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Studies on Low-temperature De-NO$_x$ System over TiO$_2$-based Photocatalysts

YAMAMOTO AKIRA

2015
Preface

Photocatalysis has been investigated since the early part of 19th century. In the history of photocatalysis, the most innovative work is the discovery of water decomposition using TiO$_2$ electrodes under UV-light irradiation (Honda–Fujishima Effect) in 1972. The discovery accelerated the researches on photocatalysis, and at present, many researchers are dealing with the photocatalysts and the related phenomena. Water decomposition is eagerly investigated not only to solve the energy problem but also to imitate plant photosynthesis (i.e., artificial photosynthesis). On the other hand, one of the most promising fields on photocatalysis is decomposition of organic pollutants for air purification. Many researches have been done in this topic, and there are some examples commercialized. However, up to date, water decomposition using photocatalysts has not been commercialized, and the application range in decomposition of organic pollutants have been limited. The essential and potential problem is the low activity (low conversion and/or low apparent quantum yield) of the photocatalysts, and the improvement is the most important theme to put the photocatalytic system into practical use.

It is assumed that the cause of the low activity is not the same in these two systems. In water decomposition, a large amount of substrate (i.e., H$_2$O) exists in the system and is fully supplied to a catalyst surface in the reaction condition. Thus, the low activity is related to a material itself used as a photocatalyst. In contrast, substrate concentrations are typically low in decomposition of organic pollutants if the target is air purification. In such a low concentration system, the catalytic activity is limited by diffusion and adsorption of substrates. Although there were many investigations to improve the adsorption of substrates, the kind of substrate and environments of the target (e.g., temperature, concentration, and co-existential gas) restrict the activity ultimately. The limitation would narrow the application range in photocatalysts in air purification.

Considering the concentration range of substrates, the optimum concentration, at which photocatalysts show high performance, should be exist (naturally, it depends on the kind of substrate). At a high concentration of substrates, the conversion become low because it defined as a ratio of products to substrates added into the system. Lowering the concentration of substrates leads to low conversion because of the limitation of its diffusion and adsorption. Thus, the optimum target concentration should be chosen to draw the maximum performance of photocatalysts. In addition, a
clear advantage is required in economic and environmental viewpoints for the practical use of photocatalysts because light energy is not inexpensive compared to thermal energy.

On the other hand, emission of nitrogen oxide (NO\(_x\)) causes serious environmental problems such as acid rain and photochemical smog. In developed countries, the acid rain and the photochemical smog have been actualized and become visible since the first part of 19th century. The acid rain killed plants, polluted rivers and lakes, and damaged stone figures and buildings. The photochemical smog damaged eyes and skin of human and caused serious health problems. In Japan, it was recognized that these environmental problems are serious in both human health and ecological system during the era of high-speed economic growth. The first regulation of NO\(_x\) emission was introduced based on the air pollution control act (1973) in Japan. The regulation accelerated the research on the removal technology of NO\(_x\) (de-NO\(_x\)). At present, the regulation is becoming stricter step by step, and the researchers in academia and company are challenging the improvement of the de-NO\(_x\) technology.

NO\(_x\) exhausted from motor vehicles has been strictly regulated in these years, and thereby the novel and innovative approaches are strongly required to control it. As a matter of course, decomposition of NO\(_x\) is difficult once NO\(_x\) is exhausted and diffused into the air because of the above-mentioned reason. Thus, NO\(_x\) is removed in a concentrated condition prior to its diffusion into the air. Even in such a concentrated condition, the actual concentration of NO\(_x\) is not high in the exhaust gas from motor vehicles (< 1000ppm). Although photocatalysts would have a potential to decompose it effectively in terms of its concentration range, the performance of photocatalysts has not been evaluated adequately. Thus, in this thesis, the target was fixed in NO\(_x\) removal in the exhaust gas using photocatalysts. To meet the future’s regulation of NO\(_x\) emission, the photocatalyst is one of the candidates even though it has a potential disadvantage of use of light energy.

The theme on this thesis is evaluation, application, and developments of photocatalysts for de-NO\(_x\) system under practical exhaust gas conditions, and elucidation of the working mechanism. Two types of photocatalytic systems were investigated in this viewpoint. One is selective catalytic reduction of NO with NH\(_3\) over TiO\(_2\)-based photocatalysts; in this study, the activity was improved into a satisfactory level at a practical gas hourly space velocity (GHSV) by means of the improvement of both the system and the photocatalyst based on the reaction mechanism. Effects of the reaction temperature were investigated in detail, and were clearly explained using kinetic and
thermodynamic parameters by the aid of kinetic analysis. This is a novel approach to interpret the
effect of the reaction temperature on photocatalysis using kinetic analysis. Besides, the author
successfully developed visible-light-sensitive photocatalysts combining various dyes with TiO$_2$. In
both investigations, improvements of the activity were achieved and the reasonable mechanisms of
the activity improvements were proposed. In addition, effect of SO$_2$ gas, which is a poisoning gas for
the catalysts, was investigated, and the poisoning mechanism was proposed in the photocatalytic
system. Another approach for the NO$_x$ removal at low temperatures is NO$_x$ storage on TiO$_2$-based
photocatalysts. In this research, the author demonstrated the modification of TiO$_2$ with Ba species
greatly enhanced the performance of NO$_x$ storage under UV-light irradiation. The role of Ba was
investigated by means of various spectroscopic methods and the Ba–Ti mixed oxide phase was
proposed to be active components for NO$_x$ storage. In the above two types of de-NO$_x$ systems using
photocatalysts, the author demonstrated the effectiveness of the photocatalysis for de-NO$_x$ system in
the exhaust gas by means of development of the photocatalytic system and the photocatalysts. The
author hopes that the photocatalytic de-NO$_x$ system is commercialized into practical use in exhaust
gas and contributes to the solution of the environmental problems.

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Akira Yamamoto

Kyoto,
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General Introduction

De-NO\textsubscript{x} technology in stationary emission sources

Nitrogen oxide (NO\textsubscript{x}, \(x = 1, 2\)), which is one of the air pollutants, causes acid rain and photochemical smog. Emission of NO\textsubscript{x} was strictly regulated in terms of the environmental protection. Emission sources of NO\textsubscript{x} were classified into two types: stationary emission sources (e.g., thermal power plants and incinerators) and mobile emission sources (e.g., automobiles, ships, and trucks). In both NO\textsubscript{x} emission sources, catalytic technologies have been investigated and developed for NO\textsubscript{x} emission control. Reduction of NO\textsubscript{x} to harmless N\textsubscript{2} is intrinsically difficult because the exhaust gas includes excess O\textsubscript{2} in the air; the reduction of NO\textsubscript{x} should be done under such a oxidative condition. In the stationary emission sources, selective catalytic reduction with NH\textsubscript{3} (NH\textsubscript{3}-SCR) is used to control the NO\textsubscript{x} emission in the presence of excess O\textsubscript{2}. The NH\textsubscript{3}-SCR systems were at first installed in Japan in the late 1970s, and nowadays, are used worldwide for the control of NO\textsubscript{x} emission from the stationary emission sources due to the high efficiency and economics.\textsuperscript{1-3} A typical catalyst for the NH\textsubscript{3}-SCR is a supported vanadium oxide (V\textsubscript{2}O\textsubscript{5}) catalysts promoted by tungsten and molybdenum oxide. The operating temperature is typically over 573 K, at which NO\textsubscript{x} is efficiently decomposed to N\textsubscript{2} over the catalyst.\textsuperscript{2,4} In the NH\textsubscript{3}-SCR, NH\textsubscript{3} functions as a reductant and reacts with NO to form N\textsubscript{2}. The detail reaction mechanisms were reviewed in the previous reports.\textsuperscript{5} One of the problems in the NH\textsubscript{3}-SCR system is a deactivation of the catalyst by poisoning materials such as SO\textsubscript{x}, halogen compounds, and particulate matter (PM) in the exhaust gas. To avoid the catalyst deactivation, the removal equipment for the poisoning materials are installed prior to the de-NO\textsubscript{x} system (i.e., desulfurization, de-halogen, dust collection, and PM combustion). As a result, the temperature of the exhaust gas decreased to approximately 473 K, and below 473 K the above-mentioned V\textsubscript{2}O\textsubscript{5} catalysts do not work efficiently.\textsuperscript{5} Thus, undesired re-heating process in the V\textsubscript{2}O\textsubscript{5} catalysts is necessary to obtain the high-efficiency of NO\textsubscript{x} removal in the NH\textsubscript{3}-SCR system.

De-NO\textsubscript{x} technology in mobile emission sources

NO\textsubscript{x} emission from the mobile sources is a serious problem. In Japan, the regulation in mobile NO\textsubscript{x} emission sources was introduced in 1973 based on the air pollution control act, and have become stricter step by step to date. In addition, new emission standards are planned to be introduced.
and the emission amount is restricted more strictly in the near future.\textsuperscript{6} The typical de-NO\textsubscript{x} catalyst is a three-way catalyst and it is installed in motor vehicles with gasoline engines. The three way catalyst, which is composed of Pt, Pd, and Rh, works efficiently around the stoichiometric air-to-fuel (A/F) ratio of 14.7. A typical A/F dependence of the conversion of NO, HC, and CO is shown in Fig. 1.\textsuperscript{7} The removal efficiency of NO\textsubscript{x} drastically decreased with increasing the A/F ratio from 14.7. In motor vehicles with gasoline engines, the A/F ratio is controlled by adjusting engine operation in response to a signal output from a gas sensor, such as an oxygen sensor, to obtain the high efficiency.

![Figure 1](image-url)

**Figure 1.** Effect of air-to-fuel ratio on the conversion of NO, CO, and HC. Reprinted with modifications from ref. 7.

**NO\textsubscript{x} emission in lean conditions**

Diesel engines and lean-burn gasoline engines have an advantage in the fuel economy compared to the gasoline engines operated at the stoichiometric point, and use of these engines lowers the fuel consumption up to 30\%.\textsuperscript{8} In the near future, use of the diesel and lean-burn engines will spread due to the fuel economy and low CO\textsubscript{2} emission because the emission amount of CO\textsubscript{2} from motor vehicles is regulated as well as the NO\textsubscript{x} emission.\textsuperscript{6} The diesel and lean-burn engines are operated at a high A/F ratio of 25–60, where three way catalysts cannot decompose the NO\textsubscript{x}. 
efficiently. Mainly three technologies have been developed for NO\textsubscript{x} removal at high A/F ratio: direct decomposition, NH\textsubscript{3}-SCR, and NO\textsubscript{x} storage and reduction (NSR).

Direct decomposition of NO\textsubscript{x} is an ideal route for NO\textsubscript{x} removal without any reductant as shown in eq. 1;

\[ \text{NO} \rightarrow 1/2 \text{N}_2 + 1/2 \text{O}_2 \] (1).

Several catalysts were reported for the direct decomposition such as Cu-zeolites\textsuperscript{9-10}, perovskite-type oxides\textsuperscript{11-13}, and Ag/La\textsubscript{0.6}Ce\textsubscript{0.4}CoO\textsubscript{3}\textsuperscript{14}. However, the reaction proceeded efficiently only at high temperatures, and the activity decreased drastically in the presence of O\textsubscript{2}, H\textsubscript{2}O, and SO\textsubscript{2}\textsuperscript{8}. Although many researches have been carried out, it is not applicable in the practical situations at least in this stage.

The NH\textsubscript{3}-SCR technology was developed for the stationary emission sources at first, and then was applied to the mobile emission sources such as diesel engines in ships, trucks, and buses. In the NH\textsubscript{3}-SCR, urea is typically used as a NH\textsubscript{3} source (urea-SCR). Urea is introduced to the exhaust gas and the introduced urea decomposes to NH\textsubscript{3} prior to the catalyst bed. The urea-SCR was widely commercialized in the mobile emission sources because it can decompose the NO\textsubscript{x} to N\textsubscript{2} selectively with high activity under lean conditions. However, in the mobile emission sources, a problem of the urea-SCR is low activity below 473 K as well as the stationary emission sources. Recently, International Council for Clean Transportation (ICCT) pointed out the impact of the NO\textsubscript{x} emission in the initial stage of start-up of engines on the total emission amounts; in the cold start condition below 473 K (approximately 800 s), urea cannot be injected because of the low activity of the catalyst\textsuperscript{15}. Thus, improving the activity at low temperatures is a serious challenge in NH\textsubscript{3}-SCR.

A concept of NSR technology was proposed by TOYOTA researchers in Japan in the mid-1990s\textsuperscript{16-17}. The typical NSR catalyst is composed of three components: precious metal (e.g., Pt), basic materials such as alkali and alkali earth metal oxides (e.g., BaO), and supports (e.g., Al\textsubscript{2}O\textsubscript{3}). The mechanism of NSR was shown in Fig. 2 using as an example of a Pt/BaO/Al\textsubscript{2}O\textsubscript{3} catalyst. In the exhaust gas, NO is a main component in NO\textsubscript{x} even in the presence of excess O\textsubscript{2}. Under the lean conditions, NO in the exhaust gas is oxidized to NO\textsubscript{2} on Pt sites and then trapped onto BaO sites as nitrate (NO\textsubscript{3}⁻) forms. As the catalyst surface becomes saturated with NO\textsubscript{x} species, it needs to be regenerated. After the storage period under the lean conditions, fuels are added to the catalysts for a short period, and the injected fuels reduce the stored NO\textsubscript{x} to N\textsubscript{2} (fuel-rich condition). The alternative
operation of the lean and rich conditions leads to the effective removal of NO\textsubscript{x} from lean-burn engines. The problems in the NO\textsubscript{x} storage systems are the low tolerance to SO\textsubscript{x} and the use of precious metals such as Pt and Rh. Typically, the exhaust gas includes SO\textsubscript{2}, and it drastically deactivates the catalyst performance. In the NSR catalyst, the use of precious metals is inevitable to both oxidize NO into NO\textsubscript{2} under lean conditions and reduce NO\textsubscript{x} to N\textsubscript{2} under the rich conditions.

**Figure 2.** Schematic representation of NO\textsubscript{x} storage and reduction in Pt/BaO/Al\textsubscript{2}O\textsubscript{3} system.

**Demand for low-temperature de-NO\textsubscript{x} system**

The NH\textsubscript{3}-SCR technology is used in not only the stationary emission sources but also the mobile emission sources. In both of the emission sources, a common and fundamental problem of V\textsubscript{2}O\textsubscript{5} catalysts is its high operating temperature (623–673 K)\textsuperscript{4} as mentioned above, and low-temperature catalysts for NH\textsubscript{3}-SCR are strongly desired. Several researchers have investigated the low temperature catalyst for NH\textsubscript{3}-SCR.\textsuperscript{4} Fe- and Cu-zeolite catalysts show high activity for the NH\textsubscript{3}-SCR at 473–573 K.\textsuperscript{18-22} Although these catalysts are commercially used, the activity decreased below 473 K.\textsuperscript{4} Mn-based catalysts were reported for effective low-temperature catalysts below 473 K.\textsuperscript{23-26} The Mn-based catalysts were investigated in morphology, oxidation state of active Mn sites, loading of Mn on metal oxides, and addition of third components into the catalysts.\textsuperscript{27-28} However,
problems of the Mn-based catalysts were generation of undesired by-products of N$_2$O and the low SO$_2$ tolerance.\textsuperscript{29} The activity in Mn-based catalysts was drastically decreased in the presence of SO$_2$ poisoning gas due to the generation of MnSO$_4$. The generated MnSO$_4$ is stable even at high temperature (\textit{>} 1000 K),\textsuperscript{29} which means that the re-activation of the catalyst is difficult at moderate temperatures.

\textbf{NH$_3$-SCR systems using photocatalysts}

Photocatalysts are one of the promising materials in terms of such a low temperature operation in NH$_3$-SCR. In 1992, Cant et al. reported the photocatalysis of the reaction between NH$_3$ and NO on a TiO$_2$ surface under UV-light irradiation.\textsuperscript{30} In their isotopic experiment, $^{14}$N$^{15}$N was formed using $^{15}$NH$_3$ and $^{14}$NO over TiO$_2$, which clearly shows that N$_2$ was formed via the reaction between NO and NH$_3$. Although their work was pioneering, there was no report about this reaction for the 8 years after their report possibly because of the following three reasons. The two reasons were the fact that their reaction system was different from the practical NH$_3$-SCR system; they carried out the reaction (i) in the absence of O$_2$ (ii) using a closed reactor system. The researchers normally carried out the activity tests in the NH$_3$-SCR in the presence of excess O$_2$ using a continuous flow reactor because their target is the exhaust gas including O$_2$ gas. The third reason was (iii) the low activity; N$_2$ produced for 30 min was 3.6 $\mu$mol, and N$_2$ formation rate was calculated to be 7.2 $\mu$mol h$^{-1}$ (catalyst: ca. 50 mg, light source: 100W mercury lump).

In 2000, Tanaka et al. reported the NH$_3$-SCR using photocatalysts (photo-SCR) in the presence of O$_2$, and in their research, they confirmed the formation of N$_2$ over Rb-ion-modified V$_2$O$_5$/SiO$_2$ photocatalysts under UV-light irradiation. That is the first report in NH$_3$-SCR using photocatalysts in the presence of O$_2$.\textsuperscript{31} In 2002 and 2003, the same group revealed TiO$_2$/SiO$_2$\textsuperscript{32} and TiO$_2$\textsuperscript{33-34} photocatalysts showed high activity in photo-SCR. Especially in the case of TiO$_2$, the high activity was achieved using a continuous flow reactor; inlet NO (1000ppm) was converted to N$_2$ at the conversion of 80%. The N$_2$ formation rate was calculated to be 200 $\mu$mol h$^{-1}$, which was 28 times higher that by Cant et al. at the GHSV of 4000 h$^{-1}$ although a large amount of TiO$_2$ (1.2 g) was used for the reaction. (light source: 300W ultra-high pressure Xe lamp). Teramura et al. also investigated the reaction mechanism using kinetic\textsuperscript{35} and spectroscopic methods such as FT-IR spectroscopy,\textsuperscript{34} and
ESR. In this mechanism (Fig. 3), amide radicals (·NH$_2$) generated under light irradiation reacts with NO in the gas phase to form N$_2$ (Eley–Rideal mechanism). The rate-determining step of the photo-SCR was decomposition of nitrosoamide (NH$_2$NO) intermediates (step 4).\textsuperscript{35}

Yamazoe et al. investigated various kinds of TiO$_2$ photocatalysts,\textsuperscript{37} and metal oxide promoted TiO$_2$ catalysts,\textsuperscript{38} and successfully improved the activity of photo-SCR. Among the various photocatalysts investigated, WO$_3$/TiO$_2$ photocatalysts showed the highest activity, and NO conversion of 96\% and N$_2$ selectivity to N$_2$ of $> 99\%$ were obtained at a GHSV of 25,000 h$^{-1}$. The NH$_3$ adsorption experiments revealed that the loading of WO$_3$ on TiO$_2$ increased the amount of weak Lewis acid sites. The DFT calculations suggested that the decomposition rate of the NH$_2$NO intermediates on weak Lewis acid sites was faster than on strong Lewis acid sites. Thus, the increase of weak Lewis acid sites by loading of WO$_3$ promotes the decomposition of the NH$_2$NO intermediates, and it leads to the high activity.\textsuperscript{39} Their results give the important suggestion that the promoting the decomposition of the NH$_2$NO intermediates is effective to improve the activity. In addition, it is worth mentioned that the photo-SCR over TiO$_2$ proceeds under visible light ($\lambda = 400$–450 nm) although TiO$_2$ itself does not absorb the visible light. The response to visible light was explained by a unique photo-activation mechanism of NH$_3$: the direct electron transfer from N 2p level of the adsorbed NH$_3$ to the conduction band of TiO$_2$ (in situ doping).\textsuperscript{40-41} The concept would contributed to the development of new type of visible-light-sensitive photocatalysts.
Part I: Development of Photo-assisted Selective Catalytic Reduction of NO with NH₃ over Photocatalysts

To put the photo-SCR into the practical de-NOₓ system for diesel and lean-burn engines, the following two problems should be considered:

(i) Improving the activity for the practical GHSV conditions.

\[
\text{NO conversion} > 90\%, \text{N}_2 \text{ selectivity} > 90\%, \text{GHSV} = 100,000 \text{ h}^{-1}
\]

(ii) Evaluation of the tolerance to SOₓ poisoning

To improve the activity, the author focused on acceleration of elementary steps in the reaction mechanism in Fig. 3. The previous kinetic analysis revealed that the reaction order for NH₃ was approximately zero, \(^{35}\) which means that the reaction rate of NH₃ adsorption (Step 1) is faster than those of the other elementary steps. Thus, promotion of the other steps (Step 2–4) is necessary to improve the activity. Generally, effective improvement of the activity is achieved by accelerating a relatively slow step that dominates the overall reaction rate. Thus, accelerating the rate-determining...

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**Figure 3.** Proposed reaction mechanism of photo-SCR over a TiO₂ photocatalyst. Reprinted with modifications from ref. 34.
step (i.e., Step 4 in the case of photo-SCR)\textsuperscript{35} is considered to be the most effective to improve the activity. Moreover, in the case of photocatalysis, the reaction rate of the photo-excitation step (Step 2) is expected to have a great impact on the activity, and the promotion of the Step 2 should be effective to improve the activity. In addition, the tolerance to SO\textsubscript{x} poisoning should be evaluated to put photo-SCR into practical use.

**Part II: Low-temperature NO\textsubscript{x} Storage under Lean-conditions: Photo-assisted NO\textsubscript{x} Storage over Photocatalysts**

In the exhaust gas from diesel and lean-burn engines, NO\textsubscript{x} removal technology at low temperatures (< 473 K) is strongly desired to decrease the total NO\textsubscript{x} emission amount in practical driving conditions including a cold start during 800 s from the engine start-up.\textsuperscript{15} The NSR catalysts also do not work efficiently below 473 K. Thus, a new technology must be developed to achieve such a low temperature removal of NO\textsubscript{x}. In this standpoint, we focused on the concept of the above-mentioned NSR catalysts. In NO\textsubscript{x} storage period in Fig. 2, Pt works as oxidation sites for NO into NO\textsubscript{2}, and the activity is low at low temperatures.\textsuperscript{42-43} Thus, one of the reasons of the low activity in the NSR catalyst should be the low NO oxidation ability of Pt. In contrast, it was previously reported that the NO oxidation proceeded over TiO\textsubscript{2} photocatalysts and TiO\textsubscript{2}-based photocatalysts at room temperature under light irradiation.\textsuperscript{44-50} These reports indicate that the TiO\textsubscript{2} photocatalysts have a potential to replace the role of Pt (i.e., oxidation of NO) even at low temperatures. Thus, utilization of the photocatalysis has two advantages compared to the typical NSR catalyst on NO\textsubscript{x} storage; it lead to not only lowering the operation temperature but also the replacement of Pt. On this background, we investigated and evaluated the performance of photocatalysts under a practical GHSV and NO concentration conditions to develop the low temperature NO\textsubscript{x} removal technology without using precious metals.

**References**


Chapter 1

Effect of Reaction Temperature on Photocatalytic Activity for Photo-SCR of NO with NH$_3$ over a TiO$_2$ Photocatalyst

Abstract

Effects of reaction temperature on activity of photo-assisted selective catalytic reduction (photo-SCR) of NO with NH$_3$ were investigated at very high GHSV condition (100,000 h$^{-1}$). The reaction temperature had a significant effect on the photo-SCR activity over a TiO$_2$ photocatalyst. Maximum NO conversion was achieved at 433 K (NO conversion = 84%, N$_2$ selectivity = 100%). The apparent activation energies in the low and high temperature range were evaluated to be 9.0 kJ mol$^{-1}$ (353–433 K) and –2.7 kJ mol$^{-1}$ (493–593 K), respectively. Kinetic analysis revealed that the rate-determining step in the photo-SCR was decomposition of NH$_2$NO intermediates in all the range of the reaction temperature (353–593 K). The reaction temperature affects not only the rate constant of decomposition of NH$_2$NO intermediates but also the total number of active sites ($[S]_0$) and the equilibrium constant of NH$_3$ adsorption, resulting in the dynamic change of the reaction rate.
Introduction

The removal of NO\textsubscript{x} from the exhaust gas of diesel engines has become a major goal for the automotive industry in the last few years. Among the deNO\textsubscript{x} technologies, the selective catalytic reduction (SCR) is currently regarded as the most promising one for heavy-duty and light-duty diesel engines.\textsuperscript{1} The SCR process is based on the reaction between NO\textsubscript{x} present in the flue gases and NH\textsubscript{3} (produced from urea) in the presence of O\textsubscript{2}. The V\textsubscript{2}O\textsubscript{5}–WO\textsubscript{3}/TiO\textsubscript{2} catalyst, which is commonly used for stationary SCR systems, shows a relative high conversion at 623 K–723 K.\textsuperscript{2} However, this type of catalyst has insufficient performance for diesel engines because the exhaust gas from diesel engines has wide temperature range (373 K–923 K) depending on the engine load.\textsuperscript{3} Ion exchanged zeolites, which are practically used in diesel cars, convert NO\textsubscript{x} to N\textsubscript{2} with high conversion and selectivity over 433 K.\textsuperscript{4-7} However, the ion exchanged zeolites do not work efficiently under 433 K (Conversion of NO is below 40% at 423 K in the case of Cu-ZSM-5 and Fe-ZSM-5, GHSV = 100,000 h\textsuperscript{-1}).\textsuperscript{8} On the other hand, non-supported MnO\textsubscript{x}\textsuperscript{9-10} and supported MnO\textsubscript{x} catalysts\textsuperscript{11} show high activity for the NH\textsubscript{3}-SCR at low temperature, however, the selectivity to N\textsubscript{2} is low.

Photocatalyst, which works at ambient temperature, is one of promising candidates for the de-NO\textsubscript{x} process at low temperature. Pichat et al. initially reported that NO produce N\textsubscript{2}O and N\textsubscript{2} over UV-irradiated TiO\textsubscript{2} at room temperature.\textsuperscript{12} We have reported that photo-assisted selective catalytic reduction of NO with NH\textsubscript{3} (photo-SCR) in the presence of O\textsubscript{2} proceeds over a TiO\textsubscript{2} photocatalyst at room temperature.\textsuperscript{13-16} More than 90\% of NO conversion and approximately 100 \% of selectivity to N\textsubscript{2} were achieved in our systems (GHSV = 8,000 h\textsuperscript{-1}).\textsuperscript{16-18} Approximately 10,000 h\textsuperscript{-1} is suitable GHSV for use with typical stationary sources such as power plants, blast furnace, and incinerator. On the other hand, in the case of diesel engines, catalysts are required to work at a very high GHSV region because of a limited installation area of the process for the removal of NO\textsubscript{x} and a high flow rate of the exhaust gas. Ultimately, the catalyst volume must be of the order of the engine cylinder volume (typical GHSV in three-way catalyst amount to about 100,000 h\textsuperscript{-1}).\textsuperscript{3} This means that driving
at much higher GHSV is absolutely imperative in the case that the photo-SCR applies to the removal of NO\textsubscript{x} from the exhaust gas of diesel engines. Fig. 1 shows dependence of conversion of NO and selectivity to N\textsubscript{2} for the photo-SCR of NO with NH\textsubscript{3} over TiO\textsubscript{2} at room temperature on GHSV. Unfortunately, the conversion of NO decreased with increasing the GHSV, although the selectivity to N\textsubscript{2} (ca. 96 \%) did not change. The conversion of NO descended to 40\% at 100,000 h\textsuperscript{-1}. In order to use this photocatalytic system for the industrial SCR system, higher activity is required in the high GHSV region.

The mechanism of photo-SCR of NO with NH\textsubscript{3} over TiO\textsubscript{2} has already been reported by our group as shown in Scheme 1.\textsuperscript{19} The process of decomposition of NH\textsubscript{2}NO intermediates is a rate-determining step at room temperature in the presence of excess O\textsubscript{2} gas.\textsuperscript{17} This process will be promoted by increasing the reaction temperature because it proceeds without photoirradiation, indicating that the reaction rate can be dramatically accelerated by increasing the reaction temperature. Some researchers reported that increment of reaction temperature successfully improved activity for photocatalytic reactions.\textsuperscript{20-23} However, the effects of the temperature on the rate of photocatalytic reactions in the gas phase have rarely been studied. In the present study, we investigated effects of the reaction temperature on the photocatalytic activity of the photo-SCR.
**Figure 1.** Conversion of NO (●) and N₂ selectivity (▲) in the photo–SCR as a function of GHSV.
(catalyst amount: 110 mg, NO: 1000 ppm, NH₃: 1000 ppm, O₂: 2 %)

**Scheme 1.** Proposed reaction mechanism of the photo–SCR over TiO₂.
Experimental

TiO₂ (ST-01, Ishihara Sangyo Kaisha, Ltd.,) which has an anatase phase, was hydrated in distilled water for 2 h at 353 K and was dried at 353 K overnight, followed by calcination in dry air at 673 K for 3 h. The specific surface area of the prepared TiO₂ was evaluated to be 93 m² g⁻¹ by the Brunauer–Emmett–Teller (BET) method using N₂ adsorption isotherm at 77 K.

The photo-SCR was carried out in a conventional fixed bed flow system at an atmospheric pressure at various temperatures. A 110 mg of catalyst was fixed with quartz wool and filled up in a quartz reactor which has flat facets (12 mm × 10 mm × 1 mm). Before reactions, catalysts were pretreated at 673 K by flowing 10% O₂ / He gas at 50 mL min⁻¹ for 60 min. The reaction gas composition was as follows: NO 1000 ppm, NH₃ 1000 ppm, O₂ 2%, He balance gas. A 200 W Hg–Xe lamp equipped with fiber optics, collective lens, and a mirror (San-Ei Electric Co., Ltd., UVF-204S type B) was used as a light source and the sample was irradiated from one side of the flat facets of the reactor. The measured light irradiance was 360 mW cm⁻². N₂ and N₂O products were analyzed by a SHIMADZU GC-8A TCD gas chromatograph with MS-5A and Porapak Q columns, respectively.

Adsorption isotherms of NH₃ were measured by a volumetric method using a closed vacuum system. A 0.2 g of TiO₂ were evacuated at 673 K for 30 min and then pretreated by O₂ (80 Torr) at 673 K for 60 min. After evacuating at 673 K for 60 min, the catalyst was cooled down to a given temperature. Before adsorption measurements, the dead volume was measured using Ar gas at each temperature. In the first experiment, adsorption amounts of NH₃ were measured at various equilibrium pressures of NH₃ (physical adsorption and chemical adsorption). After evacuation for 90 min, the second adsorption experiment was carried out (physical adsorption). The chemical adsorption amount of NH₃ was calculated by subtracting the adsorption amount of the second experiment from the one of the first experiment.

Results and discussion

Fig. 2 shows dependence of conversion of NO and selectivity to N₂ for the photo-SCR over TiO₂ on reaction temperature. The selectivity to N₂ slightly increased with increasing the reaction
temperature and then kept up 100% above 453 K. The conversion of NO drastically increased with increasing the reaction temperature. The maximum conversion of NO (84%) was observed at 433 K. However, it decreased with further increment of the reaction temperature. Fig. 3 displays the time course for the photo-SCR over TiO$_2$ at 433 K. The conversion of NO reached to 84% as soon as the TiO$_2$ photocatalyst was irradiated and was kept for at least 480 min, indicating that the TiO$_2$ photocatalyst used in this study was very stable under the reaction condition. The conversion in the photo-SCR system below 433 K is higher than those of Fe and Cu zeolite catalysts (The conversion of NO is below 40% in the case of Cu-ZSM-5 and Fe-ZSM-5 at 423 K at GHSV = 100,000 h$^{-1}$).

Figure 2. Dependence of conversion of NO (●) and N$_2$ selectivity (▲) in the photo–SCR on the reaction temperature. (catalyst amount: 110 mg, NO: 1000 ppm, NH$_3$: 1000 ppm, O$_2$: 2 %, GHSV: 100,000 h$^{-1}$)
We carried out the photo-SCR at lower contact time (catalyst amounts: 16 mg) to evaluate the initial rates. The selectivity to N$_2$ was 100% at all the temperatures. Arrhenius plot (Ln $r$ v.s. 1/T) of the initial rates is shown in Fig. 4. The NO conversion denoted the same tendency of Fig. 2. In the low (353–433 K) and high (493–593 K) temperature range, the logarithm of N$_2$ formation rate shows a good linear relation to the inverse number of the reaction temperature. In these two temperature ranges, following equations were obtained using a linear fitting:

$$\ln r = 6.08 - 1.08 \times 10^3 / T \quad (353 - 433 \text{ K})$$

$$\ln r = 2.98 + 3.26 \times 10^2 / T \quad (493 - 593 \text{ K})$$

where, $r$ is the N$_2$ formation rate (nmol s$^{-1}$) and T is the absolute reaction temperature (K). Using the slope of these equations, the activation energies were estimated to be 9.0 kJ mol$^{-1}$ (353–433 K) and -2.7 kJ mol$^{-1}$ (493–593 K).

**Figure 3.** Time profile of conversion of NO in the photo–SCR at 323 K (●) and 433 K (▲). (catalyst amount: 110 mg, NO: 1000 ppm, NH$_3$: 1000 ppm, O$_2$: 2 %, GHSV: 100,000 h$^{-1}$)
The first increase of the photocatalytic activity at the temperature range in 353–433 K would be due to the acceleration of the rate-determining step, which is the decomposition of NH$_2$NO intermediates at room temperature.\textsuperscript{17} To determine the rate-determining step in the temperature range between room temperature and 553 K, the kinetic study was carried out at various temperatures. The reaction rate of the photo-SCR is expressed as a following formula:

$$ r = k \ P_{NO}^{\alpha} P_{NH_3}^{\beta} P_{O_2}^{\gamma} I^{\delta} $$

where $P_x$ is a partial pressure of $x$ (x = NH$_3$, NO, and O$_2$ ) and $I$ is irradience. To obtain the reaction order ($\alpha$, $\beta$, $\gamma$, and $\delta$) at various temperatures, the photo-SCR was carried out under the condition of the various partial pressures of NO, NH$_3$ or O$_2$, or different light intensities. The reaction orders at each temperature are listed in Table 1.
The rate constant and equilibrium constant of each elementary step are defined on the basis of proposed reaction mechanism as follows:

**STEP 1**\[ \text{NH}_3 + S \rightleftharpoons \text{NH}_3^- - S \] \[ K_1 = \frac{k_1}{k_1} \] \[ (4) \]

**STEP 2**\[ \text{NH}_3^- - S + h\nu \rightleftharpoons \text{NH}_2^- - S^* + H^+ \] \[ K_2 = \frac{k_2}{k_2} \] \[ (5) \]

**STEP 3**\[ \text{NO} + \text{NH}_2^- - S^* \rightleftharpoons \text{NH}_2\text{NO}^- - S^* \] \[ K_3 = \frac{k_3}{k_3} \] \[ (6) \]

**STEP 4**\[ \text{NH}_2\text{NO}^- - S^* \rightleftharpoons \text{N}_2 + \text{H}_2\text{O} + S^* \] \[ K_4 = \frac{k_4}{k_4} \] \[ (7) \]

**STEP 5**\[ \frac{1}{4} \text{O}_2 + S^* + H^+ \rightleftharpoons \frac{1}{2} \text{H}_2\text{O} + S \] \[ K_5 = \frac{k_5}{k_5} \] \[ (8) \]

We calculated the following rate equations by assuming that each step is a rate-determining step:

\[ r = \frac{k_1P_{\text{NH}_3}[S]_0}{1 + (1/K_5P_{\text{O}_2}^{1/4})} \] \[ (9) \]

\[ r = \frac{k_2k_1P_{\text{NH}_3}I[S]_0}{1 + K_5P_{\text{NH}_3} + (1/K_5P_{\text{O}_2}^{1/4})} \] \[ (10) \]

\[ r = \frac{k_3k_1k_2P_{\text{NH}_3}P_{\text{NO}}I[S]_0}{1 + K_1P_{\text{NH}_3} + K_2k_1P_{\text{NH}_3}I + (1 + 1/K_5P_{\text{O}_2}^{1/4})} \] \[ (11) \]

**Table 1.** Reaction orders at each temperature

<table>
<thead>
<tr>
<th>T / K</th>
<th>$\alpha^{*1}$</th>
<th>$\beta^{*2}$</th>
<th>$\gamma^{*3}$</th>
<th>$\delta^{*4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>323</td>
<td>0.01</td>
<td>0.58</td>
<td>0.33</td>
<td>0.75</td>
</tr>
<tr>
<td>373</td>
<td>0.09</td>
<td>0.48</td>
<td>0.19</td>
<td>0.71</td>
</tr>
<tr>
<td>433</td>
<td>0.12</td>
<td>0.46</td>
<td>0.29</td>
<td>0.6</td>
</tr>
<tr>
<td>553</td>
<td>0.17</td>
<td>0.49</td>
<td>0.29</td>
<td>0.58</td>
</tr>
</tbody>
</table>

Reaction orders of $\text{NH}_3^{*1}$, $\text{NO}^{*2}$, $\text{O}_2^{*3}$, and irradiance $^{*4}$.
where, $[S]_0$ is the total number of active sites. The reaction orders of $P_{NO}$ in the Eqs. 9, 10, 11, and 13 do not satisfy the experimental reaction orders at all the temperatures in Table 1. Consequently, Steps 1, 2, 3, and 5 are excluded from candidates for the rate-determining step. The Eq. 12 satisfies the experimental reaction orders at all the temperatures, which indicates that the rate-determining step in the photo-SCR is step of decomposition of NH$_2$NO intermediates (Step 4) in the temperature range studied. The conversion of NO increased with increasing the reaction temperature from 353 K to 433 K because the decomposition process of NH$_2$NO intermediates was promoted by the thermal effect ($k_4$ in Eq. 12 increased as the reaction temperature increased).

The increase of $k_4$ has only a positive effect on the activity. Accordingly, it is unaccountable for the reason why the NO conversion decreased as the reaction temperature increased from 433 K to 593 K. Two reasons have been proposed for the appearance of negative apparent activation energies. One is thermal deactivation of catalysts$^{24}$ and the other is the case that an exothermic and equilibrium reaction in elementary steps have an effect on the overall reaction rate.$^{25}$ To confirm whether thermal deactivation of the catalysts occurs or not, we elevated the reaction temperature in the photo-SCR to 593 K at first, and then lowered it to 353 K (Fig. 5). If the thermal deactivation occurs, NO conversion in the cooling procedure should be lower than that in the heating procedure. The hysteresis curve was not observed between the heating and cooling procedures. This result clearly indicated that the negative apparent activation energy was not due to the thermal deactivation of the catalysts.
In all the elementary steps (Step 1–5), adsorption of NH$_3$ (Step 1) is an exothermic and equilibrium reaction. NH$_3$ adsorption isotherm experiments were carried out at various temperatures as shown in Fig. 6. Amount of NH$_3$ adsorption clearly decreased as the temperature increased. The Langmuir adsorption isotherm was used to describe the NH$_3$ adsorption as follows:

$$\frac{P_a}{q_e} = \frac{P_a}{q_m} + \frac{1}{q_m K_1}$$  \hspace{1cm} (14)

where $q_e$ is the equilibrium adsorption amount ($\mu$mol g$^{-1}$), $P_a$ is the equilibrium partial pressure of NH$_3$ (atm), $q_m$ is the maximum adsorption capacity ($\mu$mol g$^{-1}$), $K_1$ is adsorption equilibrium constant (atm$^{-1}$). The $q_m$ and $K_1$ at each temperature that are obtained using Eq. 14 are listed in Table 2. The increment of the temperature decreased not only the equilibrium constant of NH$_3$ adsorption ($K_1$) but also the maximum adsorption capacity ($q_m$) of NH$_3$. The $q_m$ is corresponding to the number of ammonia adsorption sites, which is assumed to be the total number of active sites ($|S|_0$ in the Eq. 12). From the Eq. 12, the decrease of $|S|_0$ and $K_1$ leads to decline of the overall reaction rate. Thus, we

Figure 5. Temperature cycle test in heating procedure (●) and cooling procedure (△). (catalyst amount: 16 mg, NO: 1000 ppm, NH$_3$: 1000 ppm, O$_2$ 2 %, GHSV: 100,000 h$^{-1}$)
concluded that the overall reaction rate decreased because both the total number of active sites (\( S_0 \)) and the value of \( K_f \) decreased with increasing the temperature from 433 K to 593 K.

Figure 6. \( \text{NH}_3 \) adsorption isotherms on the TiO\(_2\) catalyst at various temperatures: (a) 373 K, (b) 413 K, (c) 473 K, (d) 513 K, and (e) 553 K.

Table 2. Langmuir isotherm parameters for the \( \text{NH}_3 \) adsorption on the TiO\(_2\) at various temperatures.

<table>
<thead>
<tr>
<th>T / K</th>
<th>( q_m ) / ( \mu \text{mol g}^{-1} )</th>
<th>( K_f ) / atm(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>373</td>
<td>160.9</td>
<td>( 1.65 \times 10^4 )</td>
</tr>
<tr>
<td>413</td>
<td>146.5</td>
<td>( 8.96 \times 10^3 )</td>
</tr>
<tr>
<td>473</td>
<td>90.1</td>
<td>( 3.13 \times 10^3 )</td>
</tr>
<tr>
<td>513</td>
<td>57.8</td>
<td>( 1.64 \times 10^3 )</td>
</tr>
<tr>
<td>553</td>
<td>39.8</td>
<td>( 9.45 \times 10^2 )</td>
</tr>
</tbody>
</table>

In summary, three kinetic and thermodynamic parameters should be considered as a function of temperature to describe the reaction rate of the photo-SCR: (i) the rate constant of decomposition of \( \text{NH}_2\text{NO} \) intermediates \( (k_d) \), (ii) the total number of active sites \( (S_0) \), and (iii) the
equilibrium constant of NH$_3$ adsorption ($K_i$). In the low temperature range (353–433 K), $k_4$ dominates the overall reaction rate, which results in the straight and negative line in Arrhenius plots. In the middle temperature range (433–493 K), $[S]_0$ and/or $K_i$, which decreases as the temperature increases, starts to contribute to the reaction rate, which results in the curved Arrhenius plots. In the high temperature range (493–593 K), contribution of $[S]_0$ and/or $K_i$ to the overall reaction rate becomes more dominant than that of $k_4$. As a result, the negative apparent activation energy appeared in high temperature range.

**Conclusions**

We found the reaction temperature had a significant effect on the photo-SCR activity over a TiO$_2$ photocatalyst. The photocatalytic activity was increasing with an increase of the reaction temperature from 353 K to 433 K, however decreasing from 433 to 593 K. Maximum conversion was 84% at the high GHSV of 100,000 h$^{-1}$ at 433 K. The high efficiency of the NO removal indicates that the photo-SCR system have a potential for the practical de-NO$_x$ system in diesel engines. The kinetic analysis revealed that the rate-determining step in the photo-SCR is decomposition of NH$_2$NO intermediates in all the temperature range studied. The calculated rate equation and the NH$_3$ adsorption experiment indicated that the absorption amount of NH$_3$ at high temperature affords the key to achieve the high NO conversion, because of a trade-off relationship between the absorption of NH$_3$ and the decomposition of NH$_2$NO intermediates. We believe that thermodynamics and kinetics is becoming more important in the field of photocatalysis as well as catalysis.

**References**


Chapter 2

Visible-Light-Assisted Selective Catalytic Reduction of NO with NH$_3$ on Porphyrin Derivative-Modified TiO$_2$ Photocatalysts

Abstract

Porphyrin-derivative modified TiO$_2$ photocatalysts showed high photocatalytic activity for the selective catalytic reduction of NO with NH$_3$ in the presence of O$_2$ under visible-light irradiation. Tetra(p-carboxyphenyl)porphyrin (TCPP) was the most effective photosensitizer among the five porphyrin derivatives investigated. NO conversion and N$_2$ selectivity of 79.0% and 100% respectively, were achieved at a gas hourly space velocity of 50,000 h$^{-1}$. UV–Vis and photoluminescence spectroscopies revealed the presence of two species of TCPP on the TiO$_2$ surface; one was a TCPP monomer and the other was a H-aggregate of the TCPP molecules. It was concluded that the TCPP monomer is an active species for the photo-assisted selective catalytic reduction (photo-SCR). Moreover, an increase in the fraction of H-aggregates with the increasing TCPP loading amount resulted in a decrease in the decrease of the photocatalytic activity of the photo-SCR.
Introduction

NO\textsubscript{x}, which is present in the exhaust gas of stationary emission sources, is removed by the selective catalytic reduction with NH\textsubscript{3} (NH\textsubscript{3}-SCR) over vanadium oxide-based catalysts according to the following equation: (4NO + 4NH\textsubscript{3} + O\textsubscript{2} → 4N\textsubscript{2} + 6H\textsubscript{2}O).\textsuperscript{1-3} The NH\textsubscript{3}-SCR process is performed at temperatures above 573 K. To save the energy used for heating the catalyst bed, novel catalysts are required for performing the NH\textsubscript{3}-SCR at low temperatures.\textsuperscript{4-6} Photocatalysis is one of the promising candidates for the NH\textsubscript{3}-SCR because photocatalytic reactions proceed at room temperature. We have reported the photo-assisted selective catalytic reduction (photo-SCR) of NO with NH\textsubscript{3} in the presence of O\textsubscript{2} over TiO\textsubscript{2} photocatalysts under UV-light irradiation.\textsuperscript{7-10} In this system, the NO conversion and N\textsubscript{2} selectivity of 90\% and 99\%, respectively, were achieved at a gas hourly space velocity (GHSV) of 8,000 h\textsuperscript{−1}, which is sufficient for the deNO\textsubscript{x} process in typical stationary sources such as power plants, blast furnaces, and incinerators. However, a very high GHSV was required in diesel engines owing to the limited installation space of the deNO\textsubscript{x} process and a high flow rate of the exhaust gas. The volume of the catalyst was required to be of the order of the volume of the diesel engine cylinder (typical GHSV in a three-way catalyst is approximately 100,000 h\textsuperscript{−1}).\textsuperscript{11} Unfortunately, the NO conversion decreased with the increasing GHSV in the photo-SCR system and it decreased to 40\% at a GHSV of 100,000 h\textsuperscript{−1}.\textsuperscript{10} Therefore, the photocatalytic activity of the photo-SCR has to be improved at a high GHSV region in order to remove the NO\textsubscript{x} from the exhaust gas of diesel engines.

Expansion of the adsorption wavelength to the visible-light region is an effective way of improving the photocatalytic activity. TiO\textsubscript{2} photocatalysts do not absorb visible light because of their wide band gap (> 3.2 eV). Surprisingly, the photo-SCR proceeds to some extent under visible-light irradiation over the TiO\textsubscript{2} photocatalysts. This is due to the direct electron transfer from the electron donor level of the N 2p orbital of the adsorbed NH\textsubscript{3} to the conduction band of the Ti 3d orbital of TiO\textsubscript{2} (in-situ doping).\textsuperscript{12-13} However, the photocatalytic activity under visible-light irradiation is not sufficient for the application of the photo-SCR technology to the system at a high GHSV region. Thus, the proposed study aims to increase the photocatalytic efficiency under visible-light irradiation.
Porphyridin derivatives have absorption bands in the visible region owing to the $\pi-\pi^*$ transitions. Porphyridin derivatives are widely used as sensitizers in dye-sensitized solar cells (DSSCs) and dye-sensitized photocatalysts under visible-light irradiation owing to the following properties: 1) they exhibit intense absorption bands in the visible-light region, and 2) their photochemical and electrochemical properties can be tuned by the modification of the substituents and selection of the central metal. In previous studies, the porphyridin-sensitized photocatalysts were used for performing liquid phase reactions such as the hydrogen production from water, and degradation of organic compounds. However, there are only a few reports on the reactions involving porphyridin-sensitized photocatalysts in the gas phase. Recently, Ismail et al. reported that the porphyridin-sensitized mesoporous TiO$_2$ films exhibited an improved photocatalytic activity for the photodegradation of acetaldehyde in the gas phase under visible-light irradiation. The porphyridin derivative-modified photocatalyst works efficiently as a visible-light response photocatalyst in the gas phase. In this study, we used five types of porphyrins for the modification of the TiO$_2$ photocatalyst, and investigated their performances in the photo−SCR using a gas flow reactor at a high GHSV of 50,000 h$^{-1}$.

**Experimental**

**Catalyst Preparation**

A TiO$_2$ powder (ST-01, anatase, 273 m$^2$ g$^{-1}$) was purchased from Ishihara Sangyo Kaisha, Ltd. A SiO$_2$ powder (630 m$^2$ g$^{-1}$) was prepared by hydrolysis of tetraethyl orthosilicate (TEOS) in a water–ethanol mixture at boiling point, followed by calcination in dry air at 773 K for 5 h. Tetraphenylporphyrin (TPP), Tetra($p$-carboxyphenyl)porphyrin (TCPP), Tetra($p$-sulfonatephenyl)porphyrin (TSPP), Tetra($p$-methoxyphenyl)porphyrin (TMPP), and Tetra($p$-aminophenyl)porphyrin (TAPP) were purchased from Tokyo Chemical Industry Co., Ltd. and used without further purification (see Fig. 1). The porphyridin derivatives were impregnated over the TiO$_2$ powder and the porphyrin-modified TiO$_2$ photocatalysts were abbreviated to porphyrin-TiO$_2$ (e.g. TCPP-TiO$_2$). Various loading amount of TCPP-TiO$_2$ catalysts were prepared by an impregnation method using 1 M NH$_3$ aqueous solution as a solvent (TCPP-TiO$_2$-IMP). A TCPP-modified SiO$_2$ catalyst was
prepared by the impregnation method as shown above (TCPP-SiO$_2$-IMP). A physical mixture catalyst of TCPP and the TiO$_2$ powder was prepared as a reference (TCPP-TiO$_2$-MIX).

**Photocatalytic reaction**

The photo-SCR was carried out in a conventional fixed-bed flow system at an atmospheric pressure. The catalyst was fixed with quartz wool and filled up in a quartz reactor with flat facets (H12 mm × W10 mm × D1.0 mm). The reaction gas composition was as follows: NO 1000 ppm, NH$_3$ 1000 ppm, O$_2$ 2–10%, He balance. 300 W Xe lamp (PERKIN-ELMER PE300BF) equipped with a L-42 cut-off filter was used as a light source (λ > 400 nm) and the sample was irradiated from the one side of the flat facets of the reactor. N$_2$ and N$_2$O were analyzed by SHIMADZU GC-8A TCD gas chromatographs equipped with MS-5A and Porapak Q.

**Characterization**

UV–Vis transmission adsorption and diffuse reflectance spectra were obtained with a UV–Vis spectrometer (JASCO V-650). Transmission adsorption spectra were measured using a 1 cm quartz cell at room temperature in the scan range of 300–800 nm. Photoluminescence spectra were recorded on a Hitachi F-7000 fluorospectrometer in the scan range of 550–760 nm at an excitation wavelength of 410 nm. The concentrations of TCPP in methanol solution used in the adsorption and emission spectroscopy were 3.4×10$^{-6}$ mol L$^{-1}$ and 1.0×10$^{-6}$ mol L$^{-1}$, respectively.

**Results and discussion**

**Effects of functional group in the porphyrins**

Fig. 1 shows the conversion of NO during the photo-SCR over the various porphyrin derivative-modified TiO$_2$ photocatalysts at a GHSV of 50,000 h$^{-1}$ after 6 h of visible-light irradiation. The conversion of NO over the unmodified TiO$_2$ photocatalyst was 13.4% under visible-light irradiation. Modification of the TiO$_2$ photocatalyst with the porphyrin derivatives greatly enhanced the photocatalytic conversion of NO under the visible-light irradiation as shown in Fig. 1. Among the five porphyrin derivative-modified TiO$_2$ photocatalysts, the TCPP-TiO$_2$ photocatalyst showed the highest conversion of NO (71.4%). The conversion of NO decreased in the following order:
TCPP-TiO$_2$ > TPP-TiO$_2$ > TSPP-TiO$_2$ > TMPP-TiO$_2$ > TAPP-TiO$_2$ > TiO$_2$. Hence, it can be seen that the porphyrin functional group used for the modification of TiO$_2$ had a significant effect on the photo-SCR activity.

Figure 1. Structures of porphyrin derivatives and conversion of NO in the photo–SCR over the various porphyrin derivative–modified TiO$_2$ photocatalysts after 6 h of visible–light irradiation (loading of porphyrin derivative: 18 µmol g$^{-1}$, catalyst amount: 110 mg, NO: 1000 ppm, NH$_3$: 1000 ppm, O$_2$: 2 %, GHSV: 50,000 h$^{-1}$).

Fig. 2 shows the UV–Vis DR spectra of the various porphyrin modified TiO$_2$ photocatalysts. The unmodified TiO$_2$ photocatalyst did not absorb the visible-light above 400 nm. The modification of the porphyrin derivatives increased the absorption in the visible-light region. The absorption at 420 nm (Soret band) decreased in the following order: TCPP-TiO$_2$ > TPP-TiO$_2$ ≒ TSPP-TiO$_2$ > TMPP-TiO$_2$ > TAPP-TiO$_2$ > TiO$_2$. The order of the absorption is consistent with that of the NO
conversion. The photocatalytic activities of NO were strongly dependent on the absorbance in the visible-light region, which suggested that the porphyrin derivatives functioned as photosensitizers under visible-light irradiation.

![UV–Vis diffuse reflectance spectra](image)

**Figure 2.** UV–Vis diffuse reflectance spectra of (A) TiO₂, (B) TCPP–TiO₂, (C) TSPP–TiO₂, (D) TPP–TiO₂, (E)TMPP–TiO₂, and (F)TAPP–TiO₂.

**Effect of TCPP loading on the activity of photo-SCR**

Fig. 3 shows the UV/Vis DR spectra of the different loading amounts of the TCPP-TiO₂ photocatalysts. One major peak and four minor peaks were observed in the visible region in each sample. The major peak is the Soret band (S₂ ← S₀ transition) and the four minor peaks are the Q bands (S₁ ← S₀ transition). The Q bands are attributed to the 0–0 and 0–1 components of the non-degenerated Q₁ and Q₂ bands (etio type), as expected for the D₂h symmetry. The increase in the TCPP loading amount enhanced the capability of visible-light absorption.
Figure 3. UV–Vis diffuse reflectance spectra of various loading of TCPP–TiO$_2$. (A) 0 µmol g$^{-1}$, (B) 1.3 µmol g$^{-1}$, (C) 6.3 µmol g$^{-1}$, (D) 12.5 µmol g$^{-1}$, (E) 37.5 µmol g$^{-1}$, and (F) 62.5 µmol g$^{-1}$.

The peak positions of the Soret band and Q bands as a function of TCPP loading are shown in Table 1. The peak position of the Soret band of 1.3 µmol g$^{-1}$ TCPP-TiO$_2$-IMP (417 nm) corresponded to those of the TCPP molecules dissolved in CH$_3$OH (418 nm). The TCPP molecules existed as a monomer in the CH$_3$OH solution and the peak position of the TCPP monomer coincided with that reported previously.$^{24}$ Thus, the TCPP molecules existed as monomers on the TiO$_2$ surface at the low loading amount of 1.3 µmol g$^{-1}$. The peak position of the Soret band was shifted from 417 nm to 407 nm (blue-shift) when the loading amount of TCPP was increased from 1.3 µmol g$^{-1}$ to 62.5 µmol g$^{-1}$. The origin of the blue-shift can be explained on the basis of a “face to face” stacking pattern of TCPP (H-aggregate) according to Kasha’s exciton theory.$^{25}$ Thus, the blue-shifted peak observed at 407 nm can be attributed to the Soret exciton band in the H-aggregates of the TCPP. The gradual spectral shift can be explained as the result of the relative contribution of the monomers and H-aggregates. The H-aggregates were generated with the increase in the TCPP loading. The contribution of the H-aggregates became dominant for the Soret band of adsorption spectra of various loading amount of TCPP-TiO$_2$, which results in the gradual blue shift of the Soret band.
On the other hand, the peak positions of the Q bands of 1.3 µmol g\(^{-1}\) TCPP-TiO\(_2\)-IMP (519, 555, 592, 649 nm) were slightly shifted to longer wavelengths compared to those of the TCPP monomer in CH\(_3\)OH (515, 549, 590, 646 nm). The slight red-shift can be ascribed to the aggregation of TCPP\(^{24}\) and/or the interactions between the TCPP and a solid surface.\(^{26}\) The peak positions of the four Q bands of the TCPP-TiO\(_2\)-IMP were shifted to longer wavelengths with an increase in the TCPP loading amount. The peak position of the Q bands of the H-aggregates of the TCPP is larger than that of the TCPP monomers.\(^{24}\) Thus, the red-shift of the Q bands is due to the generation of the H-aggregates. Consequently, both the monomers and H-aggregates of TCPP are generated on TiO\(_2\) and the fraction of the H-aggregates increased with the increasing TCPP loading amount.

**Table 1.** Peak positions of the sovet band and Q bands.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Loading of TCPP / µmol g(^{-1})</th>
<th>Soret / nm</th>
<th>(Q_{y(0, 1)}) / nm</th>
<th>(Q_{y(0, 0)}) / nm</th>
<th>(Q_{x(0, 1)}) / nm</th>
<th>(Q_{x(0, 0)}) / nm</th>
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<tbody>
<tr>
<td>TCPP-TiO(_2)-IMP</td>
<td>1.3</td>
<td>417</td>
<td>519</td>
<td>555</td>
<td>592</td>
<td>649</td>
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<tr>
<td>TCPP-TiO(_2)-IMP</td>
<td>6.3</td>
<td>416</td>
<td>519</td>
<td>555</td>
<td>592</td>
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<td>TCPP-TiO(_2)-IMP</td>
<td>12.5</td>
<td>411</td>
<td>520</td>
<td>557</td>
<td>592</td>
<td>651</td>
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<tr>
<td>TCPP-TiO(_2)-IMP</td>
<td>37.5</td>
<td>411</td>
<td>522</td>
<td>562</td>
<td>595</td>
<td>654</td>
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<tr>
<td>TCPP-TiO(_2)-IMP</td>
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<td>522</td>
<td>560</td>
<td>594</td>
<td>653</td>
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<tr>
<td>TCPP-TiO(_2)-MIX</td>
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<td>419</td>
<td>529</td>
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<td>600</td>
<td>658</td>
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<tr>
<td>TCPP-SiO(_2)-IMP</td>
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<td>521</td>
<td>556</td>
<td>593</td>
<td>649</td>
</tr>
<tr>
<td>TCPP in MeOH</td>
<td>–</td>
<td>418</td>
<td>515</td>
<td>549</td>
<td>590</td>
<td>646</td>
</tr>
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</table>

Fig. 4 shows the effect of various loading amounts of TCPP-TiO\(_2\)-IMP on the photo-SCR. The conversion of NO increased with the increasing TCPP loading amount up to 12.5 µmol g\(^{-1}\). The surface density of TCPP molecules on 12.5 µmol g\(^{-1}\) TCPP-TiO\(_2\)-IMP is estimated to be 2.8×10\(^{-2}\) molecule nm\(^{-2}\). As shown in Fig. 3, increasing the loading amount of TCPP enhanced the capability of the visible-light absorption, which leads to the higher conversion of NO. On the other hand, the
conversion of NO decreased when the TCPP loading was higher than 12.5 µmol g\(^{-1}\). The UV–Vis spectroscopy revealed that the H-aggregates of TCPP were generated with the increase of the TCPP loading amount. The excited state lifetime of the H-aggregates was slightly shorter than those of the monomers.\(^{24, 27}\) The generation of H-aggregates with a short excited state lifetime decreased the electron transfer efficiency from the excited state of TCPP to the conduction band of TiO\(_2\) due to non-radiative deactivation, which possibly resulted in the decrease of the photo-SCR activity.

![Graph showing the dependence of conversion of NO on TCPP loading on TiO\(_2\).](image)

**Figure 4.** Dependence of conversion of NO on TCPP loading on TiO\(_2\) (catalyst amount: 110 mg, NO: 1000 ppm, NH\(_3\): 1000 ppm, O\(_2\): 2 %, GHSV: 50,000 h\(^{-1}\)).

**Photo-SCR under various reaction conditions**

Table 2 summarizes the concentrations of N\(_2\) in the outlet gas for the photo-SCR under various reaction conditions. The conversion of NO in the photo-SCR over TCPP-TiO\(_2\)-IMP was 79.0% (Entry 1). Fig. 5 shows the time profile of the conversion of NO in the photo-SCR over TiO\(_2\), TCPP-TiO\(_2\), and TCPP-SiO\(_2\). The photocatalytic conversion of NO over TCPP-TiO\(_2\) maintained for 6 h without marked deactivation. N\(_2\) was the only product observed and N\(_2\)O was not detected in any
of the reactions. The utilization of visible-light was advantageous for the high selectivity to N$_2$, since N$_2$O was generated as a by-product of the photo-SCR over TiO$_2$ photocatalyst under UV-light irradiation. Turnover number (TON) of TCPP was calculated to be 810 after 6 h of visible-light irradiation. Thus, the total N$_2$ in the outlet gas was originated from the nitrogen atoms of NO and NH$_3$ molecules in the gas phase and not from the TCPP molecules. The reaction hardly proceeded over the TCPP-TiO$_2$ photocatalyst without a substrate such as NO, NH$_3$, and O$_2$ (Entry 2, 3, and 4). The O$_2$ concentrations did not affect the generation rate of N$_2$ over 2% (Entry 1, 5, and 6). The TCPP-SiO$_2$-IMP showed much lower activity under the same reaction conditions than that of the TCPP-TiO$_2$-IMP (Entry 7), although the TCPP on SiO$_2$ absorbed visible-light as well as that on TiO$_2$ as shown in Fig. 6. In addition, the activity of the photo-SCR over the TCPP-TiO$_2$ photocatalyst prepared by a physical mixture method (TCPP-TiO$_2$-MIX) was similar to that of the unmodified TiO$_2$, although the TCPP-TiO$_2$-MIX absorbed in the visible region as shown in Fig. 6.

Table 2. Results of photo–SCR under various reaction conditions.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Inlet gas conc. (ppm)</th>
<th>N$_2$ conc.$^a$ (ppm)</th>
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</thead>
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<tr>
<td></td>
<td></td>
<td>NO (ppm)</td>
<td>NH$_3$ (ppm)</td>
</tr>
<tr>
<td>1</td>
<td>TCPP-TiO$_2$-IMP$^b$</td>
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<td>1000</td>
</tr>
<tr>
<td>2</td>
<td>TCPP-TiO$_2$-IMP$^b$</td>
<td>0</td>
<td>1000</td>
</tr>
<tr>
<td>3</td>
<td>TCPP-TiO$_2$-IMP$^b$</td>
<td>1000</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>TCPP-TiO$_2$-IMP$^b$</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>5</td>
<td>TCPP-TiO$_2$-IMP$^b$</td>
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<td>1000</td>
</tr>
<tr>
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<td>TCPP-TiO$_2$-IMP$^b$</td>
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<td>1000</td>
</tr>
<tr>
<td>7</td>
<td>TCPP-SiO$_2$-IMP$^b$</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>8</td>
<td>TCPP-TiO$_2$-MIX$^b$</td>
<td>1000</td>
<td>1000</td>
</tr>
</tbody>
</table>

$a$ Concentration of N$_2$ in the outlet gas. Catalyst amount: 110 mg (TiO$_2$, TCPP–TiO$_2$), 50 mg (TCPP–SiO$_2$). $^b$ TCPP loading: 12.5 µmol g$^{-1}$. 
Figure 5. Time profile of conversion of NO in the photo–SCR over TiO$_2$ (▲), TCPP–TiO$_2$ (●), and TCPP–SiO$_2$ (■). (TCPP loading: 12.5 µmol g$^{-1}$, catalyst amount: 110 mg, NO: 1000 ppm, NH$_3$: 1000 ppm, O$_2$: 2%, GHSV: 50,000 h$^{-1}$).

Figure 6. UV–Vis diffuse reflectance spectra of (A) TCPP–TiO$_2$(IMP), (B) TCPP–SiO$_2$, and (C) TCPP–TiO$_2$(MIX), and adsorption spectra of $3.4\times10^{-6}$ mol L$^{-1}$ TCPP in methanol (D).
Fig. 7 shows the photoluminescence spectra of TCPP-TiO₂-IMP, TCPP-SiO₂-IMP, TCPP-TiO₂-MIX, and TCPP monomer in CH₃OH. Two emission bands were observed in the TCPP monomer in CH₃OH solution (650 and 714 nm), which coincided with the previously reported values.²⁴ The emission bands at 650 nm and 714 nm can be attributed to the transition from the vibrational ground state of \( S_1 \) to the vibrational ground state of \( S_0 \) (\( Q_{x(0,0)} \) transition) and to the vibrational excited state of \( S_0 \) (\( Q_{x(0,1)} \) transition) of the TCPP monomer, respectively.²⁴,²⁸ The peak positions of the emission bands in the TCPP-TiO₂-IMP (654 and 715 nm) were almost similar to those of the TCPP monomer in CH₃OH. It is reported that the emission bands of the H-aggregates of TCPP have lower intensity and are shifted to longer wavelengths than those of the monomers,²⁹ which is totally different from the emission spectrum of the TCPP-TiO₂-IMP. Accordingly, the emission bands of TCPP-TiO₂-IMP were mainly composed of the TCPP monomer emissions.

Two emission bands were observed at 658 and 713 nm, and the peak positions were similar to those of the TCPP in CH₃OH (650 and 714 nm) and TCPP-TiO₂-IMP (654 and 715 nm) (Fig. 7). Thus, the TCPP species on SiO₂ possesses a monomeric state, which is similar to that on TiO₂. The low activity of TCPP-SiO₂-IMP can be explained by an electron transfer mechanism, which is the key step in the DSSCs and dye-sensitized photocatalysts. In the first step of the photo-SCR over the TCPP-TiO₂-IMP, the TCPP is excited by the visible-light irradiation. In the next step, the electron transfer occurs from the photo-excited TCPP to the conduction band of TiO₂. However, the electron transfer cannot occur from the photo-excited TCPP to the conduction band of SiO₂ because the energy level of the SiO₂ conduction band is much higher than that of the lowest unoccupied molecular orbital (LUMO) of TCPP, which results in the low activity of the TCPP-SiO₂-IMP. Hence, the photo-SCR over TCPP-TiO₂-IMP under visible-light irradiation proceeds via the electron transfer from the photo-excited TCPP to the conduction band of TiO₂.

No emission peak was observed for the TCPP-TiO₂-MIX and TCPP powder (Fig. 7). The interaction between the TCPP molecules might lead to the non-radiative deactivation of the photo-excited states of TCPP, resulting in the luminescence quenching for the TCPP-TiO₂-MIX and TCPP powder. These
results explain the low activity of the TCPP-TiO$_2$-MIX, *i.e.* though the TCPP molecules on the TCPP-TiO$_2$-MIX absorb visible-light, they do not function as a photosensitizer under visible-light irradiation because of the fast non-radiative quenching.

![Graph showing photoluminescence spectra](image)

**Figure 7.** Photoluminescence spectra of (A) TCPP–TiO$_2$–IMP, (B) TCPP in methanol, (C) TCPP–SiO$_2$–IMP, (D) TCPP–TiO$_2$–MIX, and (E) TCPP powder. The excitation wavelength was 410 nm. The spectra of (A), (C), (D), and (E) were measured at the voltage of photomultiplier tube of 700 V and spectrum (B) was of 450 V. Loading of TCPP was 12.5 µmol g$^{-1}$, and the concentration of TCPP in methanol was $1.0 \times 10^{-6}$ mol L$^{-1}$.

**On–off response tests of visible light irradiation**

Fig. 8 shows the on–off response for the photo-SCR under visible-light irradiation over the TCPP-TiO$_2$ photocatalyst at a GHSV of 50,000 h$^{-1}$. The conversion of NO was about 6% without visible-light irradiation. The conversion of NO significantly increased to 86.5% under visible-light irradiation, indicating the function of the TCPP-TiO$_2$ photocatalyst as a visible-light-driven photocatalyst for the photo-SCR. The conversion of NO gradually decreased to 81.2% with the increasing irradiation time, although the conversion was restored to the original level (85.5%) after
the on–off action. The decrease in the conversion of NO with the irradiation time was not due to the decomposition of TCPP. If the TCPP on the TiO$_2$ surface was decomposed under visible-light irradiation, the initial conversion of NO was expected to decrease gradually in the second, third, and fourth times. However, we did not observe a decrease in the initial conversion of NO. The recovery of the initial conversion of NO took place reversibly.

![Conversion of NO](image.png)

**Figure 8.** Conversion of NO during several on/off cycles of visible–light irradiation over the TCPP/TiO$_2$ photocatalyst: each cycle consisted of two–hours light on and off (TCPP loading: 12.5 $\mu$mol g$^{-1}$, catalyst amount: 110 mg, NO: 1000 ppm, NH$_3$: 1000 ppm, O$_2$: 2 %, GHSV: 50,000 h$^{-1}$).

**Conclusions**

We found that porphyrin derivative-modified TiO$_2$ functions as a visible-light-driven photocatalyst for the photo-SCR. The TCPP-modified TiO$_2$ photocatalyst showed the highest activity of the photo-SCR among the TiO$_2$ photocatalysts modified with the five porphyrin derivatives investigated. We elucidated the state of TCPP on TiO$_2$ affect the photocatalytic conversion of NO.
and the active species is a TCPP monomer adsorbed on TiO$_2$ due to efficient electron transfer from the photo-excited TCPP monomer to the conduction band of TiO$_2$.

**References**


Chapter 3

Visible-Light-Assisted Selective Catalytic Reduction of NO with NH\textsubscript{3} over Dye-Modified TiO\textsubscript{2} Photocatalysts

Abstract

Dye-modified TiO\textsubscript{2} photocatalysts showed high photocatalytic activity for the selective catalytic reduction of NO with NH\textsubscript{3} in the presence of O\textsubscript{2} under visible-light irradiation. Among the 15 dyes investigated, the maximum conversion was achieved using a Ru(2,2'-bipyridyl-4,4'-dicarboxylic acid)\textsubscript{2}(NCS)\textsubscript{2} complex (N3-dye) for the modification of TiO\textsubscript{2} (NO conversion > 99%, N\textsubscript{2} selectivity > 99%). Diffuse reflectance infrared Fourier transform (DRIFT) investigation showed that nitrite (NO\textsubscript{2}^-) and nitrate (NO\textsubscript{3}^-) species were generated on the N3-TiO\textsubscript{2} surface under visible-light irradiation. In gas switch reactions, NO\textsubscript{2}^- on the N3-TiO\textsubscript{2} surface became N\textsubscript{2} by a reaction with adsorbed NH\textsubscript{3} under visible-light irradiation, although NO\textsubscript{3}^- reacted with NH\textsubscript{3} to form N\textsubscript{2} and N\textsubscript{2}O. Based on the relativity with NH\textsubscript{3}, we concluded that the NO\textsubscript{2}^- species is an intermediate in photo-SCR and reacts with NH\textsubscript{3} adsorbed on the surface of N3-TiO\textsubscript{2} under visible-light irradiation to selectively form N\textsubscript{2}.
Introduction

Nitrogen oxides (NO\textsubscript{x}) are air pollutants and cause serious environmental problems, including acid rain and town smog. In NO\textsubscript{x} emission from heavy-duty diesel engines for trucks and buses, selective catalytic reduction (SCR) technology with urea is used to remove the NO\textsubscript{x} in the exhaust gas.\textsuperscript{1} In the SCR system, the injected urea decomposes to NH\textsubscript{3} and CO\textsubscript{2}, and the formed NH\textsubscript{3} reduces NO to harmless N\textsubscript{2} according to eq. 1.

\[
4\text{NO} + 4\text{NH}_3 + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \quad (1)
\]

V\textsubscript{2}O\textsubscript{5}-based catalysts\textsuperscript{2-4} and Fe- or Cu-zeolite catalysts\textsuperscript{5-8} are used for the SCR process and these catalysts effectively decomposes the NO\textsubscript{x}.

Regulations in NO\textsubscript{x} emission have become stricter step by step, and further improvements of the de-NO\textsubscript{x} systems are required to meet the future regulations.\textsuperscript{9} The world harmonized transient cycle (WHTC) tests were introduced in Euro VI regulation (2014) for the heavy-duty diesel engines to simulate in-use driving conditions; in the WHTC, the NO\textsubscript{x} emission is monitored in transient situations including a cold start.\textsuperscript{10} However, in the SCR system, urea cannot be injected because of the low activity of the catalysts during the cold start condition (<473 K).\textsuperscript{10} Thus, novel technology is strongly desired to remove the NO\textsubscript{x} at low temperatures.

Utilizing photocatalysis is an effective way in terms of such a low temperature operation. We have reported photocatalysts that show activity for NH\textsubscript{3}-SCR at low temperatures in the presence of excess O\textsubscript{2} (referred to as photo-SCR).\textsuperscript{11-14} The reaction mechanism of photo-SCR has been investigated by us and other groups using spectroscopic,\textsuperscript{15-16} kinetic,\textsuperscript{12, 17-18} and theoretical\textsuperscript{19} methods. Over TiO\textsubscript{2} photocatalyst, the conversion of NO and the selectivity to N\textsubscript{2} becomes 90\% and 99\%, respectively, at a gas hourly space velocity (GHSV) of 8000 h\textsuperscript{-1}, which is sufficient for the De-NO\textsubscript{x} process in typical stationary sources such as power plants, blast furnaces, and incinerators. However, higher GHSV values (>50,000 h\textsuperscript{-1}) are required in engines owing to the limited installation space of the De-NO\textsubscript{x} process and a high flow rate of the exhaust gas.

Recently, we reported that porphyrin-sensitized TiO\textsubscript{2} functions as a visible-light-sensitive photocatalyst for NH\textsubscript{3}-SCR.\textsuperscript{20} In the porphyrin-sensitized TiO\textsubscript{2} system, maximum conversion of NO was 79\% at a GHSV of 50,000 h\textsuperscript{-1} under visible-light irradiation. However, the improvement of the
activity at the higher GHSV of 100,000 h\(^{-1}\) is essential from the practical application viewpoint. This reaction proceeds via electron injection from photo-excited dyes into the conduction band of TiO\(_2\) (dye-sensitization mechanism),\(^{20}\) although a detailed mechanism of the reaction is unclear. The electron injection process from photo-excited dyes into the conduction band of a semiconductor is an important step in dye-sensitized solar cells (DSSCs)\(^{21-23}\) and dye-sensitized photocatalysts,\(^{24-27}\) and has been previously investigated.\(^{28-30}\) Many researchers have tested various dyes, including Ru complexes,\(^{31-34}\) porphyrins,\(^{35-41}\) phthalocyanines,\(^{42-45}\) and other organic dyes,\(^{22,26,46-47}\) to improve the performance of DSSCs and dye-sensitized photocatalysts. The type of dye used for the modification of semiconductors has a great impact on the performance of DSSCs and dye-sensitized photocatalysts, and thus, should have a significant effect on the activity in photo-SCR under visible-light irradiation. A major problem of the dye-sensitization system is the stability of the dyes; moreover, optimization of the dye is essential to evaluate and improve the performance of photo-SCR over dye-modified TiO\(_2\) photocatalysts. Herein, we investigated photo-SCR under visible-light irradiation using TiO\(_2\) photocatalysts modified with 15 different dyes (Fig. 1) to improve the activity of this photocatalytic system. The reactivity of the adsorbed intermediates generated over the dye-modified TiO\(_2\) photocatalyst were also investigated by means of in situ diffuse reflectance infrared Fourier transform (DRIFT) and UV–Vis diffuse reflectance (DR) spectroscopies to elucidate the reaction mechanism.

**Experimental**

**Catalyst Preparation**

All dyes were used without further purification, and their structures are shown in Fig. 1. The dyes were impregnated on a TiO\(_2\) powder (ST-01, anatase, 273 m\(^2\) g\(^{-1}\)), purchased from Ishihara Sangyo Kaisha, Ltd., using appropriate solvents (Table 1). Sodium nitrite (NaNO\(_2\)) and sodium nitrate (NaNO\(_3\)) were impregnated on the N3-dye-modified photocatalyst using water as the solvent (loading of NaNO\(_2\) or NaNO\(_3\): 1000 μmol g\(^{-1}\)).

**Photocatalytic reaction**
Photo-SCR was carried out in a conventional fixed-bed flow system at atmospheric pressure, the details of which we have previously reported.\textsuperscript{12,20} In brief, two types of a quartz reactor were used in this research: reactor 1 (12 mm × 10 mm × 1.0 mm, catalyst amount: 110 mg) for a GHSV of 100,000 and 250,000 h\textsuperscript{–1}, and reactor 2 (50 mm × 15 mm × 1.0 mm, catalyst amount: 420 mg) for a GHSV of 8000 h\textsuperscript{–1}. The reaction gas (NO 1000 ppm, NH\textsubscript{3} 1000 ppm, O\textsubscript{2} 2%, He balance) was introduced to the reactors at a flow rate of 100–500 mL min\textsuperscript{–1}. A 300 W Xe lamp (PERKIN-ELMER PE300BF) equipped with an L42 cut-off filter was used as a light source (\(\lambda\) > 400 nm). N\textsubscript{2} and nitrous oxide (N\textsubscript{2}O) were analyzed using two SHIMADZU GC-8A TCD gas chromatographs.

**Characterization**

In situ DRIFT measurements were performed with a JASCO ISDR-600 FTIR spectrometer equipped with a mercury-cadmium-tellurium (MCT) detector cooled by liquid N\textsubscript{2} at a resolution of 4 cm\textsuperscript{–1} and with 16 co-added scans. The sample powder (50 mg) was placed in a DR cell, which was fitted with a KBr window at the top. The catalyst was pretreated at 353 K under a He gas flow (100 mL min\textsuperscript{–1}) for 1 h, and was then cooled to room temperature. Concentrations of gases were the same as in the reaction. The background spectrum was measured after the pretreatment in a He gas flow at room temperature. A 200 W Hg–Xe lamp equipped with a collective lens (San-Ei Electric Co. Ltd., UVF-204S type C) was used as a light source, and light was irradiated through an L42 cut-off filter. UV–Vis DR spectra were measured using a UV–Vis spectrometer (JASCO V-650) with an integrating sphere. A BaSO\textsubscript{4} plate was used as a reference. A sample powder was added to a quartz cell with flat facets and evacuated at 373 K for 1 h before the measurement. Cl\textsubscript{2} and NH\textsubscript{3} gas were added to the cell using a vacuum line.
Figure 1. Schematic representation of dyes
Results and discussion

Screening of dyes

Fig. 2 shows the results of photo-SCR over dye-modified TiO$_2$ photocatalysts. The reaction proceeded to some extent (ca. 5%) over a bare TiO$_2$ photocatalyst under visible-light irradiation, as reported in the previous paper.$^{48}$ Modification of TiO$_2$ with various dyes greatly enhanced

Table 1. Solvents used for the impregnation

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<th>Entry</th>
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<th>Solvent used for the impregnation</th>
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<td>Methanol</td>
</tr>
<tr>
<td>7</td>
<td>TCPP$^b$</td>
<td>Methanol</td>
</tr>
<tr>
<td>8</td>
<td>Methylene blue</td>
<td>Methanol</td>
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<tr>
<td>9</td>
<td>Zn phthalocyanine</td>
<td>Trifluoroacetic acid</td>
</tr>
<tr>
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<tr>
<td>11</td>
<td>Phthalocyanine</td>
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</tr>
<tr>
<td>12</td>
<td>RhCl$_3$</td>
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<tr>
<td>13</td>
<td>Indigo carmine</td>
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</tr>
<tr>
<td>14</td>
<td>Cu phthalocyanine</td>
<td>Trifluoroacetic acid</td>
</tr>
<tr>
<td>15</td>
<td>Carmine</td>
<td>10 mmol L$^{-1}$ NaOH aq.</td>
</tr>
</tbody>
</table>

$^a$ Ru(4,4’-dicarboxy-2,2’-bipyridine)$_2$(NCS)$_2$

$^b$ Tetrakis(4-carboxyphenyl)porphyrin
photo-SCR activities. The maximum conversion of NO (>99%) was obtained using an N3-dye (1 in Fig. 1)-modified TiO$_2$ photocatalyst (N3-TiO$_2$) after 30 min. The conversion of NO was significantly higher than those of other photocatalysts (e.g., UV-light irradiated TiO$_2$)$^{14,20}$ and conventional catalysts (e.g., Fe- and Cu-zeolite catalysts)$^{49}$ at low temperatures. N$_2$O was not detected in all reactions shown in Fig. 2. The high selectivity to N$_2$ is consistent with our previous reports of photo-SCR over porphyrin-modified TiO$_2$ photocatalysts under visible-light irradiation.$^{20}$ The order of activities is discussed in the last section.

![Conversion of NO in photo-SCR over the dye-modified TiO$_2$ photocatalysts under visible-light irradiation. Dye loading: 12.5 μmol g$^{-1}$. GHSV: 100,000 h$^{-1}$. The numbers in the bottom axis correspond to those in Fig. 1.](image)

**Figure 2.** Conversion of NO in photo-SCR over the dye-modified TiO$_2$ photocatalysts under visible-light irradiation. Dye loading: 12.5 μmol g$^{-1}$. GHSV: 100,000 h$^{-1}$. The numbers in the bottom axis correspond to those in Fig. 1.

In TCPP-TiO$_2$ (7), conversion of NO was 50% at 30 min of the reaction, and the decrease of the conversion was hardly observed during 180 min (Fig. 3). The high stability of TCPP agreed with the previous reports.$^{20}$ When xanthene dyes were used, relatively high conversions of NO were
obtained after 30 min: rose bengal 2 (81%), eosin Y 3 (80%), and rhodamine B 5 (63%). However, the conversions gradually decreased during 180 min of the reaction (Fig. 3). Bleaching of the catalyst colors was observed after the reaction, which suggested that the decrease of the activity was due to dye decomposition. The low stability of xanthene dyes was consistent with the previously reported DSSCs.22,50 Thus, the xanthene dyes were deemed unsuitable for photo-SCR. In Ru(bpy)_3Cl_2 4, and phthalocyanines (9, 11, and 14), the conversions of NO at 180 min were higher than those at 30 min although the color bleaching was observed in these dyes after the reaction. A relatively high stability was observed in N3-dye 1 despite the presence of O_2, and the N3-TiO_2 photocatalyst showed the highest conversion of NO even at 180 min (95%) as shown in Fig. 3. Although the bleaching of the catalyst color was also observed in N3-TiO_2 after the reaction, the total amount of generated N_2 reached to 1.4 mmol for 3 h, and the turnover number (TON) of N3-dye was calculated to be 1000 after 3 h of the reaction. As a result of the screening of dyes, N3-dye showed the highest activity and relatively high stability in photo-SCR under a practical GHSV condition.

Figure 3. Time course of the conversion of NO in photo-SCR over the dye-modified TiO_2 photocatalysts under visible-light irradiation. Dye loading: 12.5 μmol g^{-1}. GHSV: 100,000 h^{-1}.
Optimization of the catalyst preparation conditions

Effect of loading of N3-dye on the activity was investigated at a GHSV of 250,000 h\(^{-1}\) (Fig. 4). The conversion of NO drastically increased up to 37.5 μmol g\(^{-1}\), and then slightly decreased. The maximum conversion of NO was 63% after 30 min of the reaction. The tendency of the activity to the dye loading was similar to the porphyrin-TiO\(_2\) system in our previous reports although the optimized loading of N3-dye was larger than that of TCPP-TiO\(_2\) (12.5 μmol g\(^{-1}\)).\(^{20}\) Fig. 5 shows the effect of the solvent used in the impregnation on the conversion of NO. As a result of the optimization, methanol was found to be the most effective solvent for the impregnation. Ru-K edge XANES spectra were measured using 37.5 μmol g\(^{-1}\) N3-TiO\(_2\) catalysts prepared using various solvents. The edge energies of all the spectra of N3-TiO\(_2\) catalysts (a–d) were the same as that of the reference pellet of N3-dye (e), and were completely different from that of Ru foil. This result indicates the valence of Ru in all the N3-TiO\(_2\) catalysts was +2. There was no change in the shapes of the spectra of N3-TiO\(_2\) catalysts and N3-dye (a–e). In our previous research, the aggregation of dyes drastically decreased the activity.\(^{20}\) The solvents used in the impregnation may affect the aggregation state of N3-dye and change the photocatalytic activity observed in Fig. 5.

![Figure 4. Effect of loading of N3-dye on the activity. GHSV: 250,000 h\(^{-1}\). The data were obtained after 30 min of the reaction.](image)
Figure 5. Effect of the solvents used in the impregnation on the activity. N3-dye loading: 37.5 μmol g$^{-1}$, GHSV: 250,000 h$^{-1}$. The data were obtained after 30 min of the reaction.

Figure 6. Rh-K edge XANES spectra of 37.5 μmol g$^{-1}$ N3-TiO$_2$ prepared by impregnation using (a): methanol, (b) ethanol, (c) 2-propanol, and (d) 1 M NH$_3$ aq., and reference samples. (e): N3-dye, and (f) Ru foil.
Reactivity of adsorbed species of NH$_3$ and NO

Table 2 lists the results of reactions under various conditions. Efficient N$_2$ formation was observed over N3-TiO$_2$ in the presence of NO, NH$_3$, and O$_2$ under visible-light irradiation (640 ppm, Entry 2). The activity of N3-TiO$_2$ was significantly higher than that of the TiO$_2$ photocatalyst under UV and visible light irradiation (290 ppm, Entry 1). Product formation was greatly diminished without NO, NH$_3$, or O$_2$ (Entries 3, 4, and 5), which indicated that all the gases are involved in the formation of N$_2$. Furthermore, visible-light irradiation drastically promoted photo-SCR over N3-TiO$_2$ (Entry 6).

Table 2. Results of photo–SCR under various reaction conditions.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Inlet (%)$^d$</th>
<th>Lamp$^b$</th>
<th>Outlet (ppm)$^c$</th>
</tr>
</thead>
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<tr>
<td></td>
<td></td>
<td>NO</td>
<td>NH$_3$</td>
<td>O$_2$</td>
</tr>
<tr>
<td>1</td>
<td>TiO$_2$</td>
<td>0.1</td>
<td>0.1</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>N3-TiO$_2$$^d$</td>
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<td>0.1</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>N3-TiO$_2$$^d$</td>
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<td>0.1</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>N3-TiO$_2$$^d$</td>
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<td>0</td>
<td>2</td>
</tr>
<tr>
<td>5</td>
<td>N3-TiO$_2$$^d$</td>
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<td>0.1</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>N3-TiO$_2$$^d$</td>
<td>0.1</td>
<td>0.1</td>
<td>2</td>
</tr>
<tr>
<td>7</td>
<td>N3-SiO$_2$$^d$</td>
<td>0.1</td>
<td>0.1</td>
<td>2</td>
</tr>
</tbody>
</table>

$^a$ Concentration of N$_2$ and N$_2$O in the inlet gas. $^b$ Light source, UV+Vis: 300 W Xe lamp without cut-off filter, Vis: 300 W Xe lamp with L-42 cut-off filter. $^c$ Concentration of N$_2$ and N$_2$O in the outlet gas. GHSV: 250,000 h$^{-1}$, total flow rate: 500 ml min$^{-1}$, catalyst amount: 110 mg. $^d$ Loading of N3-dye: 37.5 μmol g$^{-1}$. $^e$ Not detected.
A couple of gas switch experiments were carried out to investigate the reactivity of the adsorbed species of NH$_3$ and NO on the N3-TiO$_2$ surface. In the first experiment, NH$_3$/He gas was flowed in the first 120 min in the dark (Fig. 7A), and no product was observed. Subsequently, the feed gas was switched to NO/O$_2$/He gas and visible-light irradiation was started. Selective formation of N$_2$ (910 ppm, selectivity to N$_2$ > 99%) was observed after 5 min of visible-light irradiation. The concentration of N$_2$ in the outlet gas gradually decreased with increasing visible-light irradiation time and dropped to 24 ppm after 270 min. This formation of N$_2$ presumably derived from the reaction between the initially adsorbed NH$_3$ and NO in the gas phase, because low amount of N$_2$ were formed via a reaction of NO and O$_2$ under visible-light irradiation (Table 2, Entry 4). The above gas switch reaction clearly showed the adsorbed NH$_3$ was involved in the reaction.

In the second experiment, NO/O$_2$/He gas was flowed under visible-light irradiation for 90 min, and then the feed gas was switched to NH$_3$/He gas in the dark (Fig. 7B). During this period, a small amount of N$_2$ was formed and N$_2$O was not detected. After 120 min of the NH$_3$/He gas flow in the dark, visible-light irradiation was started and N$_2$ (780 ppm) and N$_2$O (130 ppm) were observed (selectivity to N$_2$: 86%) after 5 min; the concentrations gradually decreased as the irradiation time was increased. The blank test results showed that NH$_3$ did not decompose to N$_2$ over N3-TiO$_2$ under visible-light irradiation (Table 2, Entry 3). Thus, the generation of N$_2$ and N$_2$O was due to the reaction between NO$_x$ species generated on a N3-TiO$_2$ surface and NH$_3$ molecules.

The couple of gas switch experiments revealed that the adsorbed two species (i.e., NH$_3$ and NO$_x$) were involved in the reaction. In addition, the reaction did not proceed without visible-light irradiation, which indicated that visible-light was essential for this surface reaction between NH$_3$ and NO$_x$ species. Accordingly, we concluded that the adsorbed NH$_3$ and surface NO$_x$ speices reacted under visible-light irradiation to form N$_2$ and N$_2$O.
DRIFT investigations of surface NO\textsubscript{x} species

Fig. 8 represents the DRIFT spectra before and after the addition of NO/O\textsubscript{2}/He gas in the dark. The spectrum before the addition was used as the baseline. Two peaks, at 1478 and 1198 cm\textsuperscript{-1}, gradually increased with increasing the exposure time (Fig. 8A). The peak at 1478 cm\textsuperscript{-1} was assigned to a \(\nu_3\) vibration of monodentate NO\textsubscript{2}– adsorbed on the surface of N3-TiO\textsubscript{2}. This species is also expected to have a \(\nu_1\) vibration band between 1065 and 1050 cm\textsuperscript{-1}.\textsuperscript{51-52} In the DRIFT experiment, a shoulder band was observed around that region, which supports its proposed generation. The peak at 1198 cm\textsuperscript{-1} was assigned to a bridged bidentate NO\textsubscript{2}– in a previous paper.\textsuperscript{51-52} Three negative peaks at 3697, 3659, and 3631 cm\textsuperscript{-1}, and a broad positive peak around 3500 cm\textsuperscript{-1} appeared after the addition of NO/O\textsubscript{2}/He gas (Fig. 8B). The negative peaks were assigned to isolated OH groups in different surroundings (e.g., number of coordinated Ti atom, valence of coordinated Ti atom, surface sites of TiO\textsubscript{2})\textsuperscript{53-54} and the broad positive peak was attributed to a hydrogen-bonded OH group. We did not
observe a characteristic band of deformation vibration of water molecules around 1640 cm⁻¹, which indicated that the amount of adsorbed water did not change by the co-adsorption of NO and O₂. Thus, the increase of the band intensity centered at 3500 cm⁻¹ is not due to the adsorption of water molecules generated. The change in the OH region suggests that the adsorbed NO₂⁻ species interacted with the isolated OH groups through hydrogen bonding, thus reducing the band intensities of the isolated OH groups and increasing the hydrogen-bond-related band intensity. Both NO₂⁻ species (monodentate and bridged bidentate) were generated on the surface of N3-TiO₂ by the co-adsorption of NO and O₂ in the dark.

After 30 min of NO/O₂ gas flow, O₂/He gas was introduced to the DRIFT cell, and then visible-light irradiation was started across the KBr window. As shown in Fig. 9A, the band at 1478 cm⁻¹ decreased with visible-light irradiation, which indicated that the NO₂⁻ species were consumed by the reaction with O₂ under visible-light irradiation. New bands at 1605, 1583, 1297, and 1253 cm⁻¹ increased with increasing irradiation time. Bands at 1605 and 1253 cm⁻¹ were attributed to a ν₃ vibration of the bridging bidentate nitrate (NO₃⁻), and a set of bands at 1583 and 1297 cm⁻¹ was assigned to the chelating bidentate NO₃⁻.⁵¹-⁵² Thus, the NO₂⁻ species was oxidized into the NO₃⁻ species under visible-light irradiation. In the OH region (Fig. 9B), the isolated OH bands at 3697, 3659, and 3631 cm⁻¹ decreased with visible-light irradiation, suggesting that the surface OH groups reacted with the adsorbed NO₂⁻ to form NO₃⁻. The DRIFT investigation revealed that the NO₂⁻ species appeared after the co-adsorption of NO and O₂ in the dark, and were oxidized into NO₃⁻ by O₂ under visible-light irradiation (Scheme 1).
Figure 8. DRIFT spectra of N3-TiO$_2$ in the dark before addition of NO/O$_2$/He gas (dotted line), and after 5, 10, 15, 20, 25 (grey lines), and 30 min (black line).

Figure 9. DRIFT spectra of N3-TiO$_2$ in O$_2$/He gas before visible-light irradiation (dotted line), and after 20 min, 40 min (grey lines), and 60 min (black line) from the start of visible-light irradiation.
**Reactivity of the NO$_2^-$ and NO$_3^-$ species with NH$_3$ under visible-light irradiation.**

Either NaNO$_2$ or NaNO$_3$ was impregnated over N3-TiO$_2$ in order to investigate the reactivity of NO$_2^-$ and NO$_3^-$ on the surface of N3-TiO$_2$. NH$_3$ was flowed into the reactor filled with the NaNO$_3$- or NaNO$_2$-impregnated catalysts (Fig. 10). In the dark, N$_2$ and N$_2$O were not detected in an NH$_3$/He gas flow for both catalysts. For the NaNO$_3$-impregnated N3-TiO$_2$, N$_2$ (2020 ppm) and N$_2$O (1420 ppm) were observed after 5 min of visible-light irradiation. Not much N$_2$ was observed in the NH$_3$/He gas flow under visible-light irradiation in the blank tests (Table 2, Entry 3). Thus, the generated N$_2$ shown in Fig. 10A is derived from a reaction between NH$_3$ in the gas phase and NO$_3^-$ species on the surface of N3-TiO$_2$. Surprisingly, a large amount of N$_2$O was detected in this experiment (selectivity to N$_2$ = 59%). In contrast, selective formation of N$_2$ was observed from the NaNO$_2$-impregnated N3-TiO$_2$ under visible-light irradiation (Fig. 10B, selectivity to N$_2$ = 94%), which suggested that NO$_2^-$ became N$_2$ on reacting with NH$_3$. As shown above, the reactivity of NO$_2^-$ with NH$_3$ was significantly different from that of NO$_3^-$ in terms of selectivity to N$_2$ (Scheme 1), which could explain the relatively low selectivity to N$_2$ (selectivity to N$_2$ = 86%) in the gas switch reaction shown in Fig. 7B; both the NO$_2^-$ and NO$_3^-$ species were formed in NO/O$_2$/He gas under visible-light irradiation on the surface of N3-TiO$_2$ and reacted with NH$_3$. High selectivity to N$_2$ (>99%) in photo-SCR in the presence of NO, NH$_3$, and O$_2$ (Table 2, Entry 2) over N3-TiO$_2$ strongly indicated that an intermediate in photo-SCR was NO$_2^-$ was adsorbed on the surface of N3-TiO$_2$ on the basis of the difference in their reactivity.
Scheme 1. Surface NO₃ species on N3-TiO₂ catalyst and its reactivity with NH₃ under visible light irradiation.

Figure 10. Time course of concentration of N₂ and N₂O in the outlet gas over (A) NaNO₃-imprignated N3-TiO₂ and (B) NaNO₂-imprignated N3-TiO₂. Loading of NaNO₃ or NaNO₂: 1000 μmol g⁻¹. Loading of N3-dye: 37.5 μmol g⁻¹, Reaction gas: 1000 ppm NH₃/He. GHSV: 8000 h⁻¹, light source: 300 W Xe lump equipped with a L42 cut-off filter.
Role of dyes.

As shown in Table 2, the activity of N3-SiO$_2$ catalyst was very low (conversion of NO: 1.6%, entry 7), which indicated that the N3-dye did not function independently of the support (i.e., TiO$_2$). Thus, the reaction over N3-TiO$_2$ proceeds via a dye-sensitization mechanism: visible-light irradiation induces the electron injection from photo-excited dyes to the conduction band of TiO$_2$. A similar result was obtained in porphyrin-modified TiO$_2$ photocatalysts. After the electron injection, the oxidation product of N3-dye and an electron in the conduction band of TiO$_2$ should be generated as shown in eq. 2:

$$\text{N3-dye} + h\nu \rightarrow \text{N3-dye}^+ + e^-_{cb} \quad (2)$$

Based on eq. 2, we investigated the reactivity of the oxidation product of N3-dye with NH$_3$. In a previous report, the one-electron oxidation product of Ru$^{2+}$(bpy)$_3$ (i.e., Ru$^{3+}$(bpy)$_3$) in zeolite was prepared using Cl$_2$ as an oxidant, and we attempted the corresponding oxidation of N3-dye. Fig. 11 shows the UV-Vis DR spectra of N3-dye. After evacuation, the catalyst color was the dark purple, and an absorption band at 515 nm was observed (a). The band is assigned to a MLCT band of the grand state N3-dye (Ru$^{2+}$). After addition of Cl$_2$, the catalyst color changed from dark purple into ocher, and the absorption peak was shifted to 420 nm (b). The band at 420 nm is not attributed to the one electron oxidation products (Ru$^{3+}$) of N3-dye because the one electron oxidation product have an adsorption band around 740 nm, which was observed in several transient adsorption experiments.

S. Das and P. V. Kamat investigated the oxidized form of N3-dye by using transient absorption spectroscopy using azide (N3•) radical generated by $\gamma$-Radiolysis as an oxidant. Their results provided the spectral evidence for the formation of two different species that follow the oxidation of N3-dye. One oxidized product (species 1, abs. max: 740 nm) was attributed to the one-electron oxidation product of N3-dye, and is undergone further transformations to the other oxidized form (species 2, abs. max: 440 nm) at room temperature. The identification of species 2 was not made in their report. The ocher products (abs. max: 420 nm) observed in our UV-Vis DR experiments can be assigned to the species 2 judging from the position of adsorption maximum. To
examine the reactivity of species 2, NH₃ was introduced to the cell. After addition of NH₃, the catalyst color changed into the initial dark purple as shown in Fig. 11c. This result clearly indicates that species 2 can react with NH₃ and returned to the initial ground state of N3-dye. Although the identification is not made and which oxidation products (species 1 or 2) activate NH₃ in the in situ reaction condition is unclear, the UV-Vis DR spectroscopy revealed that oxidized products (at least, species 2) of N3-dye have a potential to activate NH₃.

As discussed above, N3-dye⁺ could not be prepared because of its instability. Therefore, we used the TiO₂ photocatalyst modified with Ru²⁺(bpy)₃Cl₂ (4 in Fig. 1) in the UV–Vis spectroscopic study and investigated the reactivity of one-electron oxidation products of Ru²⁺(bpy)₃ with NH₃ (Fig. 12). After the evacuation of Ru(bpy)₃Cl₂/TiO₂, an adsorption band at 455 nm was observed (spectrum (a) in Fig. 12) and attributed to an MLCT band of Ru²⁺(bpy)₃. After the addition of Cl₂, the catalyst color changed from light orange to slightly greyish orange and the adsorption at 600–800 nm increased (spectra (b)), which was assigned to an LMCT band of Ru³⁺(bpy)₃. As previously mentioned, Ru³⁺(bpy)₃ was successfully prepared on the TiO₂ surface by using Cl₂ as an oxidant. Subsequent introduction of NH₃ to the cell resulted in a decrease in the adsorption at 600–800 nm (spectra (c)), which clearly showed the reaction of Ru³⁺(bpy)₃ with NH₃ and reduction to the initial Ru²⁺(bpy)₃ species. The UV–Vis spectroscopic result shows that Ru³⁺(bpy)₃ has the potential to oxidize NH₃. We concluded that Ru³⁺(bpy)₃, generated after the electron injection, activates NH₃ to an NH₂ radical (eq. 3), which reacts with NO₂⁻ to form N₂ selectively.¹², 48

Ru³⁺(bpy)₃ + NH₃ → Ru²⁺(bpy)₃ + NH₂ radical + H⁺ \tag{3}

On the other hand, the electron injected to the conduction band of TiO₂ is consumed by the reaction with O₂ and H⁺ (surface OH group) to form H₂O according to eqs. 4 and 5.¹², 15-16

\begin{align*}
Ti^{4⁺} + e^{-}_{cb} & \rightarrow Ti^{3⁺} \tag{4} \\
Ti^{3⁺} + 1/4O₂ + H^+ & \rightarrow Ti^{4⁺} + 1/2H₂O \tag{5}
\end{align*}
Figure 11. UV-Vis DR spectra and photographs of 37.5 μmol g⁻¹ N3-TiO₂ photocatalyst after evacuation (a), after addition of Cl₂ (b), and after addition of NH₃ (c).

Figure 12. UV–Vis DR spectra of the TiO₂ photocatalyst modified with Ru(bpy)₃Cl₂ after evacuation (a), after addition of Cl₂, and after addition of NH₃. Dye loading: 37.5 μmol g⁻¹.
Proposed reaction mechanism and effects of dyes on the activity.

Based on the results obtained thus far, we proposed the reaction mechanism of photo-SCR over Ru-dye-modified TiO₂ photocatalysts under visible-light irradiation (Scheme 2). The mechanism is composed of five steps: (1) adsorption of NO and NH₃ on the catalyst surface, (2) electron injection from photo-excited Ru dyes into the conduction band of TiO₂, (3) activation of NH₃ by oxidized Ru dyes, (4) surface reaction between an NH₂ radical and NO₂⁻, and (5) re-oxidation of Ti³⁺ sites by O₂.

In DSSCs, Ru complexes have shown the best photovoltaic properties among a huge number of dyes,²² and N3-dye was known to be an effective Ru dye for DSSCs due to 1) the wide adsorption range to 800 nm, 2) strong adsorption on the semiconductor surface due to binding with up to four carboxyl groups, and 3) sufficiently long excited state life-time (~20 ns).²² In our research, N3-dye showed the highest activity in photo-SCR under visible-light irradiation among the 15 dyes studied. The adsorption of N3-dye was not larger than other dyes as shown in Fig. 13. This result indicated that the highest activity was not due to the adsorption amount in the visible region, although this should be a significant factor. In the case of DSSCs, carboxylic groups were necessary in terms of the strong adsorption of dyes on the semiconductor surface, and the strong adsorption led to strong photovoltaic properties. In this research, Ru(bpy)₃Cl₂ dye, which does not possess a carboxylic group, also showed high activity (conversion of NO = 70.5%). A similar result for photo-SCR was obtained in our previous reports using the porphyrin-modified TiO₂ photocatalysts with different functional groups.²⁰ Therefore, carboxylic groups were not important to improve the activity, unlike the DSSCs system. Thus, the life-time of the photo-excited state and the reactivity of the oxidized product of dyes with NH₃, which should affect reaction steps 2 and 3 in Scheme 2, would have a significant effect on the photo-SCR activity.
Scheme 2. Proposed reaction mechanism of photo-SCR under visible-light irradiation over Ru complexes modified TiO$_2$ photocatalyst.

Figure 13. UV–Vis DR spectra of the dye-modified TiO$_2$ photocatalysts. Dye loading: 12.5 $\mu$mol g$^{-1}$. 
Conclusions

We demonstrated high-performance photocatalysts for NH$_3$-SCR under visible-light irradiation by combining popular dyes with TiO$_2$ photocatalysts. The screening of 15 dyes displayed that N3-dye was most effective for the modification of TiO$_2$. Complete conversion of NO and selectivity to N$_2$ were achieved over N3-TiO$_2$ at a high GHSV of 100,000 h$^{-1}$ after 30 min of visible-light irradiation. We proposed a reasonable reaction mechanism of the photo-SCR over dye-modified TiO$_2$ photocatalysts under visible light irradiation by using in situ DRIFT and UV–Vis DR spectroscopies. The reaction proceeds via electron injection from dyes excited by visible-light irradiation into the conduction band of TiO$_2$ (dye-sensitization). The dye oxidation product, generated after the electron injection, oxidatively activates NH$_3$, which then reacts with surface NO$_2^-$ to provide selective formation of N$_2$.

References


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Chapter 4

Effects of SO$_2$ on Selective Catalytic Reduction of NO with NH$_3$ over a TiO$_2$ Photocatalyst

Abstract

The effect of SO$_2$ gas was investigated on the activity of the photo-assisted selective catalytic reduction of nitrogen monoxide (NO) with ammonia (NH$_3$) over a TiO$_2$ photocatalyst in the presence of excess oxygen (photo-SCR). Introduction of SO$_2$ (300ppm) greatly decreased the activity of the photo-SCR at 373 K. Increment of the reaction temperature enhanced the resistance to SO$_2$ gas and, at 553 K, the conversion of NO was stable for at least 300 min of the reaction. X-ray diffraction, Fourier transform infrared spectroscopy, thermogravimetry and differential thermal analysis, X-ray photoelectron spectroscopy, elemental analysis, and N$_2$ adsorption measurement revealed that the ammonium sulfate species were generated after the reaction. There was a strong negative correlation between the deposition amount of the ammonium sulfate species and the specific surface area. Based on the above relationship, we concluded that the deposition of the ammonium sulfate species decreased the specific surface area by plugging the pore structure of the catalyst and the decrease of the specific surface area resulted in the deactivation of the catalyst.
Introduction

The emission of nitrogen oxides (NO\textsubscript{x}) causes air pollution problems such as acid rain and photochemical smog. Selective catalytic reduction (SCR) of NO\textsubscript{x} with ammonia (NH\textsubscript{3}) is a commercial de-NO\textsubscript{x} process in the stationary and mobile NO\textsubscript{x} emission sources. The main reaction is as follows:

\[
4\text{NO} + 4\text{NH}_3 + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \quad (1)
\]

In the stationary emission sources, the industrial catalyst for the process is vanadium oxide based catalysts, such as V\textsubscript{2}O\textsubscript{5}–WO\textsubscript{3}/TiO\textsubscript{2} \textsuperscript{1-2}. The catalysts show the high activity and high selectivity to N\textsubscript{2} in the temperature window of 523–673 K. This type of catalyst has to be installed upstream the particulate collector and the flue-gas desulfurization unit in order to meet the optimum working temperature. However, the catalysts are not available in the diesel engine because of the wide temperature window (423–773 K) of the exhaust gas. A promising catalyst which shows high activity at low temperatures is strongly desired for the diesel engine.

Mn based catalysts were eagerly investigated due to the high activity at low temperatures \textsuperscript{3-8}. The Mn based catalysts show almost 100% of the conversion in the temperature range of 373–473 K although the selectivity to N\textsubscript{2} is slightly low in some reaction conditions \textsuperscript{3-4}. The problem of the Mn based catalysts is low resistance to SO\textsubscript{2} poisoning. Kijlstra et al. \textsuperscript{9} proposed that the formation of MnSO\textsubscript{4} is the main reason for the deactivation of the MnO\textsubscript{x}/Al\textsubscript{2}O\textsubscript{3} catalysts. The formed sulfates decomposed at 1020 K, which means regeneration of the catalysts is only possible at much higher temperatures than the reaction temperature. On this point, the simultaneous pursuit of the operation at low temperatures and the high resistance to SO\textsubscript{2} gas is a challenging and important topic in the de-NO\textsubscript{x} technology.

We have previously reported the photo-assisted SCR of NO with NH\textsubscript{3} over TiO\textsubscript{2} photocatalysts in the presence of excess oxygen (O\textsubscript{2}) at ambient temperature. In the photocatalytic system, high conversion and high selectivity were achieved at the gas hourly space velocity (GHSV) of 25,000 h\textsuperscript{-1} (conversion of NO > 90\%, selectivity to N\textsubscript{2} > 95\%) \textsuperscript{10}. We have carried out various investigations: the elucidation of the reaction mechanism using spectroscopic methods \textsuperscript{11} and kinetic analysis \textsuperscript{12}, the improvement of the activity by metal doping \textsuperscript{13} and combining the temperature effect
with the photo-SCR\textsuperscript{14}, and the development of visible-light-sensitive photocatalyst with dye-sensitization\textsuperscript{15}. Other research groups also carried out a theoretical study\textsuperscript{16}, which verified the proposed reaction mechanism by our group\textsuperscript{11,17}, and a kinetic study using an annular fixed-film photoreactor\textsuperscript{18}. However, the potential of the photocatalyst for the resistance to SO\textsubscript{2} gas has not been investigated yet although the resistance is essential to make the photo-SCR system practicable. Thus, our objective is to investigate the effect of SO\textsubscript{2} gas on the performance of the photo-SCR over the TiO\textsubscript{2} photocatalyst. In addition, the systematic characterization of the catalyst after the reaction was carried out to elucidate the deactivation mechanism of the TiO\textsubscript{2} photocatalyst.

**Experimental**

**Materials**

TiO\textsubscript{2} (ST-01) powder was purchased from Ishihara Sangyo Kaisha, Ltd. Before use, the TiO\textsubscript{2} powder was hydrated in distilled water for 2 h at 353 K, and then evaporated to dryness at 353 K. The powder after the hydration was tableted (diameter 20 mm) and calcined at 673 K for 3 h in a furnace under a dry air flow. The tablet was granulated using 25 and 50 mesh sieves to obtain the granules with a diameter of 300–600 \(\mu\text{m}\). Ammonium sulfate (wako), and sodium sulfate (wako) were used as reference samples without further purification.

**Photocatalytic reaction**

Photo-SCR was carried out using a conventional fixed bed flow reactor at an atmospheric pressure in the same way as in our previous reports\textsuperscript{14}. A quarts reactor was used for the reaction and the reactor volume was 0.12 mL (12×10×1 mm). 110 mg of TiO\textsubscript{2} granules with a diameter of 300–600 \(\mu\text{m}\) were introduced to the reactor and pretreated at 673 K in a 10% O\textsubscript{2}/He gas at a flow rate of 50 mL min\textsuperscript{-1} for 60 min. The reaction gas composition was as follows: NO (1000ppm), NH\textsubscript{3} (1000ppm), O\textsubscript{2} (2%), SO\textsubscript{2} (300ppm, if present), He balance. A 200 W Hg–Xe lamp equipped with fiber optics, collective lens, and a mirror (San-Ei Electric Co., Ltd., UVF-204S type B) was used as a light source. The measured light irradiance was 360 mW cm\textsuperscript{-2}. N\textsubscript{2} and N\textsubscript{2}O products were analyzed by a SHIMADZU GC-8A TCD gas chromatograph with MS-5A and Porapak Q columns, respectively.
Characterization

Crystalline phase of the TiO$_2$ powder was determined by X-ray diffraction (XRD) technique using a Rigaku Ultima IV X-ray diffractometer with Cu-K$\alpha$ radiation ($\lambda = 1.5406$ Å). The crystallite size was determined from the full width at half maximum (FWHM) of the diffraction peak of the anatase TiO$_2$ (101) plane ($2\theta=25.2^\circ$) using the Scherrer's equation. Fourier transform infrared (FTIR) transmission spectra were recorded on a JASCO FT/IR-4200 spectrometer at room temperature at a spectral resolution of 4 cm$^{-1}$ accumulating 16 scans. The background spectrum was measured without any sample in air and was subtracted from the sample spectra. The catalysts before and after the reaction and the reference samples (ammonium sulfate and sodium sulfate) were diluted with KBr by the sample-to-KBr ratio of 1.5:98.5 and 0.2:99.8 (w/w), respectively, and then pressed into pellets. Thermo-gravimetric analysis (TG) and differential thermal analysis (DTA) were performed on a Rigaku Thermo plus TG 8120 apparatus at a heating rate of 5 K min$^{-1}$ under a dry air flow condition at a flow rate of 80 mL min$^{-1}$ in the range of 298–1173 K using Al$_2$O$_3$ pans. X-ray photoelectron spectroscopy (XPS) measurement was conducted on a Shimadzu ESCA-3400 spectrometer. Samples were mounted on a silver sample holder by using a conductive carbon tape and analyzed using Mg K$\alpha$ radiation in a vacuum chamber in 0.1 eV steps. The position of the carbon peak (284.6 eV) for C1s was used to calibrate the binding energy for all the samples. The surface composition was estimated from the band areas of XP spectrum of S2p, N1s, Ti2p, and O1s and the corresponding relative sensitivity factors. Elemental analyses (EA) were performed on two CHN analyzers (MT-5, Yanaco Co. Ltd. and JM10, J-Science Lab Co. Ltd.) to analyze the contents of C, H, and N and a combustion ion chromatography (Dionex ICS-1500, Mitsubishi Chemical Analytech AQF-2100H) to analyze the S content. N$_2$ adsorption/desorption isotherm was measured at 77 K using liquid nitrogen. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface areas ($S_{\text{BET}}$). The total specific surface area ($S_{\text{tot}}$) and the external specific surface area ($S_{\text{ext}}$) were calculated from the linear fitting of the $V$–$t$ plots (fitting range: 0–0.6 nm for the $S_{\text{tot}}$, and 3.6–4.6 nm for the $S_{\text{ext}}$. The internal specific surface ($S_{\text{int}}$) area for the mesoporous materials was obtained by subtracting the $S_{\text{ext}}$ from the $S_{\text{tot}}$. The pore-size distribution was calculated from the Barrett–Joyner–Halenda (BJH) plots.
Results and discussion

Effect of SO\textsubscript{2} addition on the activity of the photo-SCR

Fig. 1 shows the time course of the photo-SCR over the TiO\textsubscript{2} photocatalyst under illumination in the presence or absence of SO\textsubscript{2} (300ppm) gas at various temperatures. The conversion of NO was stable for 300 min at 433 K in the absence of SO\textsubscript{2} gas as we reported previously\textsuperscript{14}. In the presence of SO\textsubscript{2} at 433 K, the conversion of NO decreased with the reaction time, which indicates that the SO\textsubscript{2} poisoned the catalyst, as in the case of the Mn based catalysts\textsuperscript{9}. The reaction temperature had a significant effect on the deactivation rate of the TiO\textsubscript{2} photocatalyst. At 373 K, the conversion decreased more rapidly than at 433 K and the conversion was almost stable for at least 300 min at 553 K. For simplification, the sample before the reaction was abbreviated as BR, and the samples after the reactions at 373 K, 433 K, and 553 K as AR-373K, AR-433K, and AR-553K, respectively.

![Figure 1. Time course of the photo-SCR in the presence or absence of SO\textsubscript{2} gas at various temperatures. (◆) SO\textsubscript{2}: 0ppm, 433 K, (▲) SO\textsubscript{2}: 300ppm, 373 K, (■) SO\textsubscript{2}: 300ppm, 433 K, (●) SO\textsubscript{2}: 300ppm, 553 K. NO: 1000 ppm, NH\textsubscript{3}: 1000 ppm, O\textsubscript{2}: 2%, He: balance gas, flow rate: 200 mL min\textsuperscript{-1}, GHSV: 100,000 h\textsuperscript{-1}, Light source: 200 W Hg–Xe lamp.](image-url)
XRD patterns

XRD patterns of the catalysts are shown in Fig. 2. In all the catalysts, only the diffraction pattern of anatase TiO$_2$ was observed. Crystalline sizes of anatase TiO$_2$ were estimated from Scherrer equation using the diffraction peaks of (101) and the results are listed in Table 1. The crystalline size did not change (ca. 15 nm) after the reaction, revealing that the aggregation of TiO$_2$ particles did not occur under the reaction conditions at the all reaction temperatures.

![XRD patterns of the catalysts before and after the reaction. (a) BR, (b) AR-373K, (c) AR-433K, and (d) AR-533K. Patterns are offset for clarity.](image)

**Figure 2.** XRD patterns of the catalysts before and after the reaction. (a) BR, (b) AR-373K, (c) AR-433K, and (d) AR-533K. Patterns are offset for clarity.
N₂ adsorption/desorption experiments

In N₂ adsorption/desorption experiments at 77 K (Fig. 3), all the samples exhibited a typical IV-type isotherm and had a vertically long hysteresis loop in the relative pressure (P/P₀) range of 0.8–1.0, suggesting that all the samples had a porous structure. The pore-size distribution of the catalyst before the reaction had a sharp peak at 10 nm (Fig. 4A) and the size was the same order of the crystalline size of TiO₂ (15 nm). These results indicate that the mesopores were formed by the gaps between primary TiO₂ particles. The peak became smaller after the reaction in the presence of SO₂ gas. The specific surface area calculated from the V–t plots (Fig. 4B) is summarized in Table 1. The Sₜₒ­t calculated from the V–t plots was in good agreement in the Sₜₐₓₑₜ. The Sₜₑₓᵗ of all the samples were estimated from the V–t plots as 9.0–10.8 m² g⁻¹. The Sᵢₜₑₓ was calculated by subtracting the Sₑₓᵗ from the Sₜₒ­t. The Sᵢₜₑₓ was 76.2–112 m² g⁻¹, which shows that the most part of the Sₜₒ­t was derived from the mesopores.

Table 1. Crystalline size and specific surface area of catalysts.

<table>
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<tr>
<th>Sample</th>
<th>dᵃ (nm)</th>
<th>Sₜₐₓₑᵗᵇ (m² g⁻¹)</th>
<th>Sₜₒᵗᶜ (m² g⁻¹)</th>
<th>Sₑₓᵗᵈ (m² g⁻¹)</th>
<th>Sᵢₜₑₓᵉ (m² g⁻¹)</th>
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</tr>
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<td>15.3</td>
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<td>118</td>
<td>9.0</td>
<td>109</td>
</tr>
</tbody>
</table>

ᵃ Crystalline size calculated from the FWHM of the diffraction peak of the anatase TiO₂ (101) plane. ᵇ Specific surface area determined by N₂ adsorption isotherm at 77 K using the BET method. ᶜ Total specific surface area calculated from the V–t plots. ᵈ External specific surface area calculated from the V–t plots. ᵉ Internal specific surface area calculated by subtracting the external specific surface area from the total specific surface area.
Figure 3. N\textsubscript{2} adsorption/desorption isotherms at 77 K of (A) BR, (B) AR-373K, (C) AR-433K, and (D) AR-553K. ●: adsorption, △: desorption, pretreatment: evacuation at 398 K for 2 h.

Figure 4. (A) BJH (Barrett-Joyner-Halenda) pore size distribution plots, and (B) V–t plots of the catalysts. ◆: BR, ▲: AR-373 K, ■: AR-433 K, ●: AR-553 K.
FTIR spectra

Fig. 5A shows the FTIR spectra of the catalysts in the region of 900–1800 cm$^{-1}$. In all the catalysts, a band at 1633 cm$^{-1}$ was observed and was attributed to the deformation vibration of water molecules adsorbed on the TiO$_2$ surface. New bands at 1401, 1242, 1116, 1054, and 978 cm$^{-1}$ appeared after the reaction in the presence of SO$_2$ at 373 K. The sharp band at 1401 cm$^{-1}$ was assigned to the bending vibration of ammonium (NH$_4^+$) ions$^{20}$ and was also observed in the case of the reference (NH$_4$)$_2$SO$_4$ powder. Free sulfate ions (SO$_4^{2-}$, $T_d$ symmetry) show two infrared peaks at 1104 ($\nu_3$) and 613 ($\nu_4$) cm$^{-1}$ $^{20}$. The band at 1116 cm$^{-1}$ was due to $\nu_3$ vibration of free sulfate ions, and was also observed in both the cases of (NH$_4$)$_2$SO$_4$ and Na$_2$SO$_4$. When a SO$_4^{2-}$ ion is bound to the TiO$_2$ surface, the symmetry can be lowered to either $C_{3v}$ or $C_{2v}$. The lowering symmetry causes the split of the $\nu_3$ vibration band into two peaks for a $C_{3v}$ symmetry and splits into three peaks for a $C_{2v}$ symmetry $^{20}$. Thus, the bands at 1242, 1054, and 978 cm$^{-1}$ are assigned to the surface coordinated SO$_4^{2-}$ ions. The surface coordinated SO$_4^{2-}$ ions could have the $C_{2v}$ symmetry based on the number of bands. The SO$_4^{2-}$ ion with a $C_{2v}$ configuration is either chelating bidentate or bridge bidentate $^{20}$. In AR-433K, the shape of the spectrum was similar to that of AR-373K although the absorbance of the bands at 1401 and 1116 cm$^{-1}$ were slightly weaker than those of AR-373K. In AR-553K, the band at 1116 cm$^{-1}$ disappeared, which means that the deposition of free sulfates was inhibited in the reaction at 553 K although the other bands at 1401, 1054, and 978 cm$^{-1}$ remained. In the region of 2400–4000 cm$^{-1}$ (Fig. 5B), three adsorption bands at 3425, 3136, 3023 cm$^{-1}$ were observed after the reaction at 373 K. The broad band between 3600–2800 cm$^{-1}$ is the stretching vibration of OH groups derived from surface hydroxyl groups and adsorbed water molecules, which also appeared in the sample before the reaction. The other two bands were observed in the catalysts after the reaction. The bands at 3136 and 3023 cm$^{-1}$ are attributed to the asymmetric stretching vibration ($\nu_3$) and symmetric stretching vibration ($\nu_1$) of NH$_4^+$ ions, respectively. The two bands also appeared in the case of (NH$_4$)$_2$SO$_4$, which strongly advocated the generation of NH$_4^+$ ions after the reaction. The peak intensity at 3136 and 3023 cm$^{-1}$ decreased as the reaction temperature increased, which was consistent with the decrease of the band at 1401 cm$^{-1}$ in Fig. 5A. The FTIR results clearly revealed generation of the free and surface coordinated SO$_4^{2-}$ ions and NH$_4^+$ ions on the TiO$_2$ surface after the reaction. The conversion of NO after 300 min of the reaction decreased in the following order:
AR-553K (80.1%) > AR-433K (37.2%) > AR-373K (12.9%). The order was consistent with that of the peak intensities of the free $\text{SO}_4^{2-}$ ions and $\text{NH}_4^+$ ions, which suggests that generation of ammonium sulfate species (e.g. $(\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4)\text{HSO}_4$) induced the deactivation of the catalyst.

**TG-DTA analysis**

TG profiles of the catalysts are shown in Fig. 6A. Several steps of the weight loss were observed in all the catalysts after the reaction, although the TiO$_2$ has only one step of the weight loss around 330 K. From room temperature to 1173 K, the weights of BR, AR-373K, AR-433K, and AR-553K decreased by 3.9, 16.1, 12.5, 8.1%, respectively. Fig. 6B shows the DTA profiles of the catalysts. All the profiles had a strong exothermic band around 1150 K without a weight loss, which was derived from the phase transition of TiO$_2$ from anatase to rutile. In the DTA profile of BR (see inset of Fig. 6B), a broad exothermic band was observed around 820 K without the weight loss. The peak was observed in all the catalysts before and after the reaction and was possibly due to the

**Figure 5.** FTIR spectra of the catalysts and the reference samples in the region of (A) 900–1800 cm$^{-1}$ and (B) 2400–4000 cm$^{-1}$. (a) BR, (b) AR-373K, (c) AR-433K, (d) AR-533K, (e) $(\text{NH}_4)_2\text{SO}_4$, and (f) Na$_2$SO$_4$. Spectra are offset for clarity.
crystallization of TiO$_2$. Besides, other exothermic bands were observed around 500 and 700 K in the case of the catalysts after the reaction.

Fig. 6C shows the first derivatives of the TG profiles (DTG) in Fig. 6A. The negative band around 330 K was observed in all the catalysts and assigned to desorption of molecular water. Other weight loss peaks were observed around 496 K, 648 K, 740 K, and 940 K. DTG profiles of the (NH$_4$)$_2$SO$_4$ powder and a physical mixture sample of the (NH$_4$)$_2$SO$_4$ powder and the TiO$_2$ powder are also shown in Fig. 6C. In the (NH$_4$)$_2$SO$_4$ powder, two peaks were observed at 530 K and 620 K, which were attributed to the following reactions (2) and (3), respectively.

\[
2(NH_4)_2SO_4 \rightarrow (NH_4)_2S_2O_7 + 2NH_3 + H_2O \quad (2)
\]

\[
3(NH_4)_2S_2O_7 \rightarrow 6SO_2 + 2NH_3 + 2N_2 + 9H_2O \quad (3)
\]

In the physical mixture sample of the (NH$_4$)$_2$SO$_4$ powder and the TiO$_2$ powder, the weight loss profile had negative peaks around 313 K, 508 K, 648 K, 760 K, and 940 K and the peak positions were in good agreement with those of the profile of AR-373K. The analogy of the profiles strongly supports the generation of (NH$_4$)$_2$SO$_4$ species on the TiO$_2$ surface after the reaction at 373 K. The bands around 500, and 650 K decreased as the reaction temperature increased from 373 K to 553 K, which suggests that the increase of the reaction temperature inhibits the deposition of the (NH$_4$)$_2$SO$_4$ species on the TiO$_2$ surface.
In the S 2p XP spectra of BR (Fig. 7A), no band was observed in the range of 165–175 eV. In all the catalysts after the reaction, asymmetric bands were observed at the peak position of 168.6–168.8 eV. The asymmetry of the bands is because of the overlap of the split sublevels of 2p$^{3/2}$ and 2p$^{1/2}$ states of S atoms (separation of bands: 1.2 eV) by spin-orbit coupling. The spectra of the catalysts after the reaction were reasonably fitted using two Gaussian functions (Fig. 8 and Table 2). In all the catalysts after the reaction, the peak positions were 168.5–168.6 and 169.7–169.9 eV.

**Figure 6.** (A) TG profiles, (B) DTA profiles, and (C) derivative thermogravimetry (DTG) profiles of the catalysts and the reference samples. (a) BR, (b) AR-373K, (c) AR-433K, (d) AR-533K, (e) (NH$_4$)$_2$SO$_4$, and (f) physical mixture of (NH$_4$)$_2$SO$_4$ and TiO$_2$ ((NH$_4$)$_2$SO$_4$: 10 % by weight).

**XPS**

In the S 2p XP spectra of BR (Fig. 7A), no band was observed in the range of 165–175 eV. In all the catalysts after the reaction, asymmetric bands were observed at the peak position of 168.6–168.8 eV. The asymmetry of the bands is because of the overlap of the split sublevels of 2p$^{3/2}$ and 2p$^{1/2}$ states of S atoms (separation of bands: 1.2 eV) by spin-orbit coupling. The spectra of the catalysts after the reaction were reasonably fitted using two Gaussian functions (Fig. 8 and Table 2). In all the catalysts after the reaction, the peak positions were 168.5–168.6 and 169.7–169.9 eV,
which corresponded to the peak positions of S 2p$_{3/2}$ and S 2p$_{1/2}$ of sulfate (SO$_4^{2-}$) species, respectively $^{20}$. The ratios of the peak areas of S 2p$_{3/2}$ to those of S 2p$_{1/2}$ were 1.96–1.99 in all the catalysts after the reaction and the values were in good agreement with the theoretical value of 2. The FWHM of the each peak was the same in all the catalysts (ca. 1.6 eV), which suggests that the S 2p XP spectra of the catalysts are derived from a single sulfur species of SO$_4^{2-}$ (S$^{6+}$). N 1s XP spectra are shown in Fig. 7B. The peak positions of N bands of NO$_2^-$ and NO$_3^-$ species on the TiO$_2$ surface were reported to be 403.5 eV and 407.0 eV, respectively $^{24-25}$. There was no band in the region of 403.5–407.0 eV, indicating that the NO$_2^-$ and NO$_3^-$ species did not exist in all the catalysts after the reaction. In AR-373K, there were two bands with the peak positions at 399.9 and 401.8 eV. The shoulder band at 399.9 eV was attributed to N atoms of NH$_3$ adsorbed on Lewis acid sites of TiO$_2$, and the band at 401.8 eV was N atoms of NH$_4^+$ species adsorbed on Brønsted acid sites and/or ammonium salts $^{20}$. The band at 401.8 eV decreased with increasing the reaction temperature and disappeared in the spectrum of AR-533 K. In Ti 2p XP spectra (Fig. 7C), the binding energies of the band of Ti 2p$_{3/2}$ and 2p$_{1/2}$ were 458.6–458.8 and 464.4–464.6 eV in all the catalysts before and after the reaction (Table 3). The values were consistent with those reported in the literature $^{20}$.

Table 4 shows the surface composition estimated from the XPS analysis. The ratio of S atoms to Ti atoms (S/Ti) decreased in the order of AR-373K > AR-433K > AR-553K. The N atoms to Ti atoms (N/Ti) ratio also decreased with increasing the reaction temperature. The decreases of S/Ti and N/Ti ratio should be mainly due to the decomposition of (NH$_4$)$_2$SO$_4$ species based on the FTIR and TG-DTA analyses. The ratio of N atoms to S atoms (N/S) decreased from 0.41 (373K) to 0.10 (553K) with the reaction temperature. The N/S values of the catalysts were lower than that of (NH$_4$)$_2$SO$_4$ powder (0.85). The low N/S values of the catalysts suggests the existence of sulfur species other than (NH$_4$)$_2$SO$_4$. From the XPS analysis, SO$_3^{2-}$ species were not detected and the valence of all the sulfur species was +6. The FTIR spectroscopy revealed the generation of the surface coordinated SO$_4^{2-}$ species with the $C_{2v}$ and/or $C_{3v}$ symmetries. Thus, the low N/S values were due to the generation of the surface coordinated SO$_4^{2-}$ species. Based on the above discussion, the decease of the N/S values with the increase of the reaction temperature is interpreted by the preferential decrease of the (NH$_4$)$_2$SO$_4$ species compared to the surface coordinated SO$_4^{2-}$ species with increasing the reaction temperature.
**Figure 7.** XP spectra of (A) S 2p, (B) N 1s, and (C) Ti 2p of the catalysts. (a) BR, (b) AR-373K, (c) AR-433K, and (d) AR-533K. Patterns are offset for clarity.
Figure 8. Result of the peak fitting of S 2p XP spectra of AR-373K (A), AR-433K (B), and AR-533K (C). Back circles: experimental data, dashed line: base line (linear function), solid lines: the result of the peak fitting.
Table 2. Results of the peak fitting of S 2p XP spectra.

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$^a$ Counts per second

$^b$ Ratio of the peak area of S 2p$_{3/2}$ to that of S 2p$_{1/2}$.

Table 3. Peak positions of XP spectra of Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$.

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<td>AR-553 K</td>
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Table 4. Surface composition estimated from XPS.

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<tr>
<td>AR-553K</td>
<td>0.14</td>
<td>0.01</td>
<td>0.10</td>
</tr>
<tr>
<td>(NH$_4$)$_2$SO$_4$</td>
<td>–</td>
<td>–</td>
<td>0.85</td>
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</tbody>
</table>
Elemental analysis (EA)

Concentrations of sulfur atoms and nitrogen atoms were estimated from EA (Table 5). The concentration of S atoms and N atoms increased after the reaction and decreased with increasing the reaction temperature. The tendency corresponded to the results of XPS analysis. Surface densities of each atom were calculated by dividing the concentrations by the BET specific surface area of BR (Table 1). The surface density of Ti atoms was calculated to be 7.0 nm$^{-2}$ using a (100) plane of anatase TiO$_2$ and the BET specific surface area of BR. In AR-373K, the surface densities of sulfur atoms and nitrogen atoms were 5.5 and 9.3 nm$^{-2}$, respectively, and the sum of the values were almost twice as much as that of Ti atoms. The result suggests the generation of a bulk (NH$_4$)$_2$SO$_4$ species.

The N/S ratio estimated from EA (Table 5) had a same tendency as that evaluated by XPS: the N/S ratio decrease with increasing the reaction temperature. In AR-373K, the N/S ratio was 1.7 and was close to 2, which was the theoretical value of chemical composition of (NH$_4$)$_2$SO$_4$. Thus, most part of SO$_4^{2-}$ species is present as a (NH$_4$)$_2$SO$_4$ salt in AR-373K. However, the N/S ratio by the XPS analysis is 0.41, which was almost half of the experimental value of the reference (NH$_4$)$_2$SO$_4$ powder (Table 4). The discrepancy between N/S ratios estimated from EA and XPS could be interpreted by considering the generation of the bulk (NH$_4$)$_2$SO$_4$ species. XPS analysis is more sensitive to surface-coordinated SO$_4^{2-}$ species than bulk (NH$_4$)$_2$SO$_4$ species. The N/S ratio estimated from XPS should be lower than the real amount of the (NH$_4$)$_2$SO$_4$ species, which was estimated from the EA, when the (NH$_4$)$_2$SO$_4$ species has a bulk structure. Thus, the lower N/S ratio by XPS than that by EA also implies the generation of the bulk (NH$_4$)$_2$SO$_4$ species.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration (wt%)</th>
<th>Surface density (nm$^{-2}$)</th>
<th>N/S (atom/atom)</th>
</tr>
</thead>
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<tr>
<td></td>
<td>S</td>
<td>N</td>
<td>S</td>
</tr>
<tr>
<td>BR</td>
<td>0.06</td>
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</tr>
<tr>
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</tr>
<tr>
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</tr>
<tr>
<td>AR-553K</td>
<td>1.7</td>
<td>0.64</td>
<td>2.7</td>
</tr>
</tbody>
</table>

Table 5. Results of elemental analysis
Structure of the ammonium sulfate species and deactivation mechanism

N₂ adsorption/desorption experiments revealed the decrease of the $S_{tot}$ after the reaction, which was mainly due to the decrease of the $S_{int}$. The decrease of the $S_{int}$ is not due to the aggregation of the TiO₂ particles during the reaction because the crystalline size of the TiO₂ particles did not change after the reaction (Table 1). FTIR, TG-DTA, XPS, and EA revealed the generation of the bulk (NH₄)₂SO₄ species on the TiO₂ surface after the reaction. The amount of (NH₄)₂SO₄ in AR-373K, which contains the largest amount of S and N atoms among the three catalysts after the reaction, is calculated to be 12wt% assuming that all the N atoms, which were estimated from EA, exist in the (NH₄)₂SO₄ form. However, the XRD diffraction peak of the bulk (NH₄)₂SO₄ species was not observed in AR-373K, which implies that the generated bulk (NH₄)₂SO₄ species has amorphous structure. Thus, the generated bulk (NH₄)₂SO₄ species plugged the pores of the catalysts, which resulted in the decrease of the $S_{int}$ (Fig. 9).

![Figure 9. Deposition model of sulfate species of the catalysts.](image-url)

The amount of the (NH₄)₂SO₄ species decreased with increasing the reaction temperature. Fig. 10 shows a correlation between the $S_{tot}$ and the contents of N and S estimated from the EA. The increment of the contents of S and N drastically decreased the $S_{tot}$. FTIR analysis revealed two SO₄$^{2-}$
species: one is the (NH$_4$)$_2$SO$_4$ species and the other is the surface coordinated SO$_4^{2-}$ species. The negative linear correlation for N contents strongly suggests that the decrease of the S$_{tot}$ is because of the generation of not the surface coordinated SO$_4^{2-}$ species but the bulk (NH$_4$)$_2$SO$_4$ species. The conversion of NO after 300 min of the reaction was plotted vs. the S$_{tot}$ (Fig. 11). The strong positive and linear correlation was obtained, which indicates that the decrease of the S$_{tot}$ results in the decrease of the conversion of NO. Based on the above discussion, we concluded that the generation of the (NH$_4$)$_2$SO$_4$ species plugged a part of the mesopores derived from the gap between the TiO$_2$ particles, which resulted in the decrease of the S$_{tot}$ and the deactivation of the catalyst.

**Figure 10.** Effect of the contents of N atoms (A) and S atoms (B) on the S$_{tot}$ estimated from the V–t plots.
Conclusions

In this study, tolerance to SO$_2$ gas was investigated in the photo-SCR of with NH$_3$ over the TiO$_2$ photocatalyst. Introduction of SO$_2$ drastically decreased the conversion of NO at 373 K. The increment of the reaction temperature drastically improved the stability of the catalyst and, at 553 K, the deactivation was not observed for 300 min of the reaction. FTIR and XPS results suggest that two SO$_4^{2-}$ species exist on the TiO$_2$ surface: the surface coordinated SO$_4^{2-}$ species and the free SO$_4^{2-}$ species as a bulk (NH$_4$)$_2$SO$_4$ formed after the photocatalytic reaction. The deactivation occurs due to a pore plugging by the deposition of (NH$_4$)$_2$SO$_4$ species on the TiO$_2$ surface on the basis of the correlation among the contents of N and S atoms after reaction, the $S_{tot}$ estimated from $V$–$t$ plots, and the photocatalytic activity.

References


Chapter 5

Noble-metal-free NO$_x$ Storage over Ba-modified TiO$_2$ Photocatalysts under UV-light Irradiation at Low Temperatures

Abstract

Photo-assisted nitrogen oxides (NO$_x$) storage was investigated over the barium-modified titanium dioxide (Ba/TiO$_2$) photocatalysts under UV-light irradiation at a high concentration of nitrogen monoxide (NO) of 200 ppm and a high gas hourly space velocity (GHSV) of 50,000 h$^{-1}$. The NO removal efficiency was kept $> 99\%$ during the 1020 s interval from the start of the reaction over the Ba/TiO$_2$ photocatalyst. The temperature-programed desorption (TPD) measurement and X-ray diffraction (XRD) technique revealed that barium oxide (BaO) species functioned as a NO$_x$ storage material even at low temperatures, which result in improvement of the performance of the photo-assisted NO$_x$ storage.
Introduction

Lean-burn and diesel engines are one of the most important technologies to improve the fuel efficiency of internal combustion engines and reduce carbon dioxide (CO$_2$) emissions. Significant fuel economy can be achieved when the engines operate under lean conditions of an air-to-fuel (A/F) ratio of approximately 20–65.\textsuperscript{1} The conventional three-way catalyst is not capable of efficiently decomposing NO$_x$ in the exhaust gas from the engines, although it can reduce NO$_x$ in the stoichiometric condition at an A/F ratio of 14.7.\textsuperscript{2,3} The NO$_x$ removal at high A/F ratios was performed using catalytic processes such as selective catalytic reduction (SCR)\textsuperscript{4-5} and NO$_x$ storage and reduction (NSR).\textsuperscript{6-8}

In the SCR system, urea is injected into the exhaust gas and decomposes into ammonia (NH$_3$) and CO$_2$. The NH$_3$ reacts with NO$_x$ in the exhaust gas to form harmless nitrogen (N$_2$) under the lean condition. This technology is widely used in diesel engines and motor vehicles using Fe- or Cu-zeolite catalysts.\textsuperscript{9-13} Alternatively, the NSR catalyst (typically, Pt/BaO/Al$_2$O$_3$) operates under lean and rich conditions. NO$_x$ was oxidised over Pt and stored as nitrite (NO$_2^-$) or nitrate (NO$_3^-$) species under the lean condition, where barium oxide (BaO) functions as a NO$_x$ storage material.\textsuperscript{14} After the NO$_x$ storage period under the lean condition (approximately 60–90 s), the engines are switched to the fuel-rich condition for a short period (approximately 3–5 s) by injecting fuels, where the stored NO$_x$ is released and reduced into harmless N$_2$ over Pt.\textsuperscript{14} The cycling operation of the lean and rich conditions provides high NO$_x$ removal efficiency.\textsuperscript{15} However, these SCR and NSR catalysts cannot reduce NO$_x$ efficiently below 423 K.\textsuperscript{16-18} In the urea-SCR system, according to the reports of the International Council for Clean Transportation (ICCT), urea injection could not start for approximately 800 s during the cold start test in the world harmonized transient cycle (WHTC) because the temperature of the exhaust gas was too low.\textsuperscript{16} Controlling the NO$_x$ emission under the cold start condition is a key and urgent task to lower the total emission of NO$_x$.

We have focused on TiO$_2$ photocatalysts as NO$_x$ storage materials to reduce NO$_x$ emissions in the cold start condition from the viewpoint of non-toxicity, low operating temperature, and rapid response to light. Under the cold start condition, utilising the photocatalysts enable the de-NO$_x$ system to work at the same time that the engine starts. There are many reports concerning the
oxidation of NO over TiO$_2$-based photocatalysts under light irradiation.$^{19-28}$ In these reports, NO in the gas phase was oxidised to NO$_2$ and surface NO$_x$ species and stored on the TiO$_2$ surface. Most of the researchers investigated the oxidation of NO over TiO$_2$ photocatalysts at very low concentrations of NO (less than 10 ppm) and/or at low gas hourly space velocity (GHSV) of 10–1000 h$^{-1}$ because their objective was the removal of NO$_x$ in air,$^{22,29}$ and elucidation of the reaction mechanism of NO oxidation.$^{24-25,30-32}$ These conditions were quite different from those of practical exhaust gas in lean-burn engines (typically, concentration of NO $> 200$ ppm and GHSV $> 50,000$ h$^{-1}$). Thus, the potential of the TiO$_2$ photocatalyst for NO$_x$ storage materials in the cold start condition has not been investigated. In this research, we investigated photo-assisted NO$_x$ storage at a high concentration of NO and high GHSV to assess the potential of the TiO$_2$ photocatalyst. In addition, the role of Ba modification was examined in the performance of the photo-assisted NO$_x$ storage.

**Experimental**

**Catalyst preparation**

TiO$_2$ powder (ST-01, anatase) was purchased from Ishihara Sangyo Kaisha, Ltd. Ba(NO$_3)_2$ (wako, 99.9%) was used without further purification. Ba(NO$_3)_2$ was impregnated on the TiO$_2$ powder using a 20 mL of water as a solvent. The catalyst powder was tabletted and grinded into granules with a diameter of 300–600 µm using 25 and 50 mesh sieves.

**Photocatalytic reaction**

Photo-assisted NO$_x$ storage was carried out using a conventional fixed bed flow system at an atmospheric pressure. A quartz reactor (H12 mm × W10 mm × D1.0 mm, the reactor volume: 0.12 mL) was used for the reaction. 0.13 g of the catalyst granules were introduced to the reactor and then pretreated at various temperatures (298–873 K) in a 10% O$_2$/He gas mixture at a flow rate of 50 mL min$^{-1}$ for 1 h. The reaction gas composition was as follows: NO (200ppm), O$_2$ (3%), He (balance). A 300 W Xe lamp (Perkin-Elmer PE300BF) was used as a light source. The outlet concentration of NO$_x$ (NO+NO$_2$) was measured using a portable gas analyzer (Horiba PG-335). N$_2$ and N$_2$O products were analyzed by Shimadzu GC-8A TCD gas chromatographs. The dead time was obtained as the time at which the concentration of NO$_x$ exceeded 2 ppm (99% of the conversion of NO) in the outlet
gas. NO₃ storage capability (NSC) was calculated as the total amount of the NOₓ stored for 1 h from the start of the reaction.

**Characterization**

The specific surface areas (SSA) was obtained by Brunauer–Emmett–Teller (BET) method using N₂ adsorption isotherm measured at 77 K. X-ray diffraction (XRD) measurement was performed on a Rigaku Ultima IV X-ray diffractometer with Cu-Kα radiation (λ = 1.5418 Å). The crystallite size was determined by the Scherrer's equation using the diffraction peak of anatase TiO₂ (101) plane (2θ = 25.2°) by the Scherrer equation:

\[
d = \frac{K\lambda}{\beta \cos \theta}
\]

where \(d\) is the crystallite size, \(\lambda\) is the wavelength of the X-ray radiation (CuKα, \(\lambda = 1.5406\) Å), \(K\) is the taken as 0.89, and \(\beta\) is the full width at half maximum (FWHM) of the diffraction peak. A diffraction peak of single-crystal silicon (111) (2θ = 28.4°) was used as the standard material to estimate instrumental peak broadening. Temperature-programed desorption (TPD) experiments were performed using the same experimental set-up as the reaction in a 10% O₂/He gas mixture at a flow rate of 50 mL min⁻¹. After the temperature was kept at 373 K for 30 min, the TPD measurement was started at a heating rate of 5 K min⁻¹ up to 923 K.

**Results and discussion**

Fig. 1 shows the time course of the outlet concentrations of NOₓ (= NO + NO₂) for NOₓ storage under various reaction conditions after the pretreatment at 773 K in a 10% O₂/He gas mixture. Without a catalyst, the concentration of NOₓ increased with the introduction of NO and immediately became 200 ppm. However, the concentration of NO was less than 2 ppm during the initial 530 s of the reaction (conversion of NO > 99%) over TiO₂. After the dead time for the breakthrough of NOₓ, the concentration of NO gradually increased with the reaction time and became 175 ppm after 3 h (not saturated), where N₂ and N₂O products were not detected by the TCD-GCs. The concentration of NO became 200 ppm after 20 h of the reaction, where the inlet NO gas slipped through the catalyst possibly because of the saturation of the TiO₂ surface by the adsorbed NOₓ species. The total
amount of the stored NO\textsubscript{x} species after 20 h was calculated to be 426 µmol g\textsuperscript{-1}. The surface density of NO\textsubscript{x} species was calculated to be 1.4 nm\textsuperscript{-2}. When the TiO\textsubscript{2} (100) surface is considered, the density of the surface Ti atoms was 7.0 nm\textsuperscript{-2}, and 20% of the surface Ti sites are occupied by the adsorbed NO\textsubscript{x} species assuming a one-to-one relationship between the stored NO\textsubscript{x} species and surface Ti sites.

The addition of Ba drastically enhanced the dead time of the NO\textsubscript{x} slip to 1020 s, which was almost twice as long as that of the TiO\textsubscript{2} photocatalyst. The dead time value meets the demand (800 s) for the cold start condition reported by the ICCT.\textsuperscript{16} The NO\textsubscript{x} storage capability (NSC) is defined as the amount of stored NO\textsubscript{x} after 1 h from the start of the reaction and was calculated to be 252 µmol g\textsuperscript{-1}. For the typical NSR catalyst, Pt/Ba/Al\textsubscript{2}O\textsubscript{3}, the NSC at 473 and 573 K was reported to be 177 and 581 µmol g\textsuperscript{-1}, respectively. The NSC of the Ba/TiO\textsubscript{2} photocatalyst was comparable to that of the typical NSR catalyst containing precious noble metals (Pt). Thus, the utilisation of photocatalysts enables us to eliminate the use of expensive and rare precious metals from the de-NO\textsubscript{x} catalyst.

The NO\textsubscript{x} storage was hardly observed without UV-light irradiation (Fig. 1, no dead time), and the NSC was calculated to be 88.4 µmol g\textsuperscript{-1}. The result clearly indicates that the UV-light irradiation accelerated the activity of the NO\textsubscript{x} storage. In the absence of O\textsubscript{2}, the reaction hardly proceeded, as observed in Fig. 1. In previous reports, active oxygen radicals derived from molecular O\textsubscript{2} (\textit{e.g.}, O\textsuperscript{2−}, O\textsuperscript{−}, and OH radicals) reacted with the NO gas to form NO\textsubscript{x} species on the TiO\textsubscript{2} surface.\textsuperscript{24-25, 29} The significant impact of UV-light and O\textsubscript{2} gas on the activity suggests that the reaction proceeded via O\textsubscript{2} radicals generated under UV-light irradiation, as displayed in the previous reports.\textsuperscript{24}
Fig. 2 shows the time course of the NO\textsubscript{x} storage at various pretreatment temperatures over the TiO\textsubscript{2} and Ba/TiO\textsubscript{2} catalysts. The NSC and dead time drastically decreased with the pretreatment temperature using the TiO\textsubscript{2} photocatalyst. Only the diffraction pattern of anatase TiO\textsubscript{2} was observed in the XRD patterns of all the TiO\textsubscript{2} samples before and after the reaction (the date is not shown). As observed in Table 1 (Entries 1–3), the crystalline size of TiO\textsubscript{2} increased from 8.9 to 28 nm, and the specific surface area (SSA) of the catalysts decreased from 292 to 50.7 m\textsuperscript{2} g\textsuperscript{−1} after the pretreatment at 873 K. The positive correlation of the NSC and SSA strongly indicates that the SSA has a significant effect on the NSC for the TiO\textsubscript{2} photocatalyst.

Ba/TiO\textsubscript{2} exhibits high resistance to the high-temperature pretreatment; the decrease in the activity of the Ba/TiO\textsubscript{2} catalysts by elevating the pretreatment temperature was smaller than that observed for the TiO\textsubscript{2} catalyst (Fig. 2 and Entry 8, 10, and 11 in Table 1). The SSA of the Ba/TiO\textsubscript{2}
catalyst was almost stable up to 773 K and then decreased at 873 K. The pretreatment at 873 K slightly decreased the crystalline size of TiO₂ in the Ba/TiO₂ photocatalyst from 7.7 to 12 nm, although this value largely decreased for the TiO₂ photocatalyst. This result clearly indicates that the Ba modification suppressed the growth of TiO₂ particles. Similar effects were previously reported for metal doping into TiO₂ (e.g., Si, Zr, La, and Al). The Ba loading enhanced the thermal stability of the catalyst, which should be one of the reasons for the higher NSC of the Ba/TiO₂ catalyst than that of the TiO₂ catalyst. The thermal stability is an advantage in the practical use of lean-burn engines.

![Figure 2. Time course of the NOx storage at the pretreatment temperatures of 673 K (a), 773 K (b), and 873 K (c). NO: 200ppm, O₂: 3%, He balance.](image-url)
The effect of the pretreatment temperature on the activity of the Ba/TiO$_2$ catalyst is summarised in Table 1. In the pretreatment temperature range of 298–573 K, the NSC of the Ba/TiO$_2$ catalyst (Entries 4–6 in Table 1) was lower than that of the bare TiO$_2$ catalyst after the pretreatment at 773 K (Entry 2) even though the crystalline size of TiO$_2$ in the Ba/TiO$_2$ catalyst was smaller than

Table 1. The result of the NO$_x$ storage, the BET specific surface area, and the crystalline size of the TiO$_2$ particle.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Temp. (^a) / K</th>
<th>SSA (b) / m$^2$ g$^{-1}$</th>
<th>(d (^c) / nm )</th>
<th>NSC (f) / μmol g$^{-1}$</th>
<th>Dead time (g) / s</th>
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</tr>
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<td>108</td>
<td>7.7</td>
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</table>

\(a\) Pretreatment temperature. \(b\) Specific surface area determined by the BET methods. \(c\) Crystalline size of the TiO$_2$ particles. \(d\) As-synthesized. \(e\) After the NO$_x$ storage reaction. \(f\) NO$_x$ storage capacity after 1 h of the reaction. \(g\) Reaction time after which the outlet concentration of NO$_x$ was less than 2 ppm. \(h\) Ba loading: 1000 μmol g$^{-1}$. 

The effect of the pretreatment temperature on the activity of the Ba/TiO$_2$ catalyst is summarised in Table 1. In the pretreatment temperature range of 298–573 K, the NSC of the Ba/TiO$_2$ catalyst (Entries 4–6 in Table 1) was lower than that of the bare TiO$_2$ catalyst after the pretreatment at 773 K (Entry 2) even though the crystalline size of TiO$_2$ in the Ba/TiO$_2$ catalyst was smaller than
that in the TiO_2 catalyst. The generation of crystalline Ba(NO_3)_2 was observed in the as-prepared Ba/TiO_2 catalyst using XRD (Fig. 3), which suggests that the decrease in the NSC occurs because the TiO_2 surface is covered with the impregnated Ba(NO_3)_2 species. The NSC increased drastically upon increasing the pretreatment temperature from 573 to 673 K. The increase in the NSC was not due to the change in the SSA because the SSA decreased from 187 to 155 m^2 g^{-1}. The crystalline size of TiO_2 did not change in the pretreatment temperature region of 573–673 K, which indicates that the growth of TiO_2 particles did not occur during the pretreatment in this temperature region. To investigate the effect of the pretreatment temperature, temperature programmed desorption (TPD) experiments were performed using the same experimental set-up as the reaction in a 10% O_2/He gas mixture, and the result of the as-prepared Ba/TiO_2 catalysts is presented in Fig. 4 (experimental detail in the ESI). By integrating the TPD profiles, the total desorption amount of NO_x (NO+NO_2) was calculated to be 242 µmol, which was consistent with the loading amount of NO_3^- ions in the Ba/TiO_2 catalyst (260 µmol). The TPD spectrum was reasonably fitted using three Gaussian functions with peaks at 694, 806, and 840 K (the fitting result is presented in Fig. 5). The intensity of crystalline Ba(NO_3)_2 in Fig. 3 decreased after the pretreatment at 773 K and completely disappeared at 873 K. The XRD results reveal that the TPD peaks at the higher temperatures of 806 and 840 K were due to the decomposition of crystalline Ba(NO_3)_2 observed in the XRD patterns. The peak at temperatures below 694 K can possibly be attributed to Ba(NO_3)_2 on the TiO_2 surface. The desorption of NO started at approximately 600 K, which corresponded to the uptake temperature of the NSC of 623 K. The generation of NO was observed in TPD experiments, as shown in Fig. 4. In addition, the concentration of NO in thermal equilibrium was calculated using the concentration of NO_x and O_2 (3%) (TPD experimental condition) and thermodynamic parameters of the following equation from the NIST Chemistry WebBook^36:

\[
\text{NO} + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{NO}_2 \quad K = \frac{P_{\text{NO}_2}}{P_{\text{NO}}P_{\text{O}_2}^{1/2}}
\]

where, \( P_x \) is the partial pressure of species \( x \). The concentration of NO detected was much lower than that calculated especially at temperatures below 760 K, which indicates that NO_2 was first generated at temperatures below 850 K. Thus, the decomposition of Ba(NO_3)_2 proceeds as described in the following reaction (2)^37-38

\[
\text{Ba(NO}_3\text{)}_2 \rightarrow \text{BaO} + 2\text{NO}_2 + \frac{1}{2}\text{O}_2
\]
Thus, we concluded that the increase of the NSC between 623 and 673 K was due to the generation of BaO, as observed in Eq. (2), and the generated BaO functions as a NO\textsubscript{x} storage material in the photo-assisted NO\textsubscript{x} storage as well as the typical NSR catalyst. The NSC decreased at the pretreatment temperature of 873 K. At this temperature, the SSA decreased, and the crystalline size of TiO\textsubscript{2} increased. In addition, the diffraction peaks of the BaTiO\textsubscript{3} mixed oxide appeared (Fig. 3). Thus, the decrease in the NSC at 873 K could be due to the decrease in the SSA of the catalyst and/or the generation of the BaTiO\textsubscript{3} mixed oxide.

Figure 3. XRD patterns of the catalysts before and after the reaction at various pretreatment temperatures. TiO\textsubscript{2} before the reaction (a), Ba/TiO\textsubscript{2} before the reaction (b), and Ba/TiO\textsubscript{2} after the reaction at pretreatment temperatures of 298 K (c), 573 K (d), 623 K (e), 673 K (f), 723 K (g), 773 K (h), and 873 K (i).
Figure 4. TPD profiles of 1000 μmol g⁻¹ Ba/TiO₂ catalyst in a 10% O₂/He gas mixture. NO (calc.) was calculated using the equilibrium constants of eq. (1) and the concentration of NOₓ and O₂ (3%) in the TPD experiment.

Figure 5. Peak deconvolution of the TPD profile of 1000 μmol g⁻¹ Ba/TiO₂ using three Gaussian functions.
Conclusions

In summary, we have developed an effective NO\textsubscript{x} storage method at a low temperature using TiO\textsubscript{2}-based photocatalysts under UV-light irradiation. We observed that the Ba modification on a TiO\textsubscript{2} surface drastically improved the performance of the catalyst. The Ba/TiO\textsubscript{2} photocatalyst exhibited 1020 s of dead time, which is sufficient for the desired value (800 s) reported by the ICCT. The effect of the pretreatment temperature was also studied, and two positive effects of Ba modification on the NSC were proposed: (i) the Ba modification inhibits the densification of TiO\textsubscript{2} particles, which helped to maintain the high SSA of TiO\textsubscript{2} and (ii) the BaO species, which was generated from the decomposition of Ba(NO\textsubscript{3})\textsubscript{2}, works as a NO\textsubscript{x} storage material over the photocatalysts at low temperatures. We concluded that TiO\textsubscript{2} and Ba/TiO\textsubscript{2} are promising for NO\textsubscript{x} storage materials at low temperatures and have the potential to reduce NO\textsubscript{x} emissions in the cold start condition.

Reference


Chapter 6

NO\textsubscript{x} Storage over Ba-modified TiO\textsubscript{2} Photocatalysts under UV-light Irradiation: Effect of Ba Loading and Structure of Ba Oxide Species

Abstract

Effect of Ba loading in photo-assisted NO\textsubscript{x} storage over Ba-modified TiO\textsubscript{2} photocatalysts under UV-light irradiation was investigated by temperature programed desorption (TPD), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and diffuse reflectance infrared Fourier transform spectroscopy (DRIFT). The Ba loading had a significant effect on the activity of NO\textsubscript{x} storage; the activity increased with increasing the Ba loading up to 500 \( \mu \text{mol g}^{-1} \), and the further increase of the Ba loading decreased the activity. Based on the TPD results, there were at least two \( \text{Ba(NO}_3\text{)}_2 \) species in the as-synthesized catalysts: surface and bulk \( \text{Ba(NO}_3\text{)}_2 \). The surface \( \text{Ba(NO}_3\text{)}_2 \) was decomposed to Ba oxide species during the pretreatment at 773 K, and the generated Ba oxide species improved the activity. On the other hand, the amount of the bulk \( \text{Ba(NO}_3\text{)}_2 \) increased with the Ba loading over 500 \( \mu \text{mol g}^{-1} \), which caused the decrease of the activity. DRIFT investigations revealed that bulk BaO was not generated on a TiO\textsubscript{2} surface because nitrate species adsorbed on Ba sites were not observed in NO/O\textsubscript{2} gas under UV-light irradiation. DRIFT, XRD, XPS, and TEM results suggested that the surface Ba–Ti mixed oxides with an amorphous structure was generated during the pretreatment. Combined with the results of NO\textsubscript{x} storage, the formed Ba–Ti mixed oxides functioned as an effective NO\textsubscript{x} storage material, which improved the NO\textsubscript{x} storage capacity.
Introduction

Control of NO\textsubscript{x} emission in exhaust gas from engines is strongly required in terms of air purification. Many researchers and engineers have been challenged to develop efficient de-NO\textsubscript{x} technologies.\textsuperscript{1} At the stoichiometric air-to-fuel (A/F) ratio of 14.7, three way catalysts are used for the NO\textsubscript{x} removal.\textsuperscript{2-3} However, under lean conditions (air-rich, A/F ratio: 20–65), typical three way catalysts cannot efficiently decompose the NO\textsubscript{x} to harmless N\textsubscript{2} although the lean operation of the engines leads to fuel economy and decreases of CO\textsubscript{2} emission.\textsuperscript{4-5} Two technologies have been developed for the removal of NO\textsubscript{x} under the lean condition: selective catalytic reduction (SCR) and NO\textsubscript{x} storage and reduction (NSR). In the SCR, NH\textsubscript{3}, which is produced by decomposition of urea, is introduced into the exhaust gas, and the introduced NH\textsubscript{3} reduces the NO\textsubscript{x} to N\textsubscript{2}. The SCR have been investigated by many researchers since 1970s. V\textsubscript{2}O\textsubscript{5}-based catalysts\textsuperscript{6-8} and Fe- or Cu- zeolite catalysts\textsuperscript{9} show high activity over 473 K. This technology is widely used in stationary emission sources and mobile emission sources including diesel engines in vehicles and trucks. However, the NO\textsubscript{x} removal efficiency is low below 473 K.

Low-temperature removal of NO\textsubscript{x} is highly desired in exhaust gas from vehicle engines. Regulation of NO\textsubscript{x} emission has become severe year by year,\textsuperscript{10} and a recent report by the International Council for Clean Transportation (ICCT) pointed out the impact of the NO\textsubscript{x} emission in the initial stage of engine start-up on the total emission amounts; in the cold start condition below 473 K (approximately 800 s), urea cannot be injected because of the low activity of the catalyst to avoid ammonia slip.\textsuperscript{11} Thus, development of low temperature technology for NO\textsubscript{x} removal is urgent task to improve the total removal efficiency of NO\textsubscript{x} in the cold start condition.

On the other hand, the NSR technology was firstly reported by Toyota researchers in 1995.\textsuperscript{5} The NSR catalyst is composed of three components: precious metals, alkali or alkali earth oxides, and supports (e.g., Pt/BaO/Al\textsubscript{2}O\textsubscript{3}).\textsuperscript{4} In the lean condition, NO is oxidized on Pt sites and stored as nitrite (NO\textsubscript{2}) or nitrate (NO\textsubscript{3}\textsuperscript{-}) species. At that time, BaO functions as a NO\textsubscript{x} storage material. After the NO\textsubscript{x} storage in the lean condition, the engine is switched to the fuel-rich condition for a short time by injecting the fuels, and the stored NO\textsubscript{3}\textsuperscript{-} is reduced by the injected fuels into N\textsubscript{2} over Pt sites.\textsuperscript{4}
The lean and rich cycle operation provides the high NO\textsubscript{x} removal efficiency.\textsuperscript{13} However, the NSR catalysts also cannot reduce the NO\textsubscript{x} efficiently at low temperatures below 473 K.\textsuperscript{14}

Photocatalysts are promising materials in terms of such a low temperature operation. Until now, several photocatalysts have been reported in the NO oxidation: TiO\textsubscript{2},\textsuperscript{15} N-doped TiO\textsubscript{2},\textsuperscript{16} metal-modified TiO\textsubscript{2},\textsuperscript{17-18} TiO\textsubscript{2}–Al\textsubscript{2}O\textsubscript{3} binary oxide.\textsuperscript{19-20} The reaction mechanism of NO oxidation was also investigated over the TiO\textsubscript{2} photocatalysts.\textsuperscript{21-28} Recently, we demonstrated the Ba-modified TiO\textsubscript{2} photocatalysts showed high activity at a practical condition (gas hourly space velocity: 50,000 h\textsuperscript{-1}, NO concentration: 200 ppm) under UV-light irradiation, and Ba modification of TiO\textsubscript{2} greatly enhanced the activity of NO\textsubscript{x} storage at low temperature.\textsuperscript{29} The activity was improved after the pretreatment in O\textsubscript{2}/He gas over 673 K, and the temperature corresponded to the decomposition temperature of Ba(NO\textsubscript{3})\textsubscript{2} used as a Ba precursor. Thus, the activated Ba oxide species were generated during the pretreatment. The structure and the role of Ba oxide species is still unclear as the case now stands.

In Pt/BaO/Al\textsubscript{2}O\textsubscript{3} system of a typical NSR catalyst, classically, BaO and BaCO\textsubscript{3} species were assumed to be NO\textsubscript{x} storage materials.\textsuperscript{4,13} On the other hand, BaO and Al\textsubscript{2}O\textsubscript{3} react at high temperature (>1073 K) to form an aluminate phase, BaAl\textsubscript{2}O\textsubscript{4}\textsuperscript{30-32} It was previously reported that the BaAl\textsubscript{2}O\textsubscript{4} was a better NO\textsubscript{x} storage material than BaO and/or BaCO\textsubscript{3},\textsuperscript{30-31} although other groups reported that the generation of BaAl\textsubscript{2}O\textsubscript{4} decreased the performance.\textsuperscript{33} In addition, TiO\textsubscript{2} was added to the NSR catalyst to improve the dispersion of Ba species using a strong interaction between Ba and Ti atoms,\textsuperscript{34} and the tolerance to sulfur poisoning,\textsuperscript{35-37} where the high temperature operations resulted in the generation of mix-oxide phase of Ti and Ba.\textsuperscript{34,38} (e.g., BaTiO\textsubscript{3}) In our photocatalytic system, BaTiO\textsubscript{3} phase was observed after the pretreatment in O\textsubscript{2}/He at 873 K, and the generation caused the decrease of NO\textsubscript{x} storage activity.\textsuperscript{29} Thus, the generation of mixed oxide phase and the effect on the activity should be considered to explain the role of Ba oxide species. In the present paper, the structure and role of Ba oxide species were investigated in the photo-assisted NO\textsubscript{x} storage at low temperature to elucidate the Ba oxide species active for the NO\textsubscript{x} storage.
Experimental

Materials

**TiO**$_2$ (ST-01, Ishihara Sangyo Kaisha, Ltd) powder was used as purchased. Barium nitrate (Ba(NO$_3$)$_2$, 99.9%) and barium titanate (BaTiO$_3$) were purchased from Wako co. ltd. (Japan). 100–1000 μmol g$^{-1}$ Ba/TiO$_2$ catalysts were prepared by impregnation using a Ba(NO$_3$)$_2$ precursor and a water (20 mL) as a solvent.

Activity tests

Photo-assisted NO$_x$ storage was carried out using a fixed bed flow system. The detail was shown elsewhere.$^{29}$ Briefly, 0.13 g catalyst granules (diameter: 300–600 μm) were added to a quartz reactor (12 mm × 10 mm × 1 mm, volume: 0.12 mL), and then pretreated at 773 K in 10% O$_2$/He gas at 50 mL min$^{-1}$ for 1 h. The reaction gas (NO: 200 ppm, O$_2$: 3%, He: balance) was flowed at 100 mL min$^{-1}$. A 300 W Xe lamp (Perkin-Elmer PE300BF) was used as a light source. The NO$_x$ (NO+NO$_2$) in the outlet gas was analyzed using a portable gas analyzer (HORIBA PG-335). Dead time for NO$_x$ breakthrough, which was defined as a time when the outlet concentration of NO$_x$ reached to 2 ppm (conversion of NO: 99%), was used for NO$_x$ breakthrough in the present research.

Characterization

N$_2$ adsorption measurement was performed on a Belsorp-miniII (BEL, Japan) at 77 K. The specific surface area ($S_{BET}$) was estimated from the N$_2$ adsorption isotherm using Brunauer–Emmett–Teller (BET) method. X-ray diffraction (XRD) measurement was carried out using a Rigaku Ultima IV X-ray diffractometer with Cu-Kα radiation ($λ = 1.5406$ Å). The crystallite size was determined by the Scherrer equation using the full width at half maximum (FWHM) of the diffraction peak of anatase TiO$_2$ (101) plane. Temperature-programed desorption (TPD) experiment was performed on the same experimental set-up as the activity test in 10% O$_2$/He gas at 50 mL min$^{-1}$. After the temperature was kept at 373 K for 30 min, the TPD measurement was started at a heating rate of 5 K min$^{-1}$ up to 973 K. The increase of temperature was also monitored using a thermocouple and an integrator. In situ diffuse reflectance infrared Fourier transform (DRIFT) spectra were measured
using an ISDR-600 FTIR spectrometer (JASCO, Japan) equipped with a mercury-cadmium-tellurium (MCT) detector cooled by liquid nitrogen at a resolution of 4 cm\(^{-1}\) with 16 co-added scans. The sample powder (50 mg) was placed in a diffuse reflectance cell, which was fitted by a potassium bromide (KBr) window at the top. The gas compositions of the pretreatment and the DRIFT experiment were the same as the activity tests. The catalyst was pretreated at 773 K, and then cooled to 373 K. A 200 W Hg–Xe lamp equipped with a collective lens (San-Ei Electric Co. Ltd., UVF-204S type C) was used as a light source. The background spectrum was measured after the pretreatment under a He gas flow at the 373 K. X-ray photoelectron spectroscopy (XPS) measurement was conducted on an ESCA-3400 spectrometer (Shimadzu, Japan). Sample was mounted on a silver sample holder by using a conductive carbon tape, and analyzed using Mg K\(\alpha\) radiation in a vacuum chamber in 0.1 eV steps. The position of the carbon peak (284.6 eV) for C1s was used to calibrate the binding energy for all the samples. The surface atomic ratio was estimated from the band areas of XPS of Ba 3d, and Ti 2p, and the corresponding relative sensitivity factors. A Transmission electron microscopy (TEM) observation was carried out with JEOL-1400 TEM (JEOL, Japan).

**Result and discussions**

**Effect of Ba loading**

Fig. 1A represents the time course of NO\(_x\) storage over Ba/TiO\(_2\) catalysts with various Ba loadings. Without a catalyst, NO\(_x\) concentration increased to 200 ppm immediately at the same time as NO/O\(_2\) gas was introduced to the reactor. TiO\(_2\) showed activity for NO\(_x\) storage under UV-light irradiation, and the dead time for the NO\(_x\) breakthrough was 530 s. Loading of Ba drastically extended the dead time for NO\(_x\) breakthrough for all the Ba loadings investigated as compared to TiO\(_2\). Fig. 1B shows the dead time in Fig. 1A as a function of Ba loading. The dead time increased with increasing the Ba loading up to 500 \(\mu\)mol g\(^{-1}\), and deceased over 500 \(\mu\)mol g\(^{-1}\). The dead time in 500 \(\mu\)mol g\(^{-1}\) Ba/TiO\(_2\) was 1020 s, which was longer than the period during the cold start condition (800 s) reported by ICCT.\(^{11}\) After the reaction after 12 h, the rates of NO\(_x\) storage were saturated, and the total amounts of stored NO\(_x\) for 12 h of 500 \(\mu\)mol g\(^{-1}\) Ba/TiO\(_2\) and TiO\(_2\) were 560 and 389 \(\mu\)mol.
g$^{-1}$, respectively. The modification of TiO$_2$ with Ba oxides species improved both the dead time and the total adsorption amount of NO$_x$.

![Graph](image)

**Figure 1.** (A) Time course of the photo-assisted NO$_x$ storage over Ba/TiO$_2$ catalysts. Pretreatment temperature: 773 K, NO: 200 ppm, O$_2$: 2%, He: balance. The numbers represent Ba loadings ($\mu$mol g$^{-1}$). (B) Effect of Ba loading on the dead time for the NO$_x$ breakthrough.

In the XRD patterns of TiO$_2$ and as-synthesized Ba/TiO$_2$ with various Ba loading showed diffraction peaks of anatase TiO$_2$ (Fig. 2). Diffraction peaks of cubic Ba(NO$_3$)$_2$ appeared in the as-synthesized Ba/TiO$_2$ catalysts over 250 $\mu$mol g$^{-1}$ of Ba loading, which indicates that the Ba species are loaded on TiO$_2$ as a nitrate form after the impregnation. Table 1 represents the crystalline size of TiO$_2$ and $S_{\text{BET}}$ of the catalysts with various Ba loading. In the as-synthesized catalysts, $S_{\text{BET}}$ decreased with increasing the Ba loading although the crystalline size of TiO$_2$ did not change after the Ba loading. The decrease of the surface area is possibly due to a plugging of pores derived from gaps of TiO$_2$ particles. Without Ba loading (bare TiO$_2$), the pretreatment at 773 K and the following reaction drastically decreased $S_{\text{BET}}$ from 292 to 185 m$^2$ g$^{-1}$ and increased the crystalline sizes of TiO$_2$ from 7.7 to 10.9 nm, which was due to sintering of TiO$_2$ particles after the pretreatment at 773 K. The crystalline sizes of TiO$_2$ (8.5–9.3 nm) in Ba/TiO$_2$ after the reaction were smaller than
that of TiO$_2$ after the reaction (10.9 nm). Thus, the Ba loading clearly suppressed the sintering of TiO$_2$ particles. To investigate the effect of $S_{BET}$, the dead time was plotted as a function of $S_{BET}$ as shown in Fig. 3. The dead time increased with increasing $S_{BET}$ in the case of TiO$_2$ after the pretreatment at 673, 773, and 873 K (blue triangles). In the several photocatalytic reactions\textsuperscript{21,41} the activity strongly depends on the surface area of the photocatalyst especially when the adsorption step of substrates is relatively slow. In this reaction, the strong positive correlation between the dead time and $S_{BET}$ was clearly observed, which suggests that the increase of $S_{BET}$ would be effective to improve the activity. On the other hand, Ba/TiO$_2$ photocatalyst (red circles) showed the significantly higher activity than those of TiO$_2$ with similar $S_{BET}$. The activity improvement by the Ba loading cannot be explained by the surface area (i.e., sintering of TiO$_2$ particles). In addition, there was no correlation between the dead time and $S_{BET}$ in Ba/TiO$_2$ with various Ba loading, which suggests that the dead time is dependent on the amount and state of Ba species. The total amount of stored NO$_x$ for 12 h of 500 $\mu$mol g$^{-1}$ Ba/TiO$_2$ was 1.4 times higher than that of TiO$_2$ although $S_{BET}$ was almost the same as shown in Table 1. The results suggested that the Ba oxide species generated after the pretreatment at 773 K functioned as an effective NO$_x$ storage material.
Figure 2. XRD patterns of the as-synthesized Ba/TiO$_2$ catalysts with various Ba loading. (a) 0, (b) 100, (c) 250, (d) 500, (e) 750, and (f) 1000 μmol g$^{-1}$.

Figure 3. Correlation between $S_{\text{BET}}$ and the dead time for the NO$_x$ breakthrough. Pretreatment temperatures were shown next to the symbols.
Correlation between the activity and TPD peak areas

TPD experiments were carried out using the as-synthesized Ba/TiO$_2$ catalysts to identify the active Ba precursors (Fig. 4A). Three desorption peaks were observed around 710, 800, and 850 K (referred to as peaks 1, 2, and 3, respectively). The peak 1 was assigned to the decomposition of Ba(NO$_3$)$_2$ in contact with a TiO$_2$ surface, and the peaks 2 and 3 were due to the decomposition of bulk Ba(NO$_3$)$_2$.\textsuperscript{29} Two desorption peaks were observed in the TPD experiment using a Ba(NO$_3$)$_2$ reference powder at 840 and 910 K, and the desorption temperatures were higher than those of Ba/TiO$_2$. The low desorption temperatures in the Ba-modified catalysts were due to the interaction between TiO$_2$ and Ba species.\textsuperscript{38} The peaks 2 and 3 were possibly due to the decomposition of the surface and inner part of bulk Ba(NO$_3$)$_2$.\textsuperscript{29} The areas of peaks 1, 2, and 3, which were estimated from a peak fitting using three Gaussians, were plotted against the Ba loading (Fig. 4B). The area of peak 1 increased with the Ba loading up to 500 µmol g$^{-1}$, and was saturated over 500 µmol g$^{-1}$. On the other hands, the areas of peaks 2 and 3 showed the same tendency; the areas of two peaks were low below 250 µmol g$^{-1}$, and the further increase of the Ba loading rapidly increased the areas of the two peaks. The same tendency supports the above assignment that peaks 2 and 3 were derived from the

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$^a$ Crystalline size of TiO$_2$. $^b$ Specific surface area estimated from the BET method. $^c$ As-synthesized. $^d$ After the pretreatment at 773 K and the following NOx storage reaction.

Table 1. Crystalline size of TiO$_2$ and BET specific surface area before and after the pretreatment and reaction.
bulk Ba(NO$_3$)$_2$. As shown above, there are at least two Ba(NO$_3$)$_2$ species in the as-synthesized Ba/TiO$_2$; one is the surface Ba(NO$_3$)$_2$ in contact with a TiO$_2$ surface, and the other one is the bulk Ba(NO$_3$)$_2$ without a contact with a TiO$_2$ surface.

The effect of the Ba loading on the activity was explained by the amount of two Ba(NO$_3$)$_2$ species estimated from the TPD spectra. The dead time in Fig. 1 increased with increasing the area of peak 1 derived from the surface Ba(NO$_3$)$_2$. The correspondence between activity and the amount of surface Ba(NO$_3$)$_2$ indicated that the surface Ba(NO$_3$)$_2$ on a TiO$_2$ is a precursor of active Ba oxide species for the NO$_x$ storage. On the other hand, over 500 μmol g$^{-1}$, the activity decreased in spite of the fact that the amount of the surface Ba(NO$_3$)$_2$ (i.e., area of peak 1) did not change. The bulk Ba(NO$_3$)$_2$, which was inactive for the reaction,$^{29}$ was generated, and the amount increased with the Ba loading. The increase of the Ba loading from 500 to 1000 μmol g$^{-1}$ decreased the TiO$_2$ content in the catalyst by 13 wt% because the 500 and 1000 μmol g$^{-1}$ corresponded to 13 and 26 wt%, respectively. The decrease of TiO$_2$ should decrease the activity because TiO$_2$ works as an oxidation site in the reaction. Thus, amounts of the surface Ba(NO$_3$)$_2$ and the inactive bulk Ba(NO$_3$)$_2$ affected the activity, which resulted in the non-correlation between $S_{BET}$ and the activity in Ba/TiO$_2$ in Fig. 3.

![Figure 4](image.png)

**Figure 4.** (A) TPD profiles of as-synthesized Ba/TiO$_2$ catalyst with various Ba loadings of (a) 100, (b) 250, (c) 500, (d) 750, and (e) 1000 μmol g$^{-1}$. (B) Desorption amounts of NO$_x$ estimated from the peaks 1, 2, and 3 as a function of Ba loading.
DRIFT investigation

DRIFT spectra were recorded at various exposure times of NO/O_2 gas in the dark. In the case of TiO_2 (Fig. 5A), the peaks at 1622, 1480, 1322, and 1194 cm\(^{-1}\) increased with the exposure time of NO/O_2 gas. The peaks at 1480, 1322, and 1194 cm\(^{-1}\) were assignable to NO_2\(^-\) species, and the peak at 1622 cm\(^{-1}\) to NO_3\(^-\) species.\(^{42}\) The co-adsorption of NO and O_2 produced NO_2\(^-\) and NO_3\(^-\) species via adsorption and oxidation, which was in line with previous reports using several transition metals including TiO_2.\(^{42-45}\) After the irradiation, the peak intensity at 1194 cm\(^{-1}\) monotonically decreased with the irradiation time, which indicates that the NO_2\(^-\) species are consumed under irradiation. On the other hand, the intensities of new peaks at 1603, 1582, 1496, 1302, and 1249 cm\(^{-1}\) increase and are saturated after 20 min of irradiation, which is due to the generation of NO_3\(^-\) species with bridging (1603, 1249 cm\(^{-1}\)), chelating (1582, 1302 cm\(^{-1}\)), and monodentate (1496 cm\(^{-1}\)) forms.\(^{21, 42-43}\) Thus, the NO_2\(^-\) species are an intermediate in NO_x storage, and are oxidized into the NO_3\(^-\) species under irradiation (eqs. 1 and 2).

\[ \text{NO} \xrightarrow{O_2, \text{dark}} \text{NO}_2^-, \text{NO}_3^- \] \hspace{1cm} (1)
\[ \text{NO}_2^- \xrightarrow{O_2, h\nu} \text{NO}_3^- \] \hspace{1cm} (2)

DRIFT spectra in 500 \(\mu\)mol g\(^{-1}\) Ba/TiO_2 were shown in Fig. 5B. In the dark, peaks at 1620, 1477, 1379, and 1210 appeared after 30 min of an NO/O_2 gas flow, and attribute to NO_2\(^-\) and NO_3\(^-\) species adsorbed on Ti sites because the peaks were observed in the case of TiO_2. Other peaks was also observed at 1379 cm\(^{-1}\) and around 1200 cm\(^{-1}\) (shoulder peaks) in Ba/TiO_2, which is possibly due to the NO_2\(^-\) species based on the wavenumber.\(^{42}\) Although a small difference was observed in the DRIFT spectra between TiO_2 and Ba/TiO_2 in the dark, the difference was not a direct evidence of the improvement of the activity by Ba loading under irradiation because the activity of NO_x storage was quite low (no dead time) in the dark over Ba/TiO_2.\(^{29}\) The DRIFT spectra of Ba/TiO_2 after irradiation in NO/O_2 gas were similar to that in the case of TiO_2; adsorption peaks at 1601, 1580, 1502, 1295, and 1254 cm\(^{-1}\) increase with increasing the irradiation time for 3 h. The previous reports using BaO/Al_2O_3 catalyst showed that NO_2 adsorbed on a BaO surface as ionic and bidentate NO_3\(^-\) species and the adsorbed NO_3\(^-\) show the IR peaks at 1550 cm\(^{-1}\) (bidentate), and 1320 and 1410 cm\(^{-1}\)
In our DRIFT investigations, the bands were not observed under irradiation. The results clearly indicates that the bulk BaO is not generated after the pretreatment. Absence of bulk BaO species suggests that Ba species are strongly interacted with TiO$_2$ as reported previously.\textsuperscript{38}

**Figure 5.** DRIFT spectra of (A) TiO$_2$ and (B) 500 μmol g$^{-1}$ Ba/TiO$_2$. (a): after the pretreatment at 773 K, (b): after addition of NO/O$_2$ gas for 30 min in the dark, (c): after irradiation for 3 h in NO/O$_2$ gas.

**XRD pattern and TEM image**

Fig. 6 shows the XRD patterns of TiO$_2$ and 500 μmol g$^{-1}$ Ba/TiO$_2$. In all the catalysts, the diffraction peaks of anatase TiO$_2$ were observed. In as-synthesized Ba/TiO$_2$, the diffraction patterns of Ba(NO$_3$)$_2$ was observed, and the pretreatment at 773 K deceaseed the peak intensities. The decrease of the peak intensities is due to the decomposition of Ba(NO$_3$)$_2$ on a TiO$_2$ surface based on the TPD results. No other peak was observed after the pretreatment at 773 K, which suggests the Ba oxide species had an amorphous structure. After the NO$_x$ storage, the peaks derived from Ba(NO$_3$)$_2$
did not change compared to Ba/TiO\textsubscript{2} after the pretreatment. From TEM images (Fig. 7), the particle size of TiO\textsubscript{2} in the as-synthesized Ba/TiO\textsubscript{2} was approximately 7–9 nm, which accorded to the crystalline size estimated from XRD (Table 1). The particle size hardly changed after the pretreatment at 773 K, and the following reaction.

![XRD patterns](image)

**Figure 6.** XRD patterns of (A) TiO\textsubscript{2} and (B) 500 \( \mu \)mol g\(^{-1}\) Ba/TiO\textsubscript{2}. (a): as-synthesized, (b): after the pretreatment at 773 K, (c): after the reaction.
XPS measurement

Fig. 8A shows Ba 3d$_{5/2}$ XPS of the Ba-modified catalysts. The peak position of Ba 3d$_{5/2}$ XPS of the as-synthesized Ba/TiO$_2$ was 779.9 eV. The peak positions in Ba/TiO$_2$ after the pretreatment and the following reaction were 780.2 and 780.1 eV, respectively, and peak shift was hardly observed. The positions in the Ba-modified catalysts were different from that in the BaTiO$_3$ reference sample (778.8 eV). In all the Ba-modified catalysts, the peak positions of Ti 2p$_{3/2}$ were 458.4–458.5 eV (Fig. 8B), which were equal to that in TiO$_2$ (458.4 eV). In the case of BaTiO$_3$, the peak position was 458.1 eV and was higher by 0.3–0.4 eV compared to the Ba-modified catalysts. The results indicate that the BaTiO$_3$ phase do not generated both after the pretreatment and the following reaction. The Ba/Ti surface atomic ratio was calculated from XPS. The pretreatment drastically increased the Ba/Ti ratio from 0.03 to 0.19, and decreased to 0.12 after the reaction. The increase in the Ba/Ti ratio clearly evidenced the structural change of Ba oxide species after the pretreatment, and
can be explained by a 2D layer structure of Ba oxide species. The 2D structure of Ba species accorded with a model proposed by Ozensoy et al. using a substrate, and suggested the above-mentioned strong interaction between Ba oxide species and TiO\textsubscript{2}.

![Figure 8. XPS of (A) Ba 3d\textsubscript{5/2} and (B) Ti 2p. (a): as-synthesized, (b): after the pretreatment at 773 K, (c): after the reaction, (d): BaTiO\textsubscript{3}, (e): TiO\textsubscript{2}.](image)

Active Ba species in photo-assisted NO\textsubscript{x} storage

NO\textsubscript{x} storage model is shown in Scheme 1. Ba(NO\textsubscript{3})\textsubscript{2} is loaded on a TiO\textsubscript{2} surface after impregnation. The O\textsubscript{2}/He pretreatment at 773 K decomposes the surface Ba(NO\textsubscript{3})\textsubscript{2} to active Ba oxide species with releasing the NO\textsubscript{x}. The active Ba oxide species has an amorphous and 2D layer structure based on the XRD and XPS analysis. The DRIFT revealed that the NO\textsubscript{3}– species were adsorbed on Ti sites after NO\textsubscript{x} storage over Ba/TiO\textsubscript{2}, which suggests that the generated NO\textsubscript{x} species do not adsorb to Ba atoms directly. In the previous report, barium orthotitanate (Ba\textsubscript{2}TiO\textsubscript{4}) was observed during the reaction between BaO/BaCO\textsubscript{3} and TiO\textsubscript{2} (110) rutile single crystal by XRD technique, and proposed that Ba\textsubscript{2}TiO\textsubscript{4} was an intermediate phase for BaTiO\textsubscript{3} formation. In addition, generation of perovskite-type Ba–Ti surface species (e.g., BaTiO\textsubscript{3}, and Ba\textsubscript{2}TiO\textsubscript{4}) was reported after Ba deposition over TiO\textsubscript{2}/Pt(111) and following oxidation with O\textsubscript{2} at 573–973 K by XPS, and their LEED images showed that the Ba–Ti surface species has an amorphous structure. In our previous reports, BaTiO\textsubscript{3}
was observed by increasing the pretreatment temperature from 773 to 873 K and at the temperature, the activity of NO\textsubscript{x} storage decreased because $S_{\text{BET}}$ decreased at the same time of the generation.\textsuperscript{29} Accordingly, Ba–Ti surface species can be generated in the O\textsubscript{2}/He pretreatment at 773 K with an amorphous structure in our photocatalytic system. Besides, adsorption of NO\textsubscript{x} on perovskite compounds including BaTiO\textsubscript{3} was investigated, and these perovskites showed a large NO\textsubscript{x} storage capacity in spite of low $S_{\text{BET}}$, (i.e., surface density of NO\textsubscript{x}– species was high on BaTiO\textsubscript{3}).\textsuperscript{48} Based on the relationship between the NO\textsubscript{x} storage capacity and $S_{\text{BET}}$, they proposed that the perovskite structure was partially decomposed during NO\textsubscript{2} adsorption process and releasing the stored NO\textsubscript{x} lead to the recovery of the perovskite structure, which resulted in the high NO\textsubscript{x} storage capacity. In our experiments, 500 $\mu$mol g$^{-1}$ Ba/TiO\textsubscript{2} showed 1.4 times higher NO\textsubscript{x} storage capacity than that of TiO\textsubscript{2} despite similar $S_{\text{BET}}$ (Table 1). Thus, the amorphous Ba–Ti mixed oxides are formed on a TiO\textsubscript{2} surface after the pretreatment and stored NO\textsubscript{x}– more densely than TiO\textsubscript{2}. We concluded that the generation of Ba–Ti mixed oxides leads to the high storage capacity of NO\textsubscript{x} under UV-light irradiation.

Scheme 1. Surface model of Ba oxide species.
Conclusions

We investigated the effect of Ba loading and active Ba oxide species in photo-assisted NO\textsubscript{x} storage over Ba-modified TiO\textsubscript{2} photocatalyst under UV-light irradiation. The Ba loading affected the amounts of the surface and bulk Ba(NO\textsubscript{3})\textsubscript{2} species in the as-synthesized catalysts with various Ba loadings, and the amounts predominated the activity. The surface Ba(NO\textsubscript{3})\textsubscript{2} was decomposed after the pretreatment at 773 K into an active Ba–Ti mixed oxides with an amorphous structure. It was firstly proposed that the surface amorphous Ba–Ti mixed oxides functioned as an effective NO\textsubscript{x} storage material.

References


In this thesis, the author investigated the two types of photocatalytic de-NO\textsubscript{x} reactions at low temperature over TiO\textsubscript{2}-based photocatalysts; part I is concerned with photo-assisted selective catalytic reduction (photo-SCR), and part II deals with photo-assisted NO\textsubscript{x} storage. In both of these photocatalytic reactions, NO was removed efficiently under UV and/or visible light irradiation. The author successfully improved the photocatalytic activities by surface modification of TiO\textsubscript{2} with organic and inorganic materials to put these photocatalytic systems into practical use. Besides, the nature of the high activity and the working mechanism were stated on the basis of the mechanistic and structural analyses using the various spectroscopic methods.

In Chapter 1, the author found the reaction temperature had a significant effect on the photo-SCR activity of a TiO\textsubscript{2} photocatalyst under irradiation. Optimization of the reaction temperature significantly increased the conversion up to 84\% with selectivity to N\textsubscript{2} of 100\% at a high GHSV of 100,000 h\textsuperscript{–1} (at 433 K). Kinetic analysis revealed that the rate-determining step of the photo-SCR was decomposition of surface NH\textsubscript{2}NO intermediates in all the range of the reaction temperature investigated (353–593 K). The author concluded that the activity improvement was due to the acceleration of the rate determining step based on the kinetic analysis. The above result suggests the utilization of residual heat from engines is effective to obtain high activity.

In Chapter 2, the author established that modification of a TiO\textsubscript{2} photocatalyst with porphyrin dyes was effective for the development of visible-light-sensitive photocatalysts. Tetra(p-carboxyphenyl)porphyrin (TCPP) was the most effective photosensitizer among the five porphyrin derivatives investigated. NO conversion and N\textsubscript{2} selectivity of 79\% and 100\% respectively, were achieved at a GHSV of 50,000 h\textsuperscript{–1} under visible-light irradiation. UV–Vis and photoluminescence spectroscopies showed that the aggregation of TCPP drastically decreased the activity. Thus, suppression of the aggregation is one of the methods to improve the photo-SCR activity of the dye-sensitized TiO\textsubscript{2} photocatalysts.

In Chapter 3, the screening of dyes significantly enhanced the photocatalytic activity in the photo-SCR over the dye-sensitized TiO\textsubscript{2} photocatalysts under visible-light irradiation. Among the 15
dyes investigated, the maximum conversion was achieved using a Ru(2,2'-bipyridyl-4,4'-dicarboxylic acid)$_2$(NCS)$_2$ complex (N3-dye) for the modification of TiO$_2$ (NO conversion > 99%, N$_2$ selectivity > 99%). The reasonable reaction mechanism was proposed using several spectroscopic methods; surface nitrite (NO$_2^-$) intermediates was found to be responsible for the high selectivity to N$_2$. The conversion obtained was enough for practical use in mobile NOx emission sources such as buses and trucks.

In Chapter 4, the effect of SO$_2$ gas was investigated on the activity in the photo-SCR over a TiO$_2$ photocatalyst in the presence of excess oxygen. Introduction of SO$_2$ (300ppm) decreased the activity at 373 K. Increment of the reaction temperature enhanced the tolerance to SO$_2$ gas, and a stable conversion of NO was obtained at 553 K. Based on the characterization of the catalysts after reactions, we concluded that the deposition of ammonium sulfate species decreased the specific surface area by plugging the pore structure of the catalysts and the decrease of the specific surface area resulted in the deactivation of the catalysts. Suppression of the generation of the ammonium sulfate species is a strategy to improve the tolerance to SO$_2$ in photo-SCR.

In Chapter 5, the photo-assisted NOx storage was investigated over the Ba/TiO$_2$ photocatalysts under UV-light irradiation at a high GHSV of 50,000 h$^{-1}$. The author clearly demonstrated that the Ba loading enhanced the activity after the O$_2$ pretreatment at 673 K. The NO removal efficiency was kept > 99% during the 1020 s interval from the start of the reaction over the Ba/TiO$_2$ photocatalyst. The TPD and XRD measurement revealed that barium oxide species functioned as a NOx storage material even at low temperatures, which resulted in the improvement of the performance of the photo-assisted NOx storage.

In Chapter 6, the author investigated the structure of Ba species active for the NOx storage under UV-light irradiation. The DRIFT investigation revealed that bulk BaO was not generated on a TiO$_2$ surface because nitrate (NO$_3^-$) species adsorbed on Ba sites were not observed in NO/O$_2$ gas under UV-light irradiation. Considering the DRIFT, XRD, XPS, and TEM results, the author proposed that the surface Ba–Ti mixed oxides with an amorphous structure was generated during the O$_2$ pretreatment and the formed Ba–Ti mixed oxides functioned as an effective NOx storage material.
In summary, TiO$_2$-based photocatalysts exhibited high activity for the photo-SCR and photo-assisted NO$_x$ storage under high GHSV conditions. The author clearly demonstrated the effectiveness of photocatalysts for the NO$_x$ emission control at low temperature in the exhaust gas. The reasonable working mechanisms were proposed throughout the researches. These findings are believe to be contribute to the development of low-temperature de-NO$_x$ systems for the exhaust gas in the future.
Appendix

Effect of a Crystalline Phase of TiO$_2$ Photocatalysts on the Photodeposition of Rh Metal Nanoparticles

Abstract

Effect of a crystalline phase of TiO$_2$ is investigated in the photodeposition processes of Rh metal nanoparticles on TiO$_2$ photocatalysts having anatase and rutile phase by means of in–situ time–resolved energy dispersive X–ray absorption fine structure spectroscopy (DXAFS), transmission electron microscopy (TEM), and X–ray photoelectron spectroscopy (XPS). The important factor was neither its crystallite size nor its specific surface area, and was the crystalline phase. In situ time–resolved DXAFS analysis clarified that the Rh metal nanoparticles with a uniform size appear on both anatase and rutile phases of TiO$_2$, whereas the appearance rate of Rh metal nanoparticles decreases with the photoirradiation time only on the rutile phase of TiO$_2$. The TEM observation and XPS depth analysis revealed that the bare surface of photodeposited Rh metal nanoparticles on the rutile is exposed, although that on the anatase is partially covered with TiO$_2$ due to strong metal–support interaction (SMSI) between Rh metal nanoparticle and TiO$_2$–δ.
Introduction

It has widely been recognized that the photodeposition, which Bard et al. have reported in 1978, is a very valuable method to recover of noble metals, to remove metal cations from aqueous effluent, and to prepare metal–supported catalysts and metal–promoted photocatalysts. Photexcited electrons in a photocatalyst reduce metal cations that have more positive reduction potential than the conduction–band level of the photocatalyst. The simultaneously generated holes in the valence band are consumed with oxidation of a reactant such as alcohol, aldehyde, or carboxylic acid. In the several studies, it is found that the metal species were photodeposited on specific sites on a photocatalyst, for example, an edge or plane of a photocatalyst crystallite. Interestingly, the morphology of the resulting metal nanoparticles greatly varies among the kinds of photocatalyst. These phenomena inspire us to study the systematic kinetics and mechanism for the formation of nanoparticles as well as the structure of resulting metal species. X–ray absorption fine structure (XAFS) spectroscopy is a powerful method to elucidate the formation process of the metal nanoparticles and reactivity of surface species. Fernandez et al. have observed the photodeposition of Au nanoparticles by an in situ XAFS measurement, where the suspension composed of an Au precursor and TiO$_2$ was pumped out from the photochemical reactor to the XAFS measurement cell under photoirradiation. We have also successfully observed the photodeposition process of Rh metal nanoparticles on TiO$_2$ using in situ time–resolved energy dispersive X–ray absorption fine structure spectroscopy (DXAFS), and proposed unique particle–formation mechanism that Rh metal nanoparticles with a uniform size constantly appear one after another on the surface of TiO$_2$. We have also successfully observed the formation process of Rh and Au nanoparticles by means of time–resolved Quick XAFS experiments.

Recently, we reported that photodeposited Rh and Pt metal nanoparticles on TiO$_2$ (JRC–TIO–8, anatase) were modified with TiO$_2$–δ which is well–known as a key species in the strong metal–support interaction (SMSI). Generally, the SMSI can be observed when group VIII noble metals (e.g., Pt, Rh, Pd, and Ir) on reducible oxide supports (e.g., TiO$_2$ and Nb$_2$O$_5$) are treated with H$_2$ at high temperature and causes the modification of metal nanoparticles with reduced supports (e.g., TiO$_2$–δ) generated by H$_2$ treatment. It is both interesting and incredible that the SMSI takes places by photoirradiation at room temperature as well as by H$_2$ treatment at high temperature. Most
probably, TiO$_{2-\delta}$ generated by the photoirradiation of TiO$_2$ cause the modification and the disorganized structure of Rh and Pt metal nanoparticles. Amount, type and property of TiO$_{2-\delta}$, therefore, may have an effect on the SMSI in the photodeposition process. Li et al. reported that the SMSI occurs by H$_2$ reduction at lower temperature on anatase TiO$_2$ than on rutile,\textsuperscript{34} suggesting that the crystalline phase of TiO$_2$ photocatalysts affects the interaction of Rh metals and TiO$_2$. In this study, we investigated the photodeposition processes of Rh metal nanoparticles on TiO$_2$ photocatalysts having anatase and rutile phases, and their structure by means of in situ time–resolved DXAFS spectroscopy, XPS with sputtering, TEM observation.

**Experimental**

**Materials**

TiO$_2$ samples used in this study (JRC–TIO–1, 3, 6, 8, and 10) were kindly supplied from the Japan Catalysis Society. All the samples were calcined in air at 673 K for 3 h before use. Crystalline phase of each TiO$_2$ was determined by X–ray diffraction technique (XRD). The crystallite size was estimated from the use of the Scherrer’s equation. The specific surface area of sample was determined using N$_2$ adsorption isotherm at 77 K. Crystalline phases, surface areas, and crystallite sizes of TiO$_2$ used in this study were listed in Table 1. In this paper, for simplicity, we denote the phase and the catalyst like N–X where N is the catalyst name JRC–TIO–N, and X is A or R meaning anatase or rutile, respectively; i.e., JRC–TIO–8 (anatase) to 8–A and JRC–TIO–3 (rutile) to 3–R.

**Photodeposition**

The photodeposition of Rh nanoparticles on TiO$_2$ was carried out in a closed batch system. As a typical photodeposition method, 500 mg of TiO$_2$ was suspended in 3.2 mL of methanol in a batch reactor made of Pyrex glass with a flat ceiling window for irradiation, followed by the addition of 0.8 mL of an aqueous solution of RhCl$_3$ (Wako Pure Chemical Industries, Ltd., 0.076 mmol of Rh). The suspension was irradiated with a 200 W Hg–Xe lamp equipped with fiber optics, a collective lens, and a mirror (San–Ei Electric Co., Ltd., UVF–204S type C) after N$_2$ bubbling for 10 min. Then the suspension was filtered, and the residual powder was washed with 100 mL of purified water and was placed in an oven at 353 K.
**Time–resolved dispersive XAFS measurements**

In situ time–resolved DXAFS measurements at the Rh–K edge (~23.2 keV) were performed at the BL28B2 beamline of the SPring–8. The DXAFS measurement system consists of a polychromator set to a Laue configuration with a Si (422) net plane and a position–sensitive detector (PSD) mounted on a $\theta–2\theta$ diffractometer. The X–ray energy was calibrated by the spectrum of a Rh foil. The above–mentioned Pyrex reactor with the suspension was set at the X–ray focal spot. Light irradiation of the reactor was synchronized with exposure to X–rays. The exposure time of the PSD was 249 ms. Fifty shots were accumulated; 12.45 s per a spectrum. We programmed the collection of 500 snapshot spectra (124.5 s) in the dark and then 7000 snapshot spectra (1743 s) under photoirradiation consecutively. The measurement program was repeated four times to obtain the spectral change at 116.2 min under photoirradiation. Analysis of XAFS spectra was performed using the REX2000 program (version 2.5.9, Rigaku Corp.). The $k^3$–weighted EXAFS oscillation in the range of 2.78–10.7 Å was Fourier–transformed.

**Characterization**

XPS spectra were acquired using an ULVAC PHI 5500MT system. Samples mounted on indium foil were analyzed using Mg K$\alpha_{1,2}$ radiation (15 kV, 400 W) in a vacuum chamber ($<1 \times 10^{-8}$ Torr). The electron takeoff angle was set at 45°. Binding energies were referenced to C 1s peak of residual carbon at 284.6 eV. Sputtering was performed by a Xe ion beam (3.0 kV) with raster size 1.1 mm $\times$ 2.1 mm. TEM, STM, and EDX mapping images were obtained with a JEOL JEM–2100F transmission electron microscope operating at an accelerating voltage of 200 kV. TEM samples were prepared by depositing drops of a methanol suspension containing small amounts of the powders onto a carbon–coated copper grid (Okenshoji Co. Ltd.).
Results and Discussion

XANES spectra

Fig. 1 shows a series of Rh–K edge XANES spectra of the suspension comprised of a methanol aqueous solution of RhCl$_3$ and 3–R under photoirradiation. The edge energy of XANES shifted to lower photon energy with the elongation of photoirradiation time. The XANES spectrum after 116 min of photoirradiation was almost identical to that of the Rh foil. This result indicates that Rh$^{3+}$ ions are reduced to Rh$^0$ metals by photoirradiation. There is no change in the spectrum from RhCl$_3$ without TiO$_2$ or photoirradiation. The XANES spectral change corresponding to the reduction of Rh$^{3+}$ ions to Rh$^0$ metals exhibits the isosbestic points, which indicates that Rh$^{3+}$ ions are reduced to Rh$^0$ metals without any intermediates within the measurable time. All the Rh–K edge XANES spectra can be represented with the linear combination of the two XANES spectra; one is that of Rh$^{3+}$ ions in the initial state and the other is that of Rh$^0$ metals in the final state. The least–squares fitting of each XANES spectrum with the linear combination allowed us to obtain the fractions of the Rh$^0$ metals and Rh$^{3+}$ ions using 3–R and 8–A as shown in Fig. 2. The fraction of Rh$^0$ metals increased with the photoirradiation time in both the cases. In the case of 3–R, the rate of an increase in Rh$^0$ metals decelerated with the photoirradiation time and the fraction of Rh$^0$ metals was saturated after 90 min. The deceleration of the increasing rate of Rh$^0$ metals means that the rate of reduction of

<table>
<thead>
<tr>
<th>Crystalline phase</th>
<th>Crystallite size (nm)</th>
<th>Specific surface area (m$^2$ g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>JRC-TIO-8</td>
<td>Anatase</td>
<td>15.5</td>
</tr>
<tr>
<td>JRC-TIO-1</td>
<td>Anatase</td>
<td>18.7</td>
</tr>
<tr>
<td>JRC-TIO-10</td>
<td>Anatase</td>
<td>16.9</td>
</tr>
<tr>
<td>JRC-TIO-3</td>
<td>Rutile</td>
<td>21.9</td>
</tr>
<tr>
<td>JRC-TIO-6</td>
<td>Rutile</td>
<td>24.0</td>
</tr>
</tbody>
</table>

Table 1. Properties of various TiO$_2$ photocatalysts.
Rh$^{3+}$ ions to Rh$^0$ metals was lowered with photoirradiation time. In the case of 8–A, the Rh$^0$ metal fraction linearly increased with photoirradiation time and became constant at 75 min, which means that the Rh$^{3+}$ ions are reduced to Rh$^0$ metals at a constant rate. On the other hand, the behavior of reduction of Rh$^{3+}$ ions to Rh$^0$ metals on 3–R is different from that on 8–A. When the other rutile phase of TiO$_2$ was used, the reduction rate of Rh$^{3+}$ ions decreased with photoirradiation time as represented by the case of 3–R, whereas, the reduction rate of Rh$^{3+}$ ions on the anatase phase of TiO$_2$ were constant with photoirradiation time as represented by the case of 8–A (Fig. 3). The behavior of reduction of Rh$^{3+}$ ions to Rh$^0$ metals on the rutile is different from that on the anatase. These results strongly suggest that the crystalline phase of TiO$_2$ has an effect on the formation rate of Rh$^0$ metals for the photodeposition.

Figure 1. XANES spectra at the Rh–K edge of reference samples and the suspension consisting of a methanol aqueous solution of RhCl$_3$ and 3–R: (a) before irradiation, (b) under irradiation, (c) after irradiation for 116 min, and (d) Rh foil.
EXAFS spectra

Figs. 4 and 5 show a series of Rh–K edge EXAFS spectra of Rh species for photodeposition on 3–R and Fourier transforms (FTs) of them. In Fig. 5, the peak located at 1.73 Å is assignable to the mixture of Rh–Cl and Rh–O scattering of RhCl₃ in solution and adsorbed on TiO₂. The height
of the peak at 1.73 Å decreased with increasing photoirradiation time, and an alternative peak appeared at 2.45 Å. The peak at 2.45 Å is assigned to the Rh–Rh scattering of Rh\(^0\) metal nanoparticles generated by photoirradiation. The peak height at 2.45 Å rose with photoirradiation time and saturated at 90 min. The structural parameters (coordination number, interatomic distance, energy shift, and Debye-Waller factor) were obtained by a curve-fitting analysis. The structural parameters at the selected photoirradiation times are listed in Table 2. Fig. 6 demonstrates dependence of the C.N.(Rh–Rh) estimated from a curve fitting analysis of EXAFS spectra in the case of 3–R and 8–A on the photoirradiation time. In the case of 3–R, the increase in the amount of change of C.N.(Rh–Rh) value was getting sluggish with the photoirradiation time and the value was saturated after 90 min of photoirradiation. In the case of 8–A, the C.N.(Rh–Rh) increased proportionally to the photoirradiation time, and attained to 10 after 75 min of photoirradiation.\(^{25}\) In both the cases, the behaviors of the C.N.(Rh–Rh) change perfectly corresponded to those of the fraction of Rh\(^0\) metals estimated from analyses of XANES spectra.

![Figure 4. Series of \(k^3\)-weighted Rh-K edge EXAFS spectra of Rh species during the photodeposition on 3-R. Before irradiation: a dotted line, and after irradiation for 116 min: a black solid line.](image-url)
Figure 5 Series of the FT of $k^3$-weighted Rh-K edge EXAFS spectra of Rh species during the photodeposition in the case of 3–R. Before irradiation: a dotted line, after irradiation for 116 min: a black solid line, and Rh foil: a dashed line.
**Table 2.** Curve-Fitting Results of the Rh-Rh Scattering of the FT of EXAFS Spectra at Selected Photoirradiation Times

<table>
<thead>
<tr>
<th>TiO₂</th>
<th>photoirradiation time / min</th>
<th>C.N.(Rh-Rh)$^b$</th>
<th>$r$/Å$^c$</th>
<th>$ΔE_0$/eV$^d$</th>
<th>$σ$/Å$^e$</th>
<th>R$^f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-R</td>
<td>29.1</td>
<td>4.5</td>
<td>2.69</td>
<td>0.3</td>
<td>0.061</td>
<td>0.47</td>
</tr>
<tr>
<td>3-R</td>
<td>58.1</td>
<td>7.1</td>
<td>2.68</td>
<td>0</td>
<td>0.060</td>
<td>0.18</td>
</tr>
<tr>
<td>3-R</td>
<td>87.2</td>
<td>9.3</td>
<td>2.69</td>
<td>0.5</td>
<td>0.062</td>
<td>0.05</td>
</tr>
<tr>
<td>3-R</td>
<td>116.2</td>
<td>9.6</td>
<td>2.69</td>
<td>0.4</td>
<td>0.063</td>
<td>0.07</td>
</tr>
<tr>
<td>8-A</td>
<td>29.1</td>
<td>4.5</td>
<td>2.70</td>
<td>0.8</td>
<td>0.062</td>
<td>0.19</td>
</tr>
<tr>
<td>8-A</td>
<td>58.1</td>
<td>8.4</td>
<td>2.69</td>
<td>1.3</td>
<td>0.062</td>
<td>0.03</td>
</tr>
<tr>
<td>8-A</td>
<td>87.2</td>
<td>10.6</td>
<td>2.69</td>
<td>0.7</td>
<td>0.062</td>
<td>0.02</td>
</tr>
<tr>
<td>8-A</td>
<td>116.2</td>
<td>10.4</td>
<td>2.69</td>
<td>0.5</td>
<td>0.061</td>
<td>0.02</td>
</tr>
</tbody>
</table>

$^a$A Rh foil is used as a reference. The R fitting range is 2.07-3.66 Å. $^b$C.N.(Rh-Rh): coordination number of Rh-Rh. $^c$r: interatomic distance. $^d$Δ$E_0$: energy shift $^e$σ: Debye-Waller factor. $^f$So-called R factor.

**Figure 6.** Photoirradiation time dependence of the C.N.(Rh–Rh) in the case of 3–R (○) and 8–A (▲).
**Generation model of Rh nanoparticles**

The C.N.(Rh–Rh) estimated from EXAFS analysis are the average for all the existing Rh\(^{3+}\) ions and Rh\(^0\) atoms. Only Rh\(^0\) atoms have Rh-Rh bonds and Rh\(^{3+}\) ions do not have. Thus, the C.N.(Rh–Rh) is given by

\[
\text{C.N.}(\text{Rh–Rh}) = \text{C.N.}_{\text{Rh}^0} \times \text{X}_{\text{Rh}^0}
\]

where the C.N.\(_{\text{Rh}^0}\) is the coordination number of Rh\(^0\) in the nanoparticles and the X\(_{\text{Rh}^0}\) is the fraction of Rh\(^0\) in the suspension. By using Eq. 1, the photoirradiation time dependence of the C.N.\(_{\text{Rh}^0}\) in the case of 3–R and 8–A is calculated from the Rh\(^0\) metal fraction and the C.N.(Rh–Rh) shown in Fig. 2 and Fig. 6. As a result, the C.N.\(_{\text{Rh}^0}\) on 3–R and 8–A were constant with photoirradiation time (Fig. 7). This result indicates that Rh metal nanoparticles with a uniform size appear one after another on both kinds of TiO\(_2\) during the photodeposition and the sizes never grow up. It is concluded that the difference in variation of C.N.(Rh–Rh) between 3–R and 8–A resulted from the difference in the appearance rate of Rh metal nanoparticles. In other words, the Rh metal nanoparticles with a uniform size appear both on the anatase and rutile, whereas the appearance rate decreases with the photoirradiation time only on the rutile.

**Figure 7.** Photoirradiation time dependence of the C.N.(Rh–Rh) of Rh\(^0\) metal in the case of 3–R (○) and 8–A (▲).
TEM, STEM and EDS analysis

Fig. 8a shows a TEM image of Rh–8A. Rh particles with a spherical shape were not observed. The particle boundaries of the Rh metal species are not identified in the TEM image although the existence of an Rh metal species is identified as green dots in the overlay of an EDS mapping image on a STEM image (Fig. 8b). Thus, we concluded that the Rh species on anatase phase of TiO$_2$ had a disordered structure, which would be due to the SMSI.$^{32}$ On the other hand, aggregated Rh species were observed on 3–R as shown in Figs. 8c and 8d. The aggregated Rh species were composed of primary Rh nanoparticles. The particle size of the primary Rh nanoparticles was smaller than 5 nm, which corresponded to the diameter estimated from EXAFS spectra. In addition, the secondary Rh metal species were not decorated by TiO$_2$, suggesting the interaction between Rh metal and rutile phase of TiO$_2$ was lower than that between Rh metal and anatase phase of TiO$_2$.

**Figure 8.** (a) TEM image and (b) overlay of EDS mapping image on STEM image of Rh–8–A, (c,d) TEM image of Rh–3–R.

XPS and sputtering by Xe ions
Fig. 9 shows the Rh 3d XPS of Rh metal nanoparticles photodeposited on 8–A (Rh–8–A) and 3–R (Rh–3–R). The peak of Rh 3ds/2 XPS of Rh–8–A appeared at 306.6 eV, which was lower energy than that of the Rh foil at 307.0 eV. The lower energy position of the peak indicates the more electron–rich surface of metal nanoparticles. It was reported that the peak of Rh 3ds/2 XPS of Rh metal nanoparticles modified by TiO$_2$–δ was found to be located at lower energy than that of the Rh foil. Rh–8–A is reasonably assumed to be in the SMSI state. On the other hand, the peak of Rh–3–R appeared at 307.2 eV, which is approximately equal to the peak energy of Rh foil (307.0 eV). The Rh metal nanoparticles of Rh–3–R would more weakly interact with TiO$_2$ than those of Rh–8–A. XPS measurements were carried out at a given sputtering time by Xe ion in these two samples. The composition ratio between Rh and Ti (Rh/Ti ratio) at a given sputtering time was evaluated from those peak areas divided by respective atomic sensitivity factors. The variation in Rh/Ti ratio with sputtering time of Rh–3–R and Rh–8–A is shown in Fig. 10. The Rh/Ti ratio of Rh–3–R was constant with the sputtering time, whereas that of Rh–8–A increased with the sputtering time and approached to 1.3% after 14 min of sputtering. This change in Rh/Ti ratio indicates that the photodeposited Rh metal nanoparticles on 3–R are not decorated, although TiO$_2$–δ generated by the photoirradiation of TiO$_2$ modifies the Rh metal nanoparticles on 8–A due to the SMSI between the Rh metal nanoparticles and TiO$_2$–δ.

**Figure 9.** Rh 3d XPS of (a) Rh–3–R and (b) Rh–8–A.
Conclusion

In the photodeposition process, the Rh metal nanoparticles with a uniform size appear on both anatase and rutile phase of TiO$_2$. The appearance rate of Rh metal nanoparticles is constant on the anatase while it decreases with the photoirradiation time on the rutile. The Rh metal species on the anatase is covered with TiO$_2$, although the aggregated Rh species, which is composed of the primary Rh nanoparticles on rutile phase of TiO$_2$, are not decorated. The crystalline phase of TiO$_2$ has a significant effect on both the formation process of Rh metal particles and the structure of photodeposited Rh species.

References


[35] In this DXAFS experiments using 8-A, the photodeposition finished after 75 min photoirradiation. That time was shorter than that in our previous paper (90 min). This is because the light intensity of this experiment is higher than that of previous one.


List of Publications

Chapter 1

1. Effect of Reaction Temperature on Photocatalytic Activity for Photo-SCR of NO with NH$_3$ over a TiO$_2$ Photocatalyst
   Akira Yamamoto, Yuto Mizuno, Kentaro Teramura, Shishido Tetsuya, and Tsunehiro Tanaka

Chapter 2

2. Visible-light-assisted selective catalytic reduction of NO with NH$_3$ on porphyrin derivative-modified TiO$_2$ photocatalysts
   Akira Yamamoto, Yuto Mizuno, Kentaro Teramura, Saburo Hosokawa, Shishido Tetsuya, and Tsunehiro Tanaka

Chapter 3

   Akira Yamamoto, Kentaro Teramura, Shishido Tetsuya, and Tsunehiro Tanaka
   DOI: 10.1002/cctc.201500207R1

Chapter 4

4. Effects of SO$_2$ on Selective Catalytic Reduction of NO with NH$_3$ over a TiO$_2$ Photocatalyst
   Akira Yamamoto, Kentaro Teramura, Saburo Hosokawa, and Tsunehiro Tanaka
Chapter 5

5. Noble-metal-free NO\textsubscript{x} storage over Ba-modified TiO\textsubscript{2} photocatalysts under UV-light irradiation at low temperatures
   Akira Yamamoto, Yuto Mizuno, Kentaro Teramura, Saburo Hosokawa, and Tsunehiro Tanaka

Chapter 6

6. Mechanism of NO\textsubscript{x} storage over Ba-modified TiO\textsubscript{2} Photocatalysts under UV-light Irradiation: Effect of Ba Loading and Structure of Ba species
   Akira Yamamoto, Yuto Mizuno, Kentaro Teramura, Saburo Hosokawa, and Tsunehiro Tanaka
   Submitted to *Applied Catalysis B*.

Appendix

7. Effect of a crystalline phase of TiO\textsubscript{2} photocatalysts on the photodeposition of Rh metal nanoparticles
   Akira Yamamoto, Junya Ohyama, Kentaro Teramura, Shishido Tetsuya, and Tsunehiro Tanaka