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Nitrogen Oxides Removal Performance of Carbonized Aggregate Coated with Titanium Dioxide

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Nitrogen oxides removal performance of carbonized aggregate coated with titanium dioxide was examined in this paper. It was possible to coat the carbonized aggregate (wood ceramics) surface with titanium dioxide of the thickness of about 5 μ m. It was proved that nitrogen oxides removal capability in the atmosphere was very high for carbonized aggregate coated with titanium dioxide. This aggregate may become an excellent material for the air pollution purification countermeasure.
Keywords: titanium dioxide, wood ceramics, nitrogen oxides, pavement, atmosphere purification

1. INTRODUCTION

Around the arterial road in the metropolis, air pollution by automobile exhaust is a still serious problem [1]. The basic countermeasure is the improvement on motor fuel and combustion equipment that are emission sources. In the meantime, the trial of atmosphere purification using soil de-nitration and photo-catalyst action of titanium dioxide are carried out as a countermeasure in the road facility. As a utilization of the titanium dioxide, two methods of addition to the organic material and to the inorganic material are considered. That is to say, one is a method for adding to the coating material used for road ancillary facility of soundproof wall, etc., and another is a method used at the pavement surface by mixing with cement materials [2].

Authors have been carried out research and development for utilizing carbonized aggregate (wood ceramics [3]) as a material for road pavement. Basic physical property of the carbonized aggregate has already been reported [4]. One of the aims of this study is purification of air pollution by the auto traffic of metropolitan area. Here, the result of examining nitrogen oxides removal performance of the carbonized aggregate coated with titanium dioxide is reported.

2. EXPERIMENTAL METHOD

2.1 Materials

(1) Carbonization of aggregate

The woody material used as raw material is medium density fiberboard (MDF) shown in Table I. First, MDF of the 15mm thickness were processed to produce the globular woodchips. The diameter of the globular woodchips became 12～13mm. Next, this woodchips were immersed in the phenol resin. The resin immersion was done in the immersion tank, while it applied under vacuum, ultrasonic wave. After the resin immersion, the resin was made to harden in the drying furnace at 130℃. Weight increase rate (the resin immersion rate) for original woodchips weight was about 50%. Next, the woodchips were carbonized in the vacuum furnace at 800℃. Treatment process and processing condition to the carbonization are shown in Table II. The diameter of the carbonized aggregate finally became about 10mm.

Table I. Specification of MDF

item	value
thickness(mm)	15
density(g/cm^3)	0.62
bending strength(N/mm^2)	33
adhesion strength(N/mm^2)	0.7
thickness expansion rate by water absorption(%)	6.5
wood screw holding force (N)	380

Table II. Process and condition of carbonization

process	condition
phenol resin immersion	1 hr with ultrasonication in vacuum vessel
curing	12hrs at 70℃→3hrs up to 130℃→keep 130℃ for 2hrs→spontaneous cooling
carbonization	3℃/min up to 800℃→keep 800℃ for 4hrs→spontaneous cooling

(2) Coating with titanium dioxide

The specification of titanium dioxide sol used for coating the carbonized aggregate is shown in Table III.

Table III. Specification of TiO_2-sol

item	value
TiO_2 (%)	30
pH	1.0
TiO_2 particle size (nm)	20
specific gravity	1.28
viscosity at 20℃ (mPa·s)	<10
deflocculant	HNO_3

Coating condition of titanium dioxide sol is shown in Table IV. Carbonized aggregate of 1kg put in the acid-resistant polyethylene fiber cloth was soaked in titanium dioxide sol for 5 minutes. The extra titanium dioxide sol was removed by centrifuge. Afterwards, taken out aggregate was spread in the container made of polyethylene, and dried at room temperature for 15 hours. Next, the aggregate was heated in vacuum furnace at 200℃ in order to firmly coat with titanium dioxide. The condition of the titanium dioxide coating was judged with the optimum as a result of measuring NOx ($NO+NO_2$) removal performance by preliminary. Weight increase rate by the titanium dioxide coating under this condition was 4.3%.

Table Ⅳ. Process and condition of TiO_2 coating

process	condition
immersion time	5min
centrifugation time	1min
vacuum heating	3 hrs up to 200℃→keep 1 hr at 200℃→4 hrs to 50℃

2.2 Measurement

The test equipment outline for evaluating nitrogen oxides removal performance is shown in Fig.1. Test gas adjusted at fixed NOx concentration and humidity (90ppm, 50% in this experiment respectively) is introduced into the reactor vessel that the aggregate was installed. The nitrogen oxides removal performance was evaluated by measuring the NOx concentration in before and behind of the reactor vessel.

The internal construction of reactor vessel is shown in Fig.2. The parts that install the aggregate are 50mm width, 300mm length. The aggregate was piled up in 5 layers. The test gas passes ventilation control board of the entrance side, and it flows into the aggregate installation part. Then, the gas escapes from 5mm clearance with pyrex glass board and exit side ventilation control board. From the upper part of the pyrex glass board, ultraviolet ray was irradiated using black light.

The test gas was introduced into the reactor vessel, and it was made to be the ultraviolet ray unirradiation for first 1 hour. Afterwards, the ultraviolet ray was irradiated for 130 minutes. NOx concentration was also measured for 30 minutes, after the ultraviolet irradiation was finished.

The measurement condition is shown in Table Ⅴ, and experiment cases are shown in Table Ⅵ. By changing the type of aggregate and stacking condition in the reactor vessel, 5 cases were examined. Alumina (Al_2O_3) sphere used in case 4 was 10mm diameter. Covering condition of titanium dioxide to the alumina sphere was similarly with the carbonized aggregate. Since there was the dispersion at the diameter of the carbonized aggregate, the number of the aggregate installed in the reactor vessel was the 94～102 piece in 1 layer. And, aggregate number used per 1 case became the 476～491 piece. Apparent TiO_2 covering area in making the diameter of the aggregate to be 10mm was shown in the right end of Table Ⅵ.

Table Ⅴ. Experimental condition for evaluating NOx removal performance of aggregate

item	condition
NOx concentration (ppm)	90 (NO≒81～84、 NO_2≒6～9)
gas flow (l/min)	4.0
UV intensity (mW/cm^2)	1.0
Relative humidity (%)	50

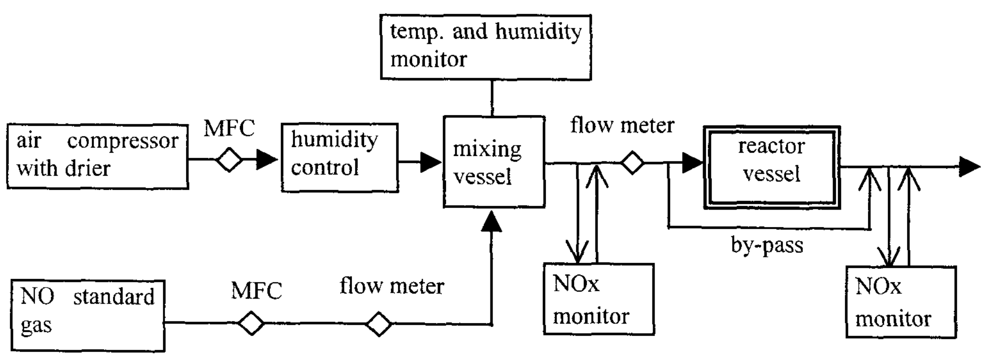

Fig.1 Test equipment outline for evaluating NOx removal performance

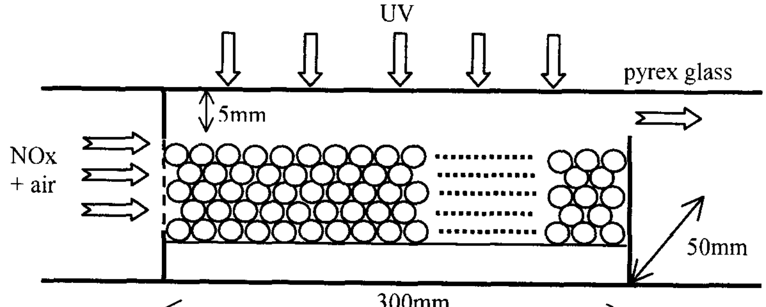

Fig.2 Scheme of reactor vessel

Table VI. Experimental case for evaluating NOx removal performance

case No.	five layers formation of aggregate in reaction vessel	total number of aggregate in one case	apparent area of TiO_2 coated (cm^2)
case1	WC for all 5 layers	487	0
case2	upper 1 layer : TiO_2-WC lower 4 layers : WC	476	298
case3	upper 1 layer : WC lower 4 layers : TiO_2-WC	490	1224
case4	upper 1 layer : Al_2O_3 aggregates with TiO_2 lower 4 layers : WC	491	298
case5	TiO_2-WC for all 5 layers	476	1494

* WC: carbonized (wood ceramics) aggregate without TiO_2
TiO_2-WC: carbonized (wood ceramics) aggregate coated with TiO_2

3.RESULTS AND DISCUSSION

3.1 Carbonized aggregate coated with titanium dioxide

The electron micrography of carbonized aggregate coated with titanium dioxide is shown in Fig.3. The photograph is a fracture surface near the aggregate surface. It was proved that the whole aggregate surface had been covered by the titanium dioxide of the thickness of about 5μm. By the coating of titanium dioxide, the specific surface changed to 35m^2/g from 46m^2/g, and was about 25% decreased. This seems to be because ruggedness of the aggregate surface and part of the gap were closed by the coating of titanium dioxide to the aggregate surface.

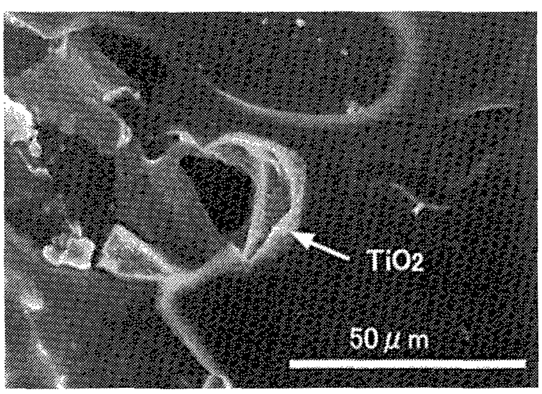

Fig.3 SEM photograph of carbonized aggregate coated with TiO_2

3.2 Nitrogen oxides removal performance

The decreasing rate of NOx ($NO+NO_2$) concentration in the exit side for entrance side was arranged as NOx removal ratio. The result is shown in Fig.4. In case 4, NOx removal ratio was about 30%. In other four cases, NOx removal ratio was high around 60%. By all cases, high NOx removal ratio was shown in the ultraviolet ray unirradiation as well as the irradiation.

Case 1 using the carbonized aggregate that had not been coated with titanium dioxide was the biggest for NOx removal ratio in the ultraviolet ray unirradiation. It is shown that adsorption effect of NOx by the carbonized aggregate is big. NOx removal ratio tended to lower with the time. The rise of NOx removal ratio by titanium dioxide in ultraviolet irradiation was smaller than the whole removal capability. Case 5 using the aggregate coated with titanium dioxide in all 5 layers was the biggest for NOx removal ratio in the ultraviolet irradiation. Removal ratio of case 4, which used alumina sphere coated with titanium dioxide in the most upper layer, was as a half of other four cases. Therefore, adsorption effect by carbonized aggregate of the most upper layer seems to greatly contribute in the whole NOx removal performance. It seems to be because the flow of the gas of the surface part excels, while there were small gas which pass through the inside in installed aggregate layer.

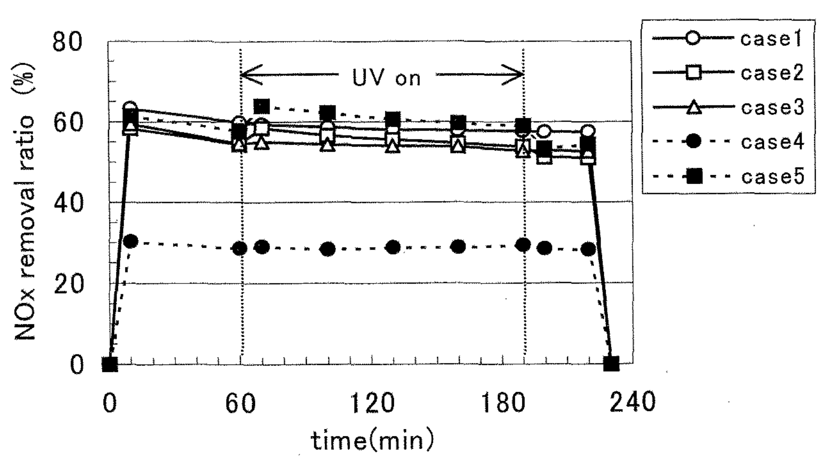

Fig.4 Variation of NOx removal ratio during experiment

3.3 Effect of titanium dioxide coating

Average NOx removal ratio and removal quantity for 2 hours in the ultraviolet irradiation are shown in Table Ⅶ. The rising part of removal ratio in ultraviolet irradiation is considered the effect by titanium dioxide, and the result of estimating the removal quantity by titanium dioxide is shown in the right end of the same table. Test specimen installation area ($0.05m \times 0.3m=0.015m^2$) was converted here into 1 m^2.

NOx removal quantity by titanium dioxide was estimated with $0.1 \sim 3.9$ mmol/$m^2 \cdot$hr. For this, the whole removal quantity including adsorption was very big with $18.3 \sim 39.1$ mmol/$m^2 \cdot$ hr. However, the absorbed amount of NOx to carbonized aggregate seems to be going to someday reach the saturation. Therefore, it is necessary to deal with adsorbed NOx so that the removal effect may continue. And, the oxidation of NOx by titanium dioxide is required in case of the physical adsorption, since desorption also occurs.

In this experiment, it was case 5 using the aggregate coated with titanium dioxide in all 5 layers that the effect of titanium dioxide was the biggest. In case 5, the NOx removal quantity by titanium dioxide in ultraviolet irradiation was estimated with 3.9 mmol/$m^2 \cdot$hr. In case 3 using the aggregate that titanium dioxide was coated at lowers of 4 layers, the effect of titanium dioxide was small. And, the effect of titanium dioxide was comparatively big in case 2 using the aggregate of which only the most upper layer was coated with titanium dioxide. This is because the ultraviolet ray that reaches lower layer is little. In case 4 that installed the alumina sphere coated with titanium dioxide in the most upper layer, the rise of the NO_2 concentration by the ultraviolet irradiation was bigger than other case. Therefore, NOx removal effect by titanium dioxide was small. It seems to be because an adsorption site of the aggregate surface was insufficient in case of the alumina sphere of the smooth surface and because the oxidation of NO was difficult to progress to NO^{3-}.

4.CONCLUSION

The carbonized aggregate (wood ceramics) was produced using the medium density fiberboard, and the surface of the aggregate was coated using the titanium dioxide sol. The NOx removal performance of produced aggregate was examined. As a result of the experiment, following fact was proved.

(1) It was possible to coat the carbonized aggregate surface by titanium dioxide of the thickness of about 5 μ m.

(2) It became clear that NOx adsorption ability of the carbonized aggregate itself was very big.

(3) NOx removal quantity of the pavement model which piled the aggregate in the 5 layers was very big with $34.6 \sim 39.1$ mmol/$m^2 \cdot$hr.

The carbonized aggregate coated with titanium dioxide is the excellent environmental cleanup material. By using this aggregate for the road pavement, it may be able to effectively remove NOx in the atmosphere. Persistence of the NOx removal effect, etc. has been left in the problem to be investigated.

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Table Ⅶ. Average of NOx removal ratio and estimated amount of removed NOx quantity

case No.	2hrs average of NOx removal ratio (%)	amount of removed NOx(mmol/$m^2 \cdot$hr)	amount of removed NOx by TiO_2(mmol/$m^2 \cdot$hr)
case1	58.2	37.2	—
case2	55.7	35.5	1.9
case3	54.0	34.6	0.1
case4	28.8	18.3	0.1
case5	53.3	39.1	3.9