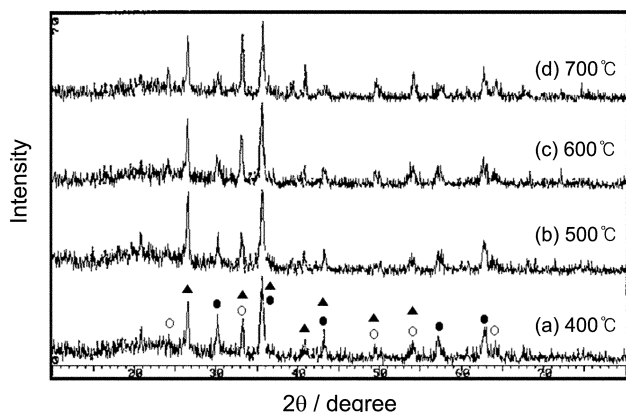


Fig. 7. X-ray diffraction patterns of refined coal fly ash that was heat-treated at various temperatures.

▲; Mullite, ●; Fe₃O₄, ○; Fe₂O₃

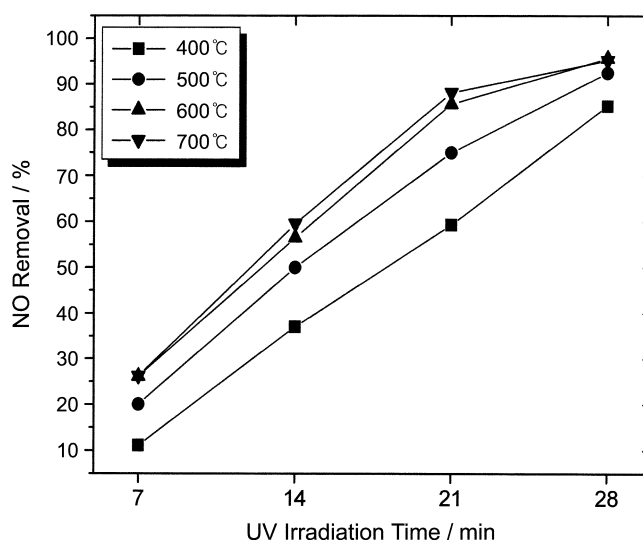


Fig. 8. The NO gas removal by TiO₂-coated coal fly ash according to the pre-heating temperature for transforming magnetite to hematite.

with Ti(OH)₄ corresponding to 10 wt% of TiO₂ by same coating method mentioned in 2.1, and the Ti(OH)₄ deposited on coal fly ashes was calcined at 300 °C for 2 hrs again for dehydration. Over the samples, the photocatalytic activity was estimated by the removal rate of NO gas. The removal rate of NO gas increases as the pre-heating temperature of coal fly ash increases, as shown in Fig. 8. The maximum removal rate found to be 95% at the temperature range of 600–700 °C when the samples were irradiated by UV lamp for 28 min. These results indicate that the transformation of magnetite in fly ash to hematite contribute to the increase of photocatalytic activity of TiO₂-coated coal fly ash. In fact, the iron oxide can be present as magnetite, maghemite and hematite or as a mixture of these phases, depending on the calcination conditions. The band gap values are different for each of the oxides, magnetite (0.1 eV), maghemite (2.3 eV) and hematite (2.2 eV). Taking the narrower band gap of magnetite into account, this is believed to lead to an increase in the incidence of electron-hole recombination rate [Ranjit and Viswanathan, 1997; Litter and Navio, 1996].

However, the removal rate of NO gas did not increase although the pre-heating temperature of coal fly ash rises to higher than 600 °C in Fig. 8. This is due to the fact that TiO₂ photocatalyst is present only on the surface of coal fly ash and all iron oxides existing on the surface were transformed into hematite by heat treatment at 600 °C. Thus, in Fig. 7, it was shown that the peaks of magnetite existed on the X-ray diffraction profile of the sample calcined at 700 °C referred to the iron oxide of magnetite phase being present inside of coal fly ash.

CONCLUSIONS

TiO₂-coated coal fly ash could be prepared by precipitation from TiCl₄ aqueous solution in this study. The crystalline structure of TiO₂ supported on coal fly ash appeared in the anatase phase, and its average crystal size was about 9 nm in the heat treatment temperature range of 300–400 °C. The removal rate of NO gas for the TiO₂-coated

coal fly ash was 63-67.5% in the same temperature range when UV was irradiated for 28 min for photoreaction.

The crystalline structure of iron oxide in coal fly ash showed magnetite phase, which was partially transformed to hematite by heat treatment in the temperature range of 400-700 °C. This phase transformation contributed to the improvement of photocatalytic activity of TiO₂-coated coal fly ash. The removal rate of NO gas for the TiO₂-coated coal fly ash, which iron oxide was transformed into hematite, increased up to 95%.

From these results above, it was found that the coal fly ash could be good as a supporter of TiO₂ photocatalyst.

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