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Removal of low concentration nitrogen oxides through photoassisted heterogeneous catalysis

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Abstract

Titanium dioxide (TiO_2) oxidized nitric oxide (NO) to nitric acid (HNO_3) very rapidly under ultraviolet light illumination, but some NO was oxidized to nitrogen dioxide (NO_2), while activated carbon (AC) adsorbed NO_2 well. A mixture of TiO_2 and AC was thus confirmed to be an excellent photoassisted catalyst for removal of low concentration (sub-ppm) NO_x from air. Addition of 1-3 wt.% of ferric oxide (Fe_2O_3) to the mixture could markedly increase the catalytic activity. Even though the catalytic activity gradually declined with the reaction time, it could be completely recovered only by washing the catalyst with water, suggesting that HNO_3 accumulated on the catalyst was removed. It is inferred that the photoilluminated TiO_2 generates reactive oxygen species which oxidize (NO and NO_2) to (NO_2 and HNO_3). AC can trap NO_2 and give TiO_2 enough time to oxidize NO_2 to HNO_3. Fe_2O_3 seems to be a promoter which can attract more NO/NO_2 to the surface of the catalyst.

Key words: heterogeneous catalysis; nitrogen oxides; photoassisted catalysis

Introduction

Despite much effort to achieve the reduction of nitrogen oxides (NO_x) from various emission sources, the concentration of NO_x in the air above Japan has been almost constant for last 10 years and often is higher than the air quality standard set for nitrogen dioxide (NO_2), particularly along roads which see heavy traffic in densely populated areas [1]. To meet with this situation, development of a new technology for removing NO_x at sub-ppm level from air of traffic roads, tunnels or other environmental emission sources has been requested. Conventional technologies used for reduction of NO_x from stationary sources like boilers have been applied to treatment of the dilute NO_x [2]. For example, the dilute NO_x was concentrated by using an absorbent such as activated carbon (AC) or zeolite. NO_x desorbed was introduced to a reactor in which nitrogen monoxide (NO) was reduced to N_2 through a selective catalytic reaction with ammonia. Although this technology can treat dilute NO_x, the

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cost of construction and operation of such a facility, and the energy consumption have been estimated to be very high. Development of a novel method which is economical and energy-saving is thus strongly desired.

We have studied the dry deposition of NO_x onto the ground and have found that the rate of NO_x adsorption onto some soil particles was enhanced by photoillumination [3]. Of the metal oxides constituting the soil particles, titanium dioxide (TiO_2) showed the highest activity for the NO_2 adsorption under photoillumination and about 60% of NO_2 was captured as nitric acid (HNO_3) on the TiO_2 surface. The photocatalytic oxidation of NO_x to HNO_3 by TiO_2 is therefore expected to be most advantageous to treatment of dilute NO_x, since any extra reactants such as ammonia are not required and HNO_3 can be trapped on the surface. In this paper, we presented our experimental results on the excellent photocatalytic activity of a mixture of TiO_2, activated carbon and ferric oxide (Fe_2O_3) particles for oxidation of NO_x to HNO_3. A reaction scheme of the NO_x photooxidation process is briefly discussed.

Experimental

TiO_2 powders were obtained from Degussa Co. (P-25, ca. 80% anatase and 20% rutile, average particle size of 20 nm) and Kokusan Kagaku Co. (reagent grade, anatase), and zinc oxide (ZnO) was purchased from New Jersey Zinc Co. AC prepared from granular coconut shell (Tsurumi Coal Co.) was mechanically ground into particles (particle size: less than 74 μm).

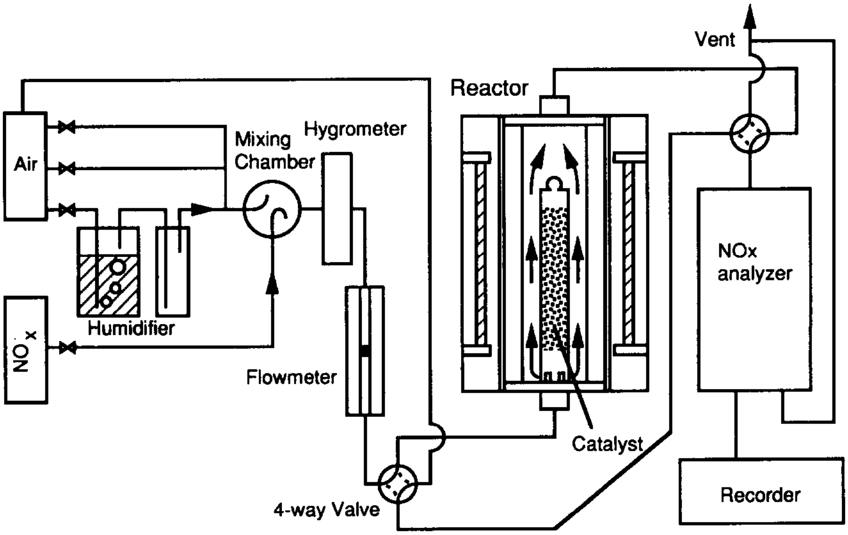

Fig. 1. Schematic diagram of a flow-type reactor for heterogeneous photocatalytic reactions of NO_x.

A flow-type photochemical reaction system as schematically shown in Fig. 1 was designed and fabricated. About 200–250 mg of catalyst powders was coated onto an inner Pyrex glass cylinder surface and was calcined overnight at 480 K under air. After cooling down to room temperature, the cylinder was placed inside an outer glass cylinder. Photoillumination was provided with a cylindrical bank of 12 black lights (wavelength: 300–400 nm). A reaction gas of 1–2 ppm NO_x in air was prepared from a NO/NO_2–N_2 mixture as well as pure O_2 in cylinder (purchased from Takachiho Chemicals Co.) and purified air. The reaction gas passed through the reactor at a flow-rate of 500 ml min^{-1} for 5–10 h at different relative humidities (dry to 72%). The experimental conditions are summarized in Table 1. After each experimental run, the inner glass cylinder was removed from the reaction system and was immersed into 185 ml

TABLE 1

Experimental conditions for NO_x photooxidation on catalyst by using a flow-type reactor

catalysts	200-250 mg (volume 0.6-0.8 ml)
reaction gas	NO, NO_2: 1-2 ppm in air flow rate: 500 ml min^{-1}
reactor volume	126 ml
space velocity	37 500 h^{-1}
gas velocity	1.2 cm s^{-1}
relative humidity	dry to 72%
reaction temperature	ca. 310 K
light intensity[a]	0.09-0.26 min^{-1}

[a] As the NO_2 photodissociation reaction rate constant.

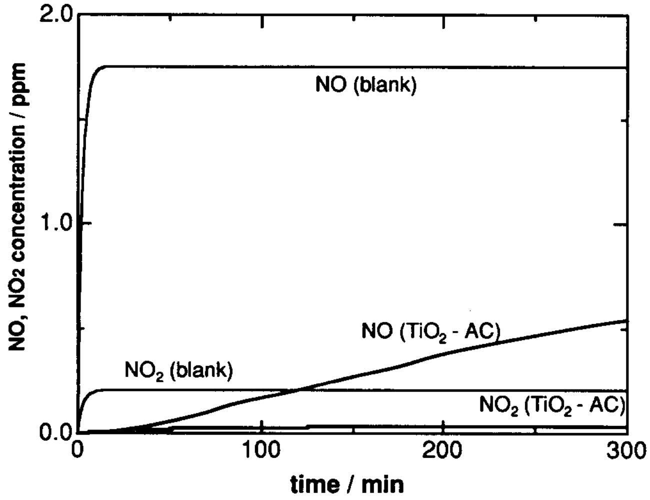

Fig. 2. Time-course of the concentration of NO and NO_2 in the presence of catalyst (a mixture of TiO_2 and activated carbon) and without catalyst (blank) under photoillumination.

of purified water. The catalyst powders were washed away from the glass cylinder with an ultrasonic cleaner. The content of HNO_3 in the water was determined as NO_3^- by ion chromatography (Shimadzu Inc., Model C-R4A). NO_x (NO and NO_2) in the gas phase was continuously monitored with a chemiluminescent NO–NO_x analyzer (Monitor Labs Inc., Model 8840).

Fig. 2 shows a typical experimental result obtained for a mixture of TiO_2–AC particles, which was exposed to ca. 2 ppm NO in air for a period of 5 h at a relative humidity of 50%. The lines of NO (blank) and NO_2 (blank) were recorded at a separate experimental run (blank test) in which NO_2 (blank) was produced by oxidation of NO in the piping lines and the reactor. In the presence of the catalyst under photoillumination, the concentration of NO was greatly reduced, although it gradually increased with the reaction time, while little NO_2 appeared in the gas phase. The area surrounded by the line of NO (blank) and that of NO (TiO_2–AC) corresponded to the amount of NO removed by the TiO_2–AC catalyst.

Results and discussion

Photocatalytic activity of some semiconductor particles

A reaction gas of 1.6 ppm NO and 0.21 ppm NO_2 in air passed over four kinds of semiconductor particles (TiO_2-1, TiO_2-2, Fe_2O_3, and ZnO) at a relative humidity of 70%. The total amount of NO and NO_2 removed and that of HNO_3 recovered were divided by the experimental period (5 h) and were normalized by the weight of catalyst used. The value in parentheses in the second column was the ratio of the amount of NO removed to the total amount of NO passing over the catalyst particles for 5 h. As can be seen from Table 2, every semiconductor particle showed the photocatalytic activity for removal of NO. TiO_2-1 and ZnO gave higher values of NO removed, while the lowest value was found for Fe_2O_3. Of the semiconductor particles, TiO_2-1 (Degussa P-25) could

TABLE 2

Removal of NO and NO_2 as well as recovery of HNO_3 by some semiconductor and activated carbon (AC) particles under photoillumination for 5 h (NO: 1.6 ppm and NO_2: 0.21 ppm, relative humidity: 70%, units: 10^{-6} mol g^{-1} h^{-1})

Catalyst (surface area: m^2/g)	NO[a]	NO_2	HNO_3
TiO_2-1 (45.6)	10.8 (0.90)	−2.3	7.7
TiO_2-2 (10.4)	7.2 (0.61)	−6.7	1.0
Fe_2O_3 (8.6)	2.1 (0.18)	−2.6	1.1
ZnO (10.5)	9.1 (0.73)	−7.8	1.1
AC (280)	2.3 (0.20)	1.4	1.4

[a] The value in parenthesis indicates the ratio of the amount of NO removed to the total amount of NO passing over the particles for 5 h.

recover the largest amount of HNO_3, which was about seven times those for the others. As indicated by the negative sign, however, about 20% of NO was released as NO_2 into the gas phase, although the amount was smaller than those for any other particles. Since the release of NO_2 into air is unfavorable to the environment, a way to diminish the formation of NO_2 should be found out. In contrast with the semiconductor particles, AC could adsorb both NO and NO_2, whereas the amount of HNO_3 formed was not large. The findings imply that a mixture of TiO_2 and AC may have a catalytic activity appropriate for removing NO_x.

Catalytic activity for NO_x removal by a mixture of TiO_2 and AC

In order to confirm this implication, several experiments have been performed with respect to TiO_2-1 (hereafter described as TiO_2), AC, and their mixture (TiO_2/AC=2/1 by weight) by using a reaction gas of 1.6 ppm NO_2 and 0.14 ppm NO in air at a relative humidity of 50% (Table 3). In this case, NO was produced by photodissociation of NO_2 in the reactor. The value in parenthesis in the second and third columns indicates the ratio of the amount of NO_2 removed to the total amount of NO_2 passing over the catalyst during the experimental period of 5 h. The results obtained in the dark are summarized as follows; (1) AC and TiO_2–AC mixture could remove much NO_2, (2) NO formation markedly took place for AC and TiO_2–AC mixture, and (3) a small amount of HNO_3 was produced for all the catalysts. Photoillumination considerably changed the activity of TiO_2 and TiO_2–AC. No NO was formed, but the formation of HNO_3 was strongly promoted for TiO_2 and TiO_2–AC, while little change was observed for AC. The removal of NO_2 and the formation of NO by AC are probably due to adsorption of NO_2 and reduction of NO_2 to NO, respectively. TiO_2 did not adsorb a large amount of NO_2 in the dark, but photoilluminated TiO_2 converted [NO and NO_2] to [NO_2 and HNO_3].

The catalytic activity of a mixture of TiO_2 and AC was examined at dif-

TABLE 3

Removal of NO_2 and NO as well as recovery of HNO_3 by TiO_2, activated carbon (AC) and TiO_2-AC at dark and under photoillumination for 5 h (NO_2: 1.6 ppm and NO: 0.14 ppm under photoillumination, relative humidity: 50%, units: 10^{-6} mol g^{-1} h^{-1})

Catalyst	NO_2 removed[a]		NO removed[b]		HNO_3 recovered	
	dark	illuminated	dark	illuminated	dark	illuminated
TiO_2	1.7 (0.16)	8.4 (0.88)	−0.1	0.30	1.7	7.8
AC	9.1 (0.87)	9.0 (0.94)	−5.1	−3.5	1.1	1.5
TiO_2-AC (2/1)	9.0 (0.86)	9.0 (0.94)	−4.7	0.87	1.6	7.3

[a] The value in parenthesis indicates the ratio of the amount of NO_2 removed to the total amount of NO_2 passing over the particles for 5 h.

[b] The negative sign indicates the formation of NO which is released into the gas phase.

ferent mixing ratios of TiO_2 to AC for a reaction gas of 1.6 ppm NO and 0.21 ppm NO_2 in air. As shown in Fig. 3, the amount of NO removed and that of HNO_3 recovered increase with the increase in the ratio of TiO_2 to AC, while the amount of NO_2 removed was decreased when the ratio became greater than 3. Consequently, it can be concluded that the optimum value of the mixing ratio of TiO_2 to AC for removing NO is approximately 2.

As a brief summary, the mixture of TiO_2 and AC powders shows excellent catalytic activity for NO_x removal, that is; the amount of NO removed and that of HNO_3 recovered are comparable to those for TiO_2 and the release of NO_2 to the gas phase is satisfactorily suppressed.

Improvement of the catalytic activity of the TiO_2-AC mixture

Addition of metal oxides (Fe_2O_3, Co_3O_4 and NiO) to the TiO_2-AC mixture was attempted to improve the catalytic activity, since it has been demonstrated that those metal oxides have relatively high adsorptive activity for NO [4,5]. It was found that each metal oxide similarly enhanced the catalytic activity for NO removal. Most of experiments, however, have been conducted with respect to Fe_2O_3, because Co and Ni oxides are not preferred from the environmental point of view. In Table 4, the results obtained for the TiO_2-AC-Fe_2O_3 mixture at a 500 ml min^{-1} flow-rate of a 1.5 ppm NO and 0.18 ppm NO_2 in air and a relative humidity of 50% are summarized. TiO_2-AC-Fe_2O_3 (I) was prepared by impregnating ferric ion to TiO_2 powders (2 wt.%) in aqueous solution, followed by filtration and calcination in air at 620 K for one day. TiO_2-AC-Fe_2O_3 (II) was made by simply mixing commercial Fe_2O_3 powders (reagent grade of Kokusan Kagaku Co., average diameter of 10 μm) with TiO_2-AC. The amount of NO removed during 10 h photoillumination by the TiO_2-AC-Fe_2O_3 (I) was

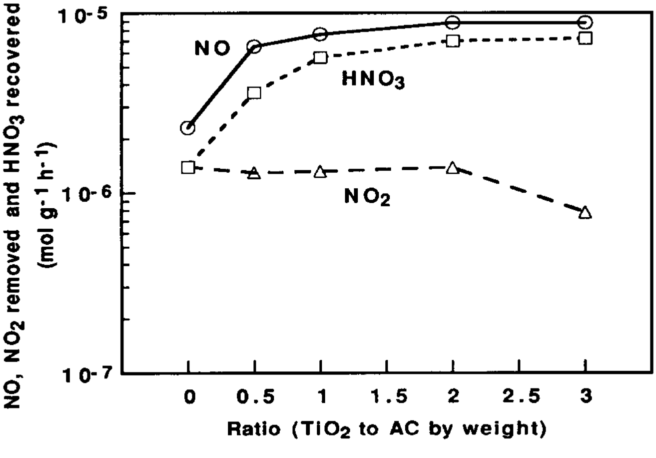

Fig. 3. Change in catalytic activity for removing NO_x (NO and NO_2 removed and HNO_3 recovered) with a mixing ratio of TiO_2 to activated carbon (AC), (reaction gas: NO 1.6 ppm and NO_2 0.21 ppm in air, a reaction time: 5 h, relative humidity: 50%).

TABLE 4

Amounts of NO and NO_2 removed and HNO_3 recovered by TiO_2-AC and TiO_2-AC-Fe_2O_3 [Ti-AC-Fe(I)[a] and Ti-AC-Fe(II)[b]] catalysts for 10 h experiment (NO: 1.5 ppm and NO_2: 0.18 ppm, relative humidity: 50%, units: 10^{-6} mol)

Catalyst	pH[c]	NO	NO_2	HNO_3
TiO_2-AC (2/1)	4.3	10.8	2.1	8.8
Ti-AC-Fe (I)	3.6	14.9	1.8	11.5
Ti-AC-Fe(II) (1)[d]	3.5	14.8	1.4	13.1
(2)	3.6	15.7	2.7	16.4
(3)	3.6	13.8	2.1	14.3

[a] Fe^{3+} was impregnated on TiO_2 (2 wt.%) and was calcined at 620 K under air. The TiO_2-Fe_2O_3 prepared was mixed with AC at a ratio of 2/1 by weight.
[b] Fe_2O_3 was mechanically mixed with TiO_2 at 2 wt.% and the mixture was further mixed with AC at a ratio of 2/1 by weight.
[c] The value of pH was measured of the water that washed the catalyst.
[d] The numbers 1, 2 and 3 indicate the time of experiment by using the same catalyst.

about 50% higher than those by TiO_2–AC and the increment of the HNO_3 yield was about 30%. The value of pH measured for the water which rinsed the TiO_2–AC–Fe_2O_3 was lower than that for TiO_2–AC. It is to be noted that the amount of HNO_3 recovered for TiO_2–AC–Fe_2O_3 (II) was greater than that for TiO_2–AC–Fe_2O_3 (I). Since an optimum value of Fe_2O_3 added was confirmed to be 1–3 wt.% of TiO_2 for TiO_2–AC, and Fe_2O_3 itself did not show a high catalytic activity (See Table 2), Fe_2O_3 may act as a promoter, probably may attract more NO to the surface of catalyst. Indeed, Kaneko has pointed out [6] that dispersion of Fe_2O_3 on AC resulted in a quite increase of NO adsorption. The higher activity of TiO_2–AC–Fe_2O_3 (II) than TiO_2–AC–Fe_2O_3 (I) may be related to the difference in the probability that Fe_2O_3 is in contact with AC. It is supposed that Fe_2O_3 in TiO_2–AC–Fe_2O_3 (II) may have more opportunities to be adjacent to AC than that deposited on the TiO_2 surface. It may also be likely that the photocatalytic activity of TiO_2 in TiO_2–AC–Fe_2O_3 (I) changes/declines to some extent owing to the deposition of Fe_2O_3 on TiO_2.

The amount of HNO_3 recovered by TiO_2–AC–Fe_2O_3 (II) catalyst was examined at different relative humidities. The HNO_3 yield obtained under humid conditions (relative humidity: 30% to 72%) seemed to be constant, although they were about 20% less than that obtained at dry condition. This low sensitivity to relative humidity is considered convenient for the catalytic oxidation of NO_x in ambient air, because relative humidity of ambient air frequently changes.

The catalytic activity seemed to be gradually decreased with the reaction time (as shown for TiO_2–AC in Fig. 2), probably due to accumulation of HNO_3 on the surface. However, by washing the used catalyst with purified water and drying it, its activity was completely recovered, as can be understood from the data indicated by the number of 1, 2 and 3 in Table 4. The result suggests that most of HNO_3 on the catalyst surface has been easily washed away. It is thus concluded that the TiO_2–AC–Fe_2O_3 powders can be repeatedly used as catalyst. In order to obtain data which are essential to the design of a practical NO_x treatment plant, a larger scale experiment will be needed, since a huge amount of air is to be treated and hence gas velocities of several meters per second, which is greater by two orders than that of this experiment (Table 1), will be necessary for the practical use. Needless to say, a more active catalyst will be a great help to this application.

Reaction scheme of NO_x removal by TiO_2-AC-Fe_2O_3 photocatalyst

The mixture of TiO_2–AC–Fe_2O_3 powders showed excellent catalytic activity for removing NO_x. This can be attributed to cooperative work by TiO_2, AC and Fe_2O_3. One is the strong and rapid photocatalytic oxidation of NO/NO_2 by TiO_2 and another is the adsorption of NO and NO_2 by AC and Fe_2O_3. Pichat et al. [7,8] have pointed out that NO is photoadsorbed on TiO_2, each NO molecule capturing one semiconductor free electron (NO^- formation), which is similar to a reaction of O_2 with electron (O_2^- formation). Since their results have been obtained in the absence of O_2, it is not clear that NO can have sufficient opportunities to interact with free electron, even with our experimental conditions where the O_2 concentration of 20% is much higher than 1–2 ppm of NO_x. To explain the present result that NO_2 and HNO_3 are formed from NO, NO should react with oxygen species produced by photoactivated TiO_2. Hori et al. [9] revealed from their experiments on photocatalytic oxidation of NO_2^- to NO_3^- in aqueous suspension of TiO_2 that the production of NO_3^- stopped when O_2 was not supplied to the solution. They suggested the contribution of HO_2 or HO_2^- radical to the NO_2^- oxidation. On the surface of photoilluminated TiO_2, production of super oxide (O_2^-) takes place. It has been reported [10–13] that some kinds of reactive oxygen species such as atomic oxygen (O), O^-, OH radical and HO_2 radical are produced through reactions among O_2^-, positive hole (p^+), O^{2-}, H^+/H_2O and OH^- on the TiO_2 surface. Based on the gas-phase chemistry concerning NO_x [14], it can be expected that reactions of ($NO+HO_2$) and ($NO+O$) rapidly proceed to form (NO_2+OH) and NO_2, respectively, and that NO_2 rapidly reacts with OH and O to produce HNO_3/NO_3 as well.

A reaction scheme as illustrated in Fig. 4 is therefore presumed, where in practice it can be imagined that much larger particles of AC and Fe_2O_3 than TiO_2 are surrounded with fine particles of TiO_2. NO diffuses to the surface of TiO_2 and rapidly reacts with the reactive oxygen species of O, HO_2 or O^- to produce NO_2. NO_2 further reacts with OH and O to form HNO_3. AC may capture NO_2 formed from NO by TiO_2 and give TiO_2 enough time to oxidize NO_2 with OH or O to HNO_3. Fe_2O_3 deposited on TiO_2 or adjacent to TiO_2 and AC may help to attract more NO which will be oxidized by the active oxygen species. The aforementioned result of the higher activity in the dry condition than

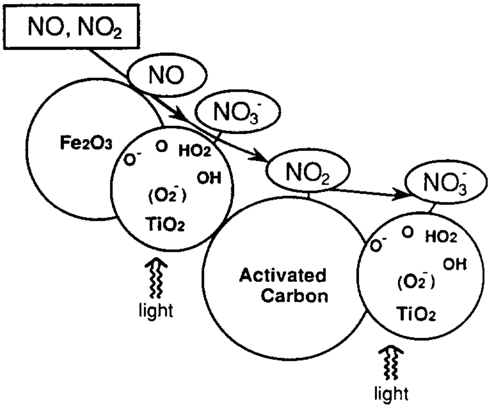

Fig. 4. A reaction scheme presumed for the catalytic oxidation of NO_x (NO and NO_2) to HNO_3 (NO_3^-) by the TiO_2-AC-Fe_2O_3 mixture under photo-illumination.

in the humid condition may reflect the change in relative contribution of each reactive species (O, OH, HO_2, and O^-) to NO/NO_2 oxidation reaction with relative humidity (the amount of H_2O or OH^- interacting with TiO_2/AC/Fe_2O_3). Further studies using some spectroscopic techniques like FTIR, ESR and others to obtain information concerning the surface species or reaction intermediates will be performed for evaluation of the reaction mechanism.

Conclusions

A very rapid photocatalytic oxidation of NO to NO_2 and HNO_3 was first confirmed for TiO_2 powders. By mixing TiO_2 with AC and Fe_2O_3 powders, most of NO and NO_2 at ppm level in air was converted to HNO_3 which was captured on the surface of the catalyst. Although the reaction mechanism has not been clearly elucidated, the important role of reactive oxygen species generated on the photoactivated TiO_2 was supposed. AC and Fe_2O_3 remarkably increased the catalytic activity for NO_x removal, probably due to their high adsorptive activity for NO/NO_2. Applicability of the photocatalyst to removal of low concentration NO_x from air has been implied.

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