Mechanism for NO Photooxidation over the Oxygen-Deficient TiO_2 Powder under Visible Light Irradiation

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The mechanism for the photooxidation of NO over hydrogen plasma-treated TiO_2 under visible light irradiation was studied by in situ Fourier transform infrared spectroscopy. It was found that the oxidation of NO over plasma-treated TiO_2 under visible light proceeded consecutively as NO $\rightarrow NO_2^- \rightarrow NO_3^-$, where the oxidation process of NO_2^- to NO_3^- was newly created by irradiation of visible light.

It is known that the TiO_2 photocatalyst can oxidize NO in air to HNO_3 (NO_3^-).[1] However, this photocatalytic reaction only proceeds under ultraviolet (UV) light irradiation with commonly used TiO_2. If the photocatalytic oxidation of NO proceeds under illumination of visible light by modifying the photocatalyst, a wider application of the TiO_2 photocatalyst can be expected. We have previously found that the TiO_2 powder slightly reduced by hydrogen plasma treatment shows a high visible light activity for the oxidation of NO.[2,3] It was considered that the appearance of visible light activity in the plasma-treated TiO_2 photocatalyst was due to a new photoexcitation process by formation of an oxygen vacancy state located between the valence and conduction bands.[3] However, the mechanism for the photooxidation of NO is not understood yet, including the information about the participation of light during each elementary step. Here, we report the mechanism for the photooxidation of NO over plasma-treated TiO_2 under visible light irradiation using in situ Fourier transform infrared (FT-IR) spectroscopy.

The TiO_2 powder (ST-01, 100% anatase, 300 $m^2\ g^{-1}$) from Ishihara Sangyo Kaisha was used in this study. The plasma treatment for the TiO_2 powder was performed by a radio-frequency discharge (13.56 MHz, 500 W) under 2 Torr H_2 for 10 min at 673 K in a quartz glass chamber. The NO oxidation was carried out at room temperature, a total pressure of 760 Torr, and a total flow rate of 50 $cm^3\ min^{-1}$ using a gas mixture of dry air containing 20 ppm NO, which was produced by the air purifier and 50 ppm of NO/N_2 from a cylinder. The FT-IR spectra were obtained using a JEOL JIR-100 FT-IR spectrometer equipped with an MCT detector and a flow-type IR cell (KBr windows) for diffuse reflectance measurement. All spectra were obtained with a resolution of 4 cm^{-1} by 200 scans in a total measurement time of 1 min. The TiO_2 sample for the IR measurements was prepared by diluting with diamond powder. It was confirmed that no adsorption and oxidation of NO was observed over only the diamond powder. The photoirradiation of the sample placed in the IR cell was carried out using a fiber-optic light source with a 150-W xenon lamp through a longpass glass filter (Schott WG320, GG455).

Figure 1 shows the in situ IR spectra obtained by exposing plasma-treated TiO_2 to a 20 ppm NO/air gas mixture for 420 min under visible light (> 455 nm) irradiation (a) and in the dark (b). Nine peaks at 1603, 1581, 1552, 1473, 1358, 1302, 1252, 1200, 1011 cm^{-1} were observed during the visible light irradiation (Figure 1 (a)). The peaks at 1603 and 1302 cm^{-1}, 1581 and 1252 cm^{-1}, 1552 and 1358 cm^{-1} were assigned to the ν_3 (split) modes of the bridging, chelating, and monodentate NO_3^- species on Ti, respectively, based on the literature data.[4–6] The broad band at 1473 cm^{-1} was due to the almost symmetrical NO_3^- ions.[7] The peak at 1011 cm^{-1} was identified as the ν_1 mode of the NO_3^- species.[4–6] No difference in the frequency of the ν_1 mode was seen by the difference in the adsorption structures of the NO_3^- species. The band at 1200 cm^{-1} was assigned to ν(NO) of the bidentate NO_2^- on Ti.[4,6] It was found that the NO_2^- species and four kinds of NO_3^- species with different adsorption structures were formed by the oxidation of NO over plasma-treated TiO_2 during visible light irradiation. We have previously confirmed that the amount of NO_3^- species accumulated on the post-reaction plasma-treated TiO_2 powder is close to that estimated from the activity of NO oxidation, indicating that no pathway to other N-compound exists in the oxidation of NO over plasma-treated TiO_2.[3]

On the other hand, only the bidentate NO_2^- species peak was detected at 1200 cm^{-1} in the dark as shown in Figure 1(b), where no formation of the NO_3^- species was observed. The oxidation of NO to NO_2^- proceeds by lattice oxygen or dissociated oxygen.[4,8] The frequency of the NO_2^- species observed in the dark was the same as that observed during visible light irradiation, indicating that the NO_2^- species formed both in the dark and during visible light irradiation had identical bonding configurations. It was thus clearly shown that visible light was needed for the formation of the NO_3^- species, while NO_2^- species was formed regardless of the light irradiation.

The formation behaviors of the NO_2^- and NO_3^- species on the plasma-treated TiO_2 photocatalyst were examined. Figure 2 shows the peak intensities of the NO_2^- and NO_3^- species formed under > 455 nm irradiation and in the dark as a function of the reaction time, where the peak intensity at high frequency for the ν_3 mode of chelating NO_3^- species was plotted as that of the NO_3^- species. The formation rate of the NO_2^- species was very fast during visible light irradiation and reached a steady state in 30 min. The formation of the NO_3^- species was observed after the NO_2^- species reached the steady state, and the amount of NO_3^- species increased with the reaction time. The formation rate of the NO_3^- species was slower than that of the NO_2^- species. Thus, it was found that the photooxidation of NO over plasma-treated TiO_2 during visible light irradiation proceeded in the consecutive oxidation reaction as follows, NO $\rightarrow NO_2^- \rightarrow NO_3^-$. The decrease in the steady state coverage of the NO_2^- species observed after 200 min is considered to be due to the decrease in the number of adsorption sites by the accumulation of the NO_3^- species formed on the catalyst surface.

On the other hand, the NO_2^- species gradually increased with the reaction time in the dark and reached a steady state in 400 min, where no NO_3^- species was formed. The formation rate of the

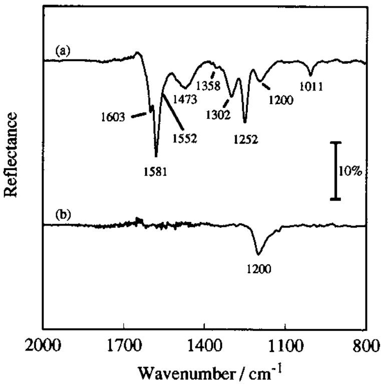

Figure 1. *In-situ* IR spectra of adsorbed species formed on plasma-treated TiO_2 by exposing to 20 ppm NO/air for 420 min under > 455 nm irradiation (a) and in the dark (b).

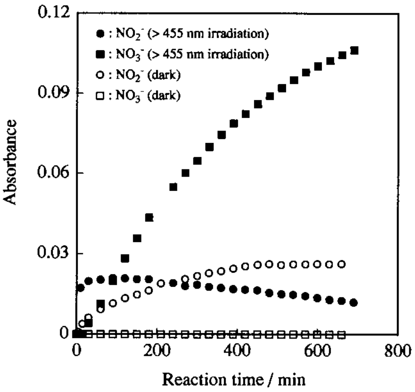

Figure 2. Peak intensities of the NO_2^- and NO_3^- species adsorbed on plasma-treated TiO_2 under > 455 nm irradiation and in the dark as a function of reaction time.

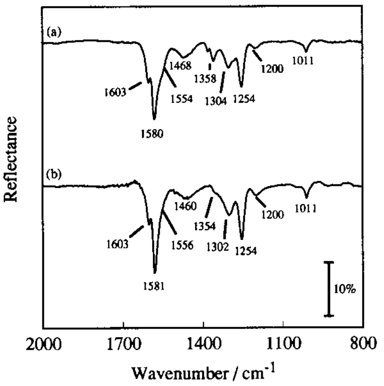

Figure 3. *In-situ* IR spectra of adsorbed species formed on plasma-treated TiO_2 (a) and raw TiO_2 (b) at 20 ppm NO/air for 30 min under > 320 nm irradiation.

NO_2^- species in the dark is obviously slow compared with that during visible light irradiation. Thus, the following two points were proved concerning the participation of visible light in the mechanism of NO oxidation over the plasma-treated TiO_2 photocatalyst: i) the oxidation process of NO_2^- to NO_3^- is newly created by irradiation of visible light, and ii) the oxidation of NO to NO_2^- is remarkably promoted by visible light.

We have previously reported that the oxygen vacancies are created by treating the TiO_2 powder in a hydrogen plasma, consequently, the oxygen vacancy state is formed between the valence and conduction bands.[3] The electrons excited to the oxygen vacancy state in plasma-treated TiO_2 were confirmed under visible light irradiation by electron spin resonance measurement, where the oxygen vacancy state was estimated to be located 1.94 eV above the valence band.[3] It was concluded that the activation of oxygen, which was considered to be important for the photocatalytic oxidation,[9] arises by the excitation of electrons to the oxygen vacancy state from the valence band under visible light irradiation, resulting in the visible light activity of NO oxidation. Thus, it is considered that NO_2^- is oxidized to NO_3^- only by activated oxygen species formed during visible light irradiation. Furthermore, the activated oxygen species significantly enhanced the rate for the oxidation process of NO to NO_2^-, compared to the oxygen species such as lattice oxygen or dissociated oxygen.

Here, a question arises whether the mechanism for the oxidation of NO is same for both the visible and UV lights. The NO oxidation under UV light irradiation was carried out to compare the mechanism under visible light. Figure 3 shows the in situ IR spectra of adsorbed species formed on plasma-treated TiO_2 (a) and raw TiO_2 (b) by exposure to 20 ppm NO/air for 30 min under > 320 nm irradiation. The IR spectra observed on both surfaces were similar to that obtained in Figure 1(a). It was found that the adsorbed species formed during the NO oxidation are identical under both conditions, clearly indicating that the oxidation process of $NO_2^- \rightarrow NO_3^-$ is created under UV light irradiation. However, the rate of the NO_3^- formation under UV light was much faster than that under visible light, considering the difference in the irradiances. These results indicate that the mechanism for the oxidation of NO under UV light is the same as that under visible light, whereas only the oxidation rate is different.

It is important for NO photooxidation that the oxidation of $NO_2^- \rightarrow NO_3^-$ proceeds by the activated oxygen species as previously described. Under UV light irradiation, the activated oxygen species is formed by the excitation of electrons to the conduction band from the valence band for a band gap energy of 3.2 eV in anatase TiO_2.[10,11] Under visible light irradiation, on the other hand, the activated oxygen species is formed by the excitation of electrons to the oxygen vacancy state from the valence band in plasma-treated TiO_2. That is, the formation path of the activated oxygen species differs between the UV and visible lights. It is considered that the rate of NO oxidation is faster under UV light irradiation because more activated oxygen species are formed.

In summary, it was found that the mechanism for the photooxidation of NO over plasma-treated TiO_2 under visible light irradiation is the consecutive oxidation of $NO \rightarrow NO_2^- \rightarrow NO_3^-$. The NO_2^- species is oxidized to NO_3^- only by the activated oxygen species, which is formed by the excitation of electrons to oxygen vacancy states in plasma-treated TiO_2 under visible light. Furthermore, it is found that the oxidation of NO proceeds with the same reaction mechanism under both UV and visible lights.

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