EPR Study of Photoinduced Electron Transfer between Adsorbent and Adsorbed Species in Photo-SCR with NH_3

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Photoformed hole and electron on TiO_2 adsrobing NH_3 are trapped, respectively, by a NH_3 species adsorbed on TiO_2 and Ti^{4+} to evolve a NH_2 radical and a Ti^{3+} species. The photoinduced electron transfer takes place between Ti^{4+} and adsorbed NH_3 species efficiently, resulting in the formation of a NH_2 radical. The NH_2 radical on TiO_2 was stably present after the photoirradiation was ceased. It is quenched rapidly just after introduction of NO leaving the Ti^{3+} species.

NO_x exhausted from the stationary emission source is removed by the selective catalytic reduction process with NH_3 (NH_3-SCR) over V_2O_5/TiO_2 based oxide catalysts.[1,2] Recently, some authors have uncovered the catalysts activated at low temperatures.[3–5] We reported photo-SCR over TiO_2 photocatalyst at room temperature where 83% of NO conversion and 96% of N_2 selectivity were achieved in the conventional fixed bed flow system.[6] We have already proposed the reaction mechanism of photo-SCR system as follows.[7] NH_3 is adsorbed on Lewis acid site of TiO_2 rapidly. One hydrogen atom of the adsorbed NH_3 species interacts with a lattice oxygen. Electron transfer takes place from N atom of NH_3 adsorbed on TiO_2 to Ti atom of TiO_2 bulk under photoirradiation. The photoformed hole is captured by the adsorbed NH_3 to form a NH_2 radical. The NH_2 radical was reacted with NO in the gas phase readily to generate a NH_2NO species as an intermediate. Thus, the formed NH_2NO species is decomposed to N_2 and H_2O and a Ti^{3+} species is reoxidized to a Ti^{4+} species by O_2. We have already detected a NH_2NO intermediate by FTIR spectroscopy.[7] However, we did not confirmed yet whether or not a NH_2 radical is generated on TiO_2 and was reacted with NO in the gas phase. In the present paper, we proposed the formation of a NH_2 radical which was readily reacted with NO in the gas phase deduced by EPR spectroscopy.

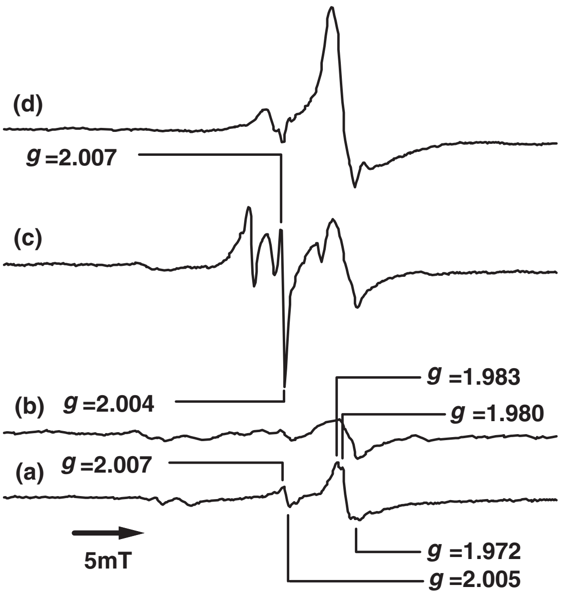

Figure 1. The EPR spectra of TiO_2 (a) after pretreatment, (b) after introduction of NH_3 in the dark, (c) under photoirradiation and (d) after introduction of NO in the dark.

JRC-TIO-4 (equivalent to Degussa P-25) supplied from the Catalysis Society of Japan was hydrated in distilled water for 2 h at 353 K, followed by filteration with a suction pump. The sample was kept at 383 K for 24 h in an oven, followed by calcination in air at 773 K for 3 h. The specific surface area was evaluated to be $48\,m^2g^{-1}$ by the BET method using N_2 adsorption isotherm at 77 K. Powder XRD tells that the treated JRC-TIO-4 consists of anatase and rutile phases. EPR spectra were recorded using an in situ quartz cell with an X-band EPR spectrometer (JOEL JES-SRE2X) with 100 kHz field modulation at 123 K. Before the measurement, the catalyst sample was heated at 673 K in air and evacuated for 30 min at the same temperature, followed by treatment with 8 kPa O_2 for 90 min and evacuation for 30 min at 673 K. The *g* value and the relative amount of radical species were determined using a Mn marker. The effect of NH_3 adsorption onto TiO_2 upon the EPR spectra was investigated by recording the spectra after the equilibrium adsorption of NH_3 at room temperature followed by evacuation. On the other hand, NO was introduced to TiO_2 adsorbing NH_3 under the measurement condition. Some spectra were recorded under illumination from a 500-W ultrahigh-pressure mercury lamp.

Figure 1 shows the EPR spectra of TiO_2 after pretreatment, after introduction of NH_3 in the dark and under photoirradiation, and after introduction of NO in the dark. The lines at $g = 1.972$, 1.980 and 1.983 assignable to a Ti^{3+} species were observed after pretreatment as shown in Figure 1a. In addition, the lines at $g = 2.005$ and 2.007 assignable to an electron trapped in an F centre appeared. It is known that a Ti^{3+} species and an F centre are formed on TiO_2 after heat treatment.[8] On introducing NH_3, these lines decreased in intensity as shown in Figure 1b. After that, new lines were observed as soon as TiO_2 adsorbing NH_3 was illuminated at 123 K in Figure 1c. This new signal was quite stably present even after more than one hour when the irradiation was ceased. Some authors clarified by EPR that a NH_2 radical is trapped on the surface of various materials under photoirradiation.[9–13] The three ^{14}N lines are further split into three lines by the hyperfine interaction with two equivalent hydrogen atoms. We measured the EPR spectra of TiO_2 adsorbing NH_3 labeled N-15 to clarify the assignment of the lines as shown in Figure 2b. In addition, we determined the magnetic parameters for $^{14}NH_2$ and $^{15}NH_2$ radical in TiO_2 as shown in Table 1. The values are consistent with earlier works.[11,13] The lines at

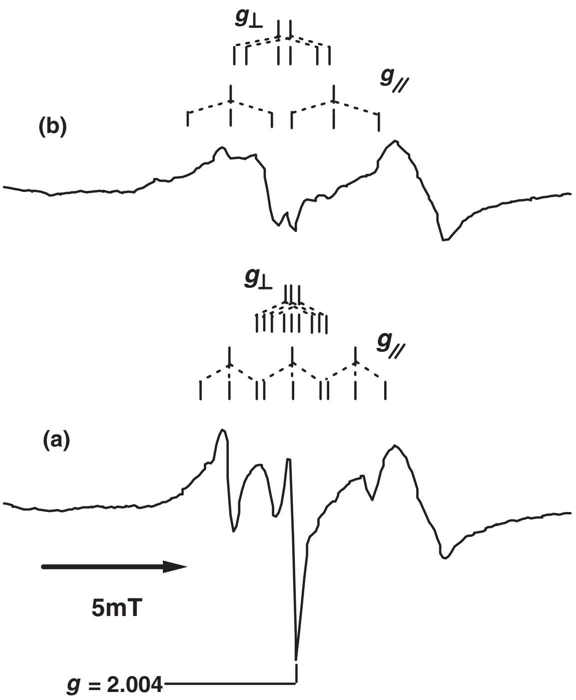

Figure 2. The EPR spectra of TiO_2 after introduction of NH_3 under photoirradiation (a) by using $^{14}NH_3$ and (b) by using $^{15}NH_3$.

$g > 2.004$ in Figure 2b were changed in comparison with those found in introduction of $^{14}NH_3$ in Figure 2a. However, the lines at $g < 2.004$ in Figure 2b remained although $^{15}NH_3$ was admitted instead of $^{14}NH_3$. The EPR spectrum of a $^{15}NH_2$ radical exhibits five lines.[9,11,12] Evidently, in our case, the lines at $g > 2.004$ were due to a NH_2 radical. On the other hand, the lines at $g < 2.004$ were attributed to the other species. Hurum et al.[8] reported the EPR spectra of Degussa P-25 under photoirradiation. They observed four characteristic lines. A couple of lines at $g = 1.990$ and 1.957 are assignable to lattice electron trapping sites in anatase and the rest two at $g = 1.975$ and 1.940 for rutile; i.e., the lines at $g < 2.004$ are assignable to Ti^{3+} species. We concluded that Figure 1c is identified to the EPR spectrum of a NH_2 radial overlapped with that of a Ti^{3+} species. Photoirradiation to TiO_2 adsorbing NH_3 contributes to the formation of a NH_2 radical and a Ti^{3+} species. This suggests that an electron transfer takes place from N atom of NH_3 adsorbed on TiO_2 to Ti atom of TiO_2 bulk. An electron reduced a Ti^{4+} cation to a Ti^{3+} cation and a hole is captured by the adsorbed NH_3 on TiO_2 to form a NH_2 radical.

After introduction of NO in the dark, the lines of the NH_2 radical vanished quickly whereas the lines of the Ti^{3+} species increased in intensity (Figure 1d). The Ti^{3+} species are restored to the Ti^{4+} species by gaseous oxygen which we confirmed by UV–vis spectroscopy. The quick disappearance of a NH_2 radical suggests whether a NH_2 radical itself changed to an EPR silent species, or NO in the gas phase attacks to a NH_2 radical on TiO_2 to form an intermediate. We have already examined the formation of a NH_2NO intermediate by FTIR spectroscopy after admittance of NO to TiO_2 adsorbing NH_3 under photoirradiation.[7] The NH_2NO intermediate is decomposed to N_2 and H_2O. This is supported by the fact that the detected nitrogen gas was only $^{15}N^{14}N$ in the $^{15}NO + {}^{14}NH_3 + O_2$ reaction. Taking into account these results, we can conclude that NO in the gas phase was reacted with NH_3 adsorbed on TiO_2. In addition, a spin state of NO, a doublet, coincides with that of a NH_2 radical. In conclusion, it is reasonable that ^{15}NO in the gas phase attacks a $^{14}NH_2$ radical anchored on TiO_2 to form a NH_2NO intermediate and O_2 reoxidized a Ti^{3+} species to a Ti^{4+} species.

Table 1. Magnetic parameters for $^{14}NH_2$ and $^{15}NH_2$ radical in TiO_2

Radical	A^{N} / G	A^{N} / G	A^{H} / G
$^{14}NH_2$	24	3	10
$^{15}NH_2$	37	6	15

Here, we clarified the charge transfer from N atom of NH_3 adsorbed on TiO_2 to Ti atom of TiO_2 (a hole and an electron are localized on a NH_3 species and a Ti^{4+} species, respectively). It is the first report that the charge transfer was confirmed between an adsorbent and an adsorbed species.

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