Available online at www.sciencedirect.com

Catalysis Today 120 (2007) 220–225

www.elsevier.com/locate/cattod

Photo-oxidation of NH_3 over various TiO_2

Seiji Yamazoe, Taro Okumura, Tsunehiro Tanaka *

Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Kyoto 615-8510, Japan

---

Abstract

Photo-oxidation of NH_3 (photo-SCO) takes place at room temperature over TiO_2 photocatalyst. From the results of photo-SCO reaction over various TiO_2, we found that JRC-TIO-8 exhibited the best activity and 100% NH_3 conversion was achieved at GHSV = 25,000 h^{-1}. ESR study revealed that the photo-SCO proceeds by the reaction between NH_2 radical and oxygen anion radical species. We found that the photo-SCO activity correlated to the amount of the NH_3 chemisorption amount of TiO_2 and the oxygen anion radical species. In particular, the produced amount of O_3^- radical is more active in the photo-SCO.

Keywords: TiO_2; Photocatalyst; Ammonia oxidation; SCO; NH_3; Oxygen anion radical; Amide radical

---

1. Introduction

The removal of ammonia from air or water is important for the environmental preservation. Many chemical processes use reactants containing ammonia and/or produce ammonia. The 'ammonia slip' is now a significant problem to be solved urgently. Currently, ammonia is removed from industrial fuel gases by absorption using biological treatment or by thermal combustion. Selective catalytic oxidation (SCO) of ammonia to nitrogen is a potentially available method in order to reduce the ammonia pollution and accordingly SCO technology attracts interest recently [1–6]. The SCO process may also be applied to the selective catalytic reduction (SCR) of NO_x with ammonia for removing unreacted ammonia in the SCR process. In this case, it is necessary to develop the SCO process operating at low temperatures.

Up to now, many efforts for the development of low temperature SCO have been made. Long and Yang reported that Cu and Fe exchanged ZSM-5 showed the good SCO performance at 623 K [1]. Recently, Gang et al. reported that Ag/Al_2O_3 catalyst showed high activity in the SCO at above 433 K [3]. A number of other catalysts were also investigated such as Pt, Pd and Rh exchanged to ZSM-5 or supported on Al_2O_3 [7], CuO/Al_2O_3 [8,9], CuO/TiO_2, V_2O_5/TiO_2 [10] and Cu, Co and Ni oxides doped on SiO_2 [11]. However, the aforementioned works were performed at high temperature (>433 K).

It is known that photocatalytic reaction proceeds at room temperature in the atmospheric pressure [12–14]. We note that photo-SCO of NH_3 to N_2 proceeds at room temperature. In a series of our studies of the photo-assisted selective catalytic reduction of NO with NH_3 over TiO_2 under irradiation [15–19], we reported that NH_3 adsorbed over TiO_2 is altered to NH_2 radical by optical excitation [16]. NH_2 radical reacts readily with oxygen anion radical because both the species are in the same electron-spin state. It is also known that oxygen anion radical species is formed over TiO_2 under irradiation [20,21]. This allows us to expect that the photo-SCO can be realized using TiO_2 photocatalyst. Actually, Cant and Cole reported that photo-SCO reaction takes place over TiO_2 [22]. However, the reaction was carried out in a closed system and the activity was very low. Therefore, it is not known exactly how the photo-SCO proceeds over TiO_2 catalytically. Despite the importance of the reaction, there have been no reports relevant to the photo-SCO over photocatalyst, after that.

In this study, we carried out the photo-SCO over various TiO_2 in a conventional fixed bed flow system. We expect that NH_2 radical and oxygen anion radical species generated by photo-excitation are the intermediates of photo-SCO. In order to observe these, we recorded the ESR spectra and investigated the reactivity of these intermediates. In addition, we examined the correlation of the NH_3 adsorption amount

---

* Corresponding author. Tel.: +81 75 383 2559; fax: +81 75 383 2561.
E-mail address: tanakat@moleng.kyoto-u.ac.jp (T. Tanaka).

0920-5861/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2006.07.053

and the produced amount of oxygen anion radical species with the photo-SCO activity.

2. Experimental

2.1. Preparation method of catalysts

TiO_2 samples used in this study were kindly supplied from the Japan Catalysis Society (JRC-TIO-1–13). These samples were hydrated in distilled water for 2 h at 353 K and followed by filtration with suction, and were dried at 383 K overnight. The catalysts were calcined in dry air at 673 K for 3 h. All calcined catalysts were grinded into powder from 26 to 50 mesh.

2.2. Catalytic reaction

Photo-SCO was carried out in a conventional fixed bed flow system at an atmospheric pressure and at room temperature. Catalysts were fixed with quartz wool and filled up in a quartz reactor, which had flat facets (12 mm × 10 mm 1 mm). Before reactions, catalysts were pretreated at 673 K by flowing 10% O_2 diluted with Ar at 50 ml/min for 1 h. The typical reaction gas composition was as follows: NH_3 1000 ppm, O_2 2%, Ar balance. A Perkin-Elmer PE300BF 300 W Xe lamp was used as a light source and samples were irradiated from the one side of the flat facets of the reactor. N_2 and N_2O products were analyzed by a SHIMADSU GC-8A TCD gas chromatograph with MS-5A column for N_2 detection and Porapak Q for N_2O. The quantity of produced NO_x was determined by a Shimadzu NOA-7000 NO_x analyzer.

2.3. ESR studies

ESR spectra were recorded with an X-band ESR spectrometer (JEOL JES-SRE2X). TiO_2 samples were packed in an in situ quartz cell. Before recording ESR spectra, samples were heated in air and evacuated for 30 min at 673 K, followed by treatment with 90 Torr (1 Torr $\approx$ 1.33 hPa) O_2 for 60 min and evacuation for 30 min at 673 K. All the ESR spectra were recorded at 123 K. As a light source, a 500 W ultrahigh-pressure mercury lamp equipped UV-33 cut filter was used for the irradiation of the light $\lambda \geq 300$ nm.

2.4. Determination of oxygen anion radical species amount

1,1-Diphenyl-2-picrylhydrazyl (TEMPOL; radical density: 97%), purchased from Wako, was used for the determination of radical amount. Fifty-two micrograms of TEMOL was dissolved in 25 ml benzene and this solution was enclosed in an quartz cell at N_2-filled ambient atmosphere. All the ESR spectra were recorded at 123 K. The radical density of TEMPOL in the benzene solution was 1.28×10^{-8} mol ml^{-1} at 123 K as a result of the volume correction of benzene. ESR spectra of TEMPOL and all the TiO_2 samples were recorded with a certain amount of Mn/MgO marker. Before recording the ESR spectra, TiO_2 samples were heated in air and evacuated for 30 min at 673 K, followed by treatment with 90 Torr O_2 for 60 min and evacuation for 30 min at 673 K. 1 Torr O_2 were introduced in all the TiO_2 samples and ESR spectra were recorded. The signals of photo-formed oxygen anion radical were obtained from the difference spectrum between the spectrum of TiO_2 sample introduced oxygen under irradiation and that before irradiation. We determined the generated oxygen anion radical amount over each sample by comparison of the double integration of oxygen anion radical signals with that of TEMPOL signals.

3. Results and discussion

3.1. Photo-SCO over TiO_2 photocatalyst

Fig. 1(a) shows the result of photo-SCO reaction over JRC-TIO-11 at GHSV = 8000 h^{-1} in the conventional fixed bed flow

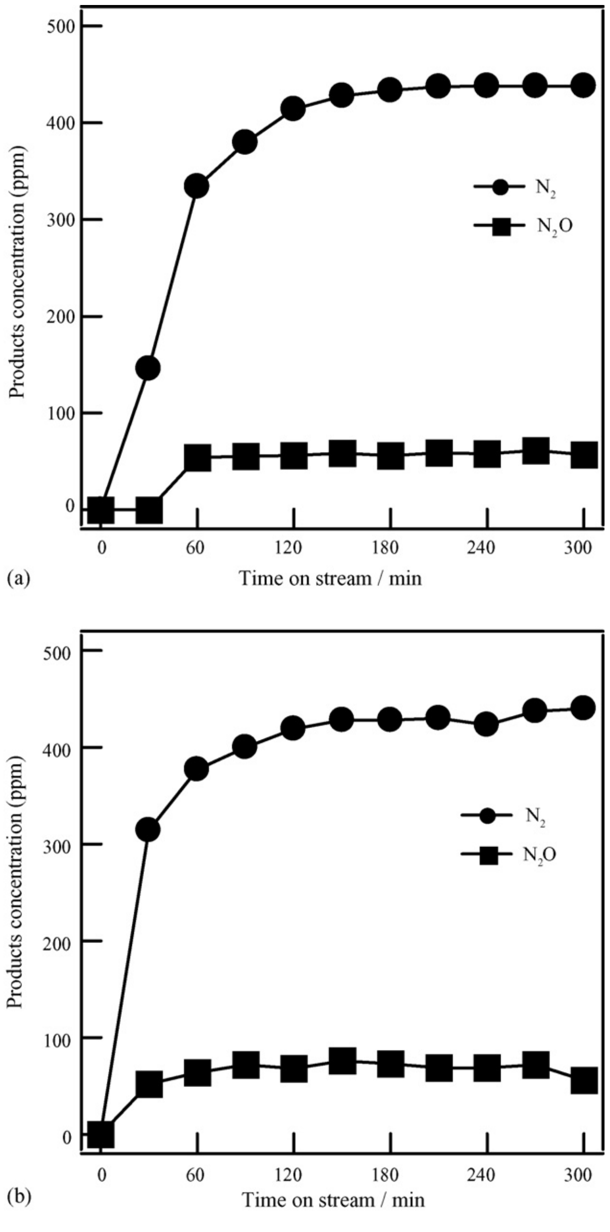

Fig. 1. The time course of photo-SCO: (a) over JRC-TIO-11 at GHSV = 8000 h^{-1} and (b) over JRC-TIO-8 at GHSV = 25,000 h^{-1}; NH_3: 1000 ppm; O_2: 2%. (●) N_2; (■) N_2O.

system. N_2 evolution rate increased gradually with irradiation time and attained a steady rate at 120 min. 100% NH_3 conversion and 88% N_2 selectivity were obtained. We confirmed that the activity was kept over 72 h. The by-product was N_2O, and NO was under detection if any. It is found that the photo-SCO proceeds over TiO_2 catalytically in the conventional fixed bed flow system.

In order to get the information to develop the effective catalyst for photo-SCO, we carried out the photo-SCO over various TiO_2. Table 1 shows the catalyst weight filled in the reactor, crystal phase, specific surface area [19], and the result of the photo-SCO over various TiO_2 at GHSV = 50,000 h^{-1}. JRC-TIO-8, which has an anatase phase, exhibited the highest activity (70% NH_3 conversion and 87% N_2 selectivity) in all TiO_2 samples. JRC-TIO-3 and JRC-TIO-11 were the most active catalysts consisting of rutile single phase and the mixture of rutile and anatase, respectively. JRC-TIO-8, which was the most active catalyst in all samples also exhibited the good activity at GHSV = 25,000 h^{-1}, and 100% NH_3 conversion and 84% N_2 selectivity were achieved as shown in Fig. 1(b). So far, there were several reports of low temperature SCO [1–3,6], but there is no report that the SCO reaction proceeds under 433 K. The photo-SCO system exhibited the higher activity at 323 K than that in other systems and this opens the door of SCO available at low temperature.

Combining the activity with the crystal phase, it is suggested that the photo-SCO proceeds over all TiO_2 samples without reference to the crystal phase. Fig. 2 shows the NH_3 conversion against the surface area of used catalysts ((surface area) = (specific surface area) × (catalyst weight)). Catalytic activity was found to be closely related to catalyst surface area. Therefore, it is suggested that the surface area is one of the factors to determine the photo-SCO activity. However, the points in Fig. 2 are scattered widely and it is thought that there are more important factors to determine the catalyst activity.

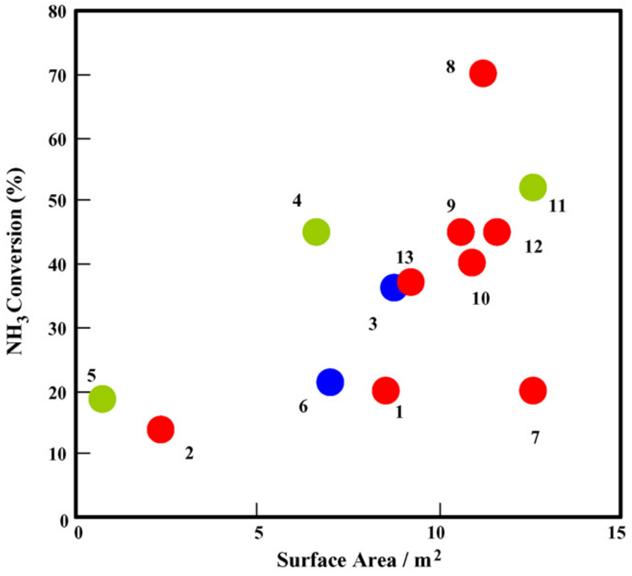

Fig. 2. Effect of the surface area on the NH_3 conversion; GHSV: 50,000 h^{-1}; NH_3: 1000 ppm, O_2: 2%. The numbers denotes the catalyst, see Table 1.

3.2. Identification and reactivity of active oxygen species

We have already reported that NH_3 adsorbed on TiO_2 changed to NH_2 radical by photo-excitation [16]. It is also reported that oxygen anion radical species is formed on TiO_2 [20–24]. Therefore, it is very likely that the photo-SCO takes place by the reaction between NH_2 radical and oxygen anion radical species. We carried out the ESR studies in order to identify the oxygen anion radical species formed by photo-excitation over TiO_2 and to investigate the reactivity of the oxygen anion radical species.

Fig. 3 shows the ESR spectra of JRC-TIO-11 at 123 K (a) after pre-treatment; (b) after O_2 introduction (1 Torr) in the dark; (c) after irradiation; (d) after NH_3 introduction (1 Torr) in the dark; (e) after re-irradiation. In Fig. 3(a), the only signal

Table 1
Photo-SCO activity and several properties of JRC-TIO series

Catalysts	Catalyst weight (g)	Crystal[a] phase	Specific surface area (m^2 g^{-1})	NH_3[b] conversion (%)	N_2 selectivity[b] (%)	NH_3 chemisorption amount (μmol g^{-1})	Oxygen anion radical amount[c] (nmol g^{-1}) (species)
JRC-TIO-1	0.12	A	71	20	91	344	19 ($O_2^{\bullet-}+O_3^{\bullet-}$)
JRC-TIO-2	0.15	A	16	14	99	92	12 ($O_2^{\bullet-}+O_3^{\bullet-}$)
JRC-TIO-3	0.19	R	46	36	92	181	25 ($O_2^{\bullet-}$)
JRC-TIO-4	0.14	R 29% A 71%	48	45	90	249	17 ($O_2^{\bullet-}+O_3^{\bullet-}$)
JRC-TIO-5	0.23	R 92%	3–4	19	93	26	12 ($O_2^{\bullet-}$)
JRC-TIO-6	0.12	A 8%	58	21	95	224	27 ($O_2^{\bullet-}$)
JRC-TIO-7	0.12	A	108	20	91	416	28 ($O_2^{\bullet-}+O_3^{\bullet-}$)
JRC-TIO-8	0.12	A	93	70	87	400	39 ($O_2^{\bullet-}+O_3^{\bullet-}$)
JRC-TIO-9	0.11	A	95	45	87	366	22 ($O_2^{\bullet-}+O_3^{\bullet-}$)
JRC-TIO-10	0.11	A	100	40	90	222	24 ($O_2^{\bullet-}+O_3^{\bullet-}$)
JRC-TIO-11	0.16	R 9% A 91%	77	52	90	446	28 ($O_2^{\bullet-}+O_3^{\bullet-}$)
JRC-TIO-12	0.12	A	99	45	90	449	31 ($O_2^{\bullet-}+O_3^{\bullet-}$)
JRC-TIO-13	0.13	A	71	37	90	328	22 ($O_2^{\bullet-}+O_3^{\bullet-}$)

[a] A: anatase; R: rutile.
[b] Photo-SCO result.
[c] The error about the obtained value is ±5%.

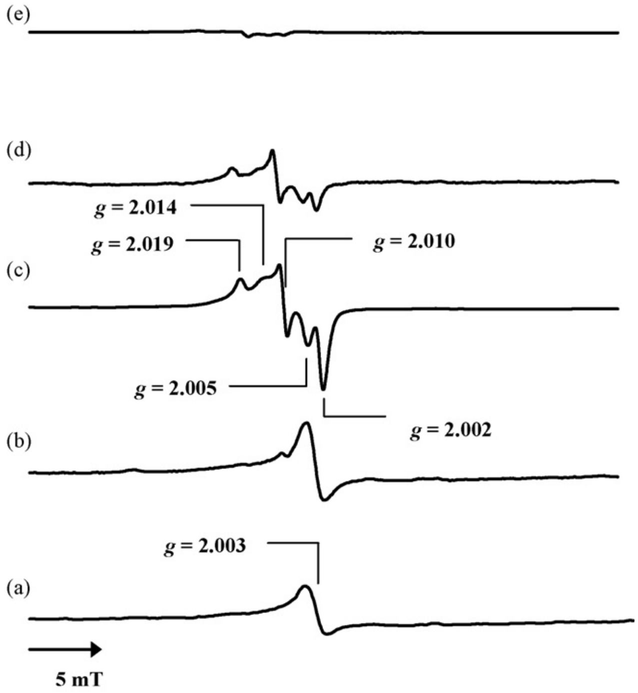

Fig. 3. ESR spectra over JRC-TIO-11 at 123 K: (a) after pretreatment; (b) after O_2 introduction (1 Torr) in the dark; (c) after irradiation; (d) after NH_3 introduction (1 Torr) in the dark; (e) after re-irradiation.

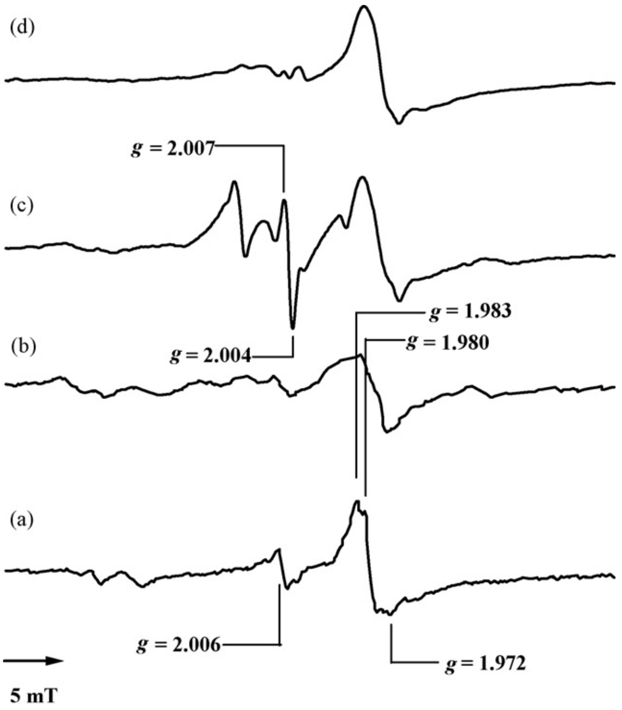

Fig. 4. ESR spectra over JRC-TIO-4 at 123 K: (a) after pretreatment; (b) after NH_3 introduction (1 Torr) in the dark; (c) after irradiation; (d) after O_2 introduction (1 Torr) in the dark.

formed at $g = 2.003$ is assignable to an electron trapped in an F center [16,25]. There was no signal of Ti^{3+} in JRC-TIO-11. O_2 introduction in the dark hardly made the spectral feature changed as shown in Fig. 3(b). However, the spectrum was changed dramatically by the irradiation after O_2 introduction as shown in Fig. 3(c). The new signals appeared and they existed stably under irradiation. These signals were due to the formation of the oxygen anion radical species. When the sample was warmed to room temperature under irradiation, some of the signals vanished keeping the signals at $g = 2.019$, 2.010 and 2.005. These signals attributed to an O_2^- radical are stable at room temperature and showed a close agreement with other reports [20,21,23–25]. The vanished signals at $g = 2.014$, 2.010 and 2.002 were thought to be assignable to O_3^- radical [20,21,23,24]. The both O_2^- and O_3^- radicals were formed at the same time over TiO_2 by irradiation. Fig. 3(d) shows the ESR spectrum of NH_3 introduced TiO_2 in the dark after (c). The signal intensity of O_2^- and O_3^- radicals decayed very leisurely but the decay-rate was the same time as that observed without NH_3 after ceasing photo-irradiation. NH_3 does not have an effect on the oxygen anion radicals in the dark. However, oxygen anion radical signals were quenched quickly by irradiation after introduction of NH_3 as shown in Fig. 3(e). The disappearance of the oxygen anion radical species indicates that these radicals reacted with the photo-activated NH_2 radical species formed by irradiation. In order to confirm this, we carried out the further ESR study.

We have already reported that NH_2 radical is generated over TiO_2 catalyst under UV illumination after NH_3 is adsorbed on TiO_2 [16]. The signal of NH_2 radical appears at $g = 1.980$–2.021. JRC-TIO-11 has a large F center signal at $g = 2.003$ as shown in Fig. 3(a), which hides the NH_2 radical if formed. Consequently, we used JRC-TIO-4 equivalent to Degussa P-25, which has a tiny signal of F center [16,25], instead of JRC-TIO-11. Fig. 4 shows the ESR spectra at 123 K over JRC-TIO-4 (a) after pre-treatment; (b) after NH_3 introduction in the dark; (c) after irradiation; (d) after O_2 introduction in the dark. In Fig. 4(a), the signals in the range of $g = 1.983$, 1.980 and 1.972 were assignable to Ti^{3+} species [23]. The signal at $g = 2.006$ is due to an electron trapped in an F center. The intensity of these signals of Ti^{3+} and F center did not vary by introduction of NH_3 (Fig. 4(b)). The irradiation of the JRC-TIO-4 adsorbing NH_3 caused the appearance of NH_2 radical formed by trapping hole [16]. The signals of NH_2 radical were stably present. This NH_2 radical kept existence for 60 min at 123 K after ceasing photo-irradiation. However, the NH_2 radical was quenched by the O_2 introduction in the dark (Fig. 4(d)). It is likely that remaining electrons by trapping holes by adsorbed NH_3 forms oxygen anion radical even in the dark, because TiO_2 is partially reduced by ammonia at that moment. We confirmed that oxygen anion radical species were formed by O_2 introduction to reduced TiO_2 in the dark (data was not shown). As a result, we conclude that NH_2 radical reacts with oxygen anion radical species formed without irradiation.

3.3. Correlation between NH_3 chemisorption amount and photo-SCO activity

We expected that the NH_3 chemisorption amount is the important factor for the photo-SCO activity, since the reaction

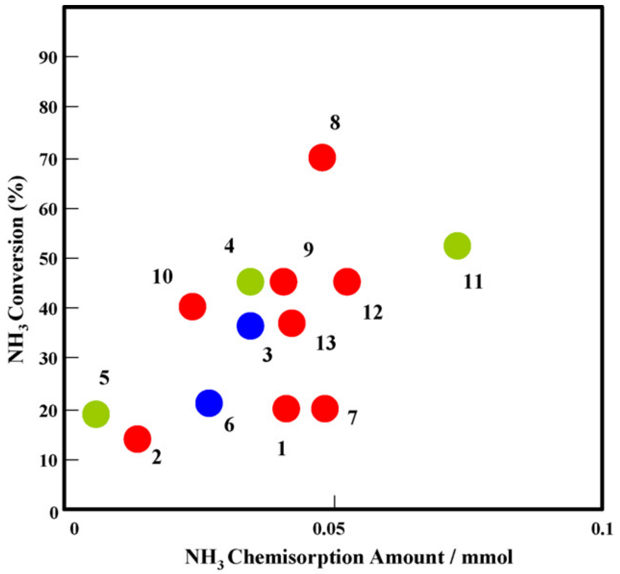

Fig. 5. Effect of the NH_3 chemisorption amount on the NH_3 conversion; GHSV: 50,000 h^{-1}; NH_3: 1000 ppm, O_2: 2%. The numbers denotes the catalyst, see Table 1.

rate is thought to be concerned with the surface population of NH_2 radicals. Table 1 shows the amount of NH_3 chemisorption on JRC-TIO-1–13. Fig. 5 displays the photo-SCO activity plotted against the NH_3 chemisorption amount on various TiO_2. JRC-TIO-8 and JRC-TIO-11, which showed the higher activities exhibited the larger NH_3 chemisorption amounts. On the contrary, JRC-TIO-2 and JRC-TIO-5, poorly active catalysts, exhibited the lower NH_3 chemisorption amounts. The photo-SCO activity has the inclination to increase as the NH_3 chemisorption amount becomes large. These results are reasonable because the adsorbed NH_3 is converted to the NH_2 radical species, which is one of the active species for the photo-SCO, by photo-excitation. Additionally, it was found that the NH_3 chemisorption amount has a good correlation with the specific surface area in Table 1. This result indicated that TiO_2 crystallites exposed the same portion of crystal planes regardless of the difference of preparation methods and the amount of acid sites where NH_3 is adsorbed depends on the surface area of catalyst. Therefore, the photo-SCO activity shows the positive correlation with the surface area in Fig. 2. We suppose that the photo-SCO activity is controlled by the NH_3 chemisorption amount and the amount of acid sites is also an important factor for photo-SCO.

3.4. Correlation between the oxygen anion radical species and the photo-SCO activity

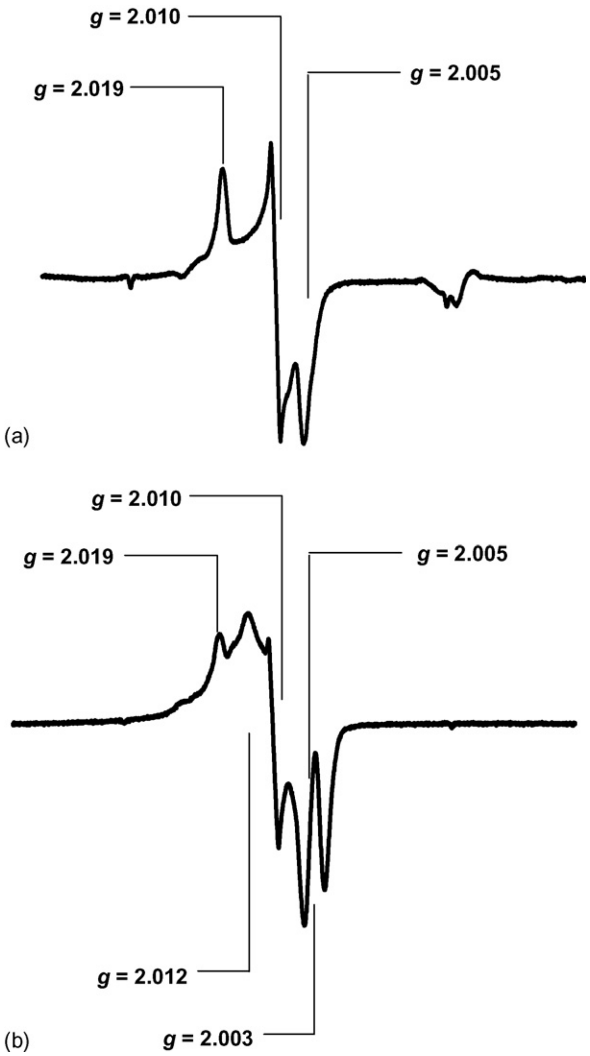

Fig. 6. The difference spectra between the ESR spectra of O_2 introduced: (a) JRC-TIO-3 and (b) JRC-TIO-11 before and after irradiation.

We demonstrated that the O_2^- and O_3^- radicals are generated on TiO_2 by irradiation and these radical species reacts with NH_2 radical. Therefore, it is expected that the photo-SCO activity depends on the oxygen anion radical species products amount as well as the NH_3 chemisorption amount. We determined the amount of the oxygen anion radical species on the basis of the amount of TEMPOL by ESR. Table 1 shows the amount of oxygen anion radical species and the kind of the produced oxygen anion radical species. It is found that O_3^- and O_2^- radicals were generated on anatase TiO_2 or rutile/anatase mixed TiO_2 containing anatase mainly, but only O_2^- radical was generated on rutile single phase. For example, Fig. 6 shows the difference spectra between the ESR spectra of O_2 introduced TiO_2 before and after irradiation. From the difference spectra of JRC-TIO-3 as shown in Fig. 6(a), O_2^- radical ($g = 2.005$, 2.010 and 2.019) was formed. The same results were obtained over JRC-TIO-5, which has mainly a rutile phase with faint fraction of anatase phase, and JRC-TIO-6. On the other hand, O_3^- radical ($g = 2.003$ and 2.012) was generated as well as O_2^- radical ($g = 2.005$, 2.010 and 2.019) over JRC-TIO-11 (Fig. 6(b)). Both O_2^- and O_3^- radicals were formed over anatase or mainly anatase TiO_2. Therefore, it is expected that the photo-SCO activity depends on not only the amount of oxygen anion radical species but also oxygen anion radical species. Fig. 7 shows the effect of the amount of the oxygen anion radical species on the photo-SCO activity at GHSV = 50,000 h^{-1}. JRC-TIO-8, which exhibited the high activity, exhibited the large value of the amount of the oxygen

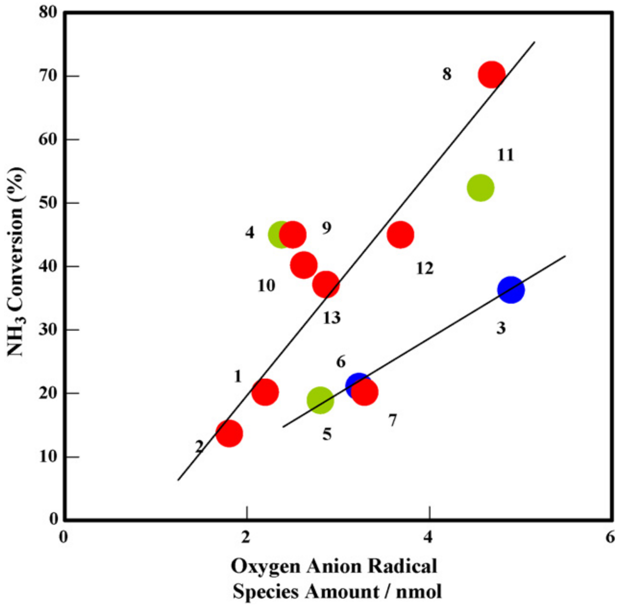

Fig. 7. Effect of the oxygen anion radical species amount on the NH_3 conversion; GHSV: 50,000 h^{-1}; NH_3: 1000 ppm, O_2: 2%. The numbers denotes the catalyst, see Table 1.

anion radical species. On the contrary, low activity JRC-TIO-2 showed the low ability against oxygen anion radical production. In comparison with the activity of JRC-TIO-3, -5 and -6, which had mainly rutile phase, the other TiO_2 having mainly anatase phase exhibited the higher activity. For example, although JRC-TIO-3 showed the largest amount of oxygen anion radical species, the activity of JRC-TIO-3 was lower than that of JRC-TIO-4, -8, -9, -10, -12 and -13. It is suggested that the difference of the activity depends on that of the reactivity between O_2^- and O_3^- radicals, and that O_3^- radical has a higher reactivity than O_2^- radical in the photo-SCO. It is known that O_3^- radical has a highly oxidation ability than O_2^- radical toward organic compounds [25]. This trend is the same for the oxidation of ammonia. In comparison with the surface area and the NH_3 chemisorption amount, the produced oxygen anion radical species amount exhibited the better linear-correlation with the photo-SCO activity. This may be due to the fact that the produced amount of oxygen anion radical species is extremely lower than chemisorption amount of NH_3. The formation of oxygen anion radicals or the association of oxygen anion radicals with the excess NH_2 radicals is presumably the rate-determining step of the photo-SCO.

4. Conclusion

The photo-SCO proceeds over TiO_2 in a conventional fixed bed flow system at atmospheric pressure. JRC-TIO-8 showed the high activity in the JRC-TIO series. The active species of photo-SCO reaction are NH_2 radical and oxygen anion radical species (O_2^- and O_3^- radicals) and the photo-SCO progresses by the reaction of these radicals. The produced species of oxygen anion radical depended on the crystal phase of TiO_2. Rutile TiO_2 generated only O_2^- radicals and anatase TiO_2 formed not only O_2^- radicals but also O_3^- radicals. The photo-SCO activity had a correlation with the amount of NH_3 chemisorption and produced oxygen anion radical species. O_3^- radical exhibited the higher activity than O_2^- radical.

Acknowledgement

This work was supported in a great-in-aid from Japan Ministry of Education, Culture, Sports and Science and from Japan Science and Technology Agency.

References

[1] R. Long, R. Yang, Chem. Commun. (2000) 1651.
[2] M. Yang, C. Wu, C. Zhang, H. He, Catal. Today 90 (2004) 263.
[3] L. Gang, B. Anderson, J. van Grondelle, R. van Santen, Appl. Catal. B: Environ. 40 (2003) 101.
[4] E. Slavinskaya, S. Veniaminov, P. Notte, A. Ivanova, A. Boronin, Y. Chesalov, I. Polukhina, A. Noskov, J. Catal. 222 (2004) 129.
[5] L. Gang, B. Anderson, J. van Grondelle, R. van Santen, Catal. Today 61 (2000) 179.
[6] R. Long, R. Yang, J. Catal. 207 (2002) 158.
[7] W. Kijlstra, D. Brands, E. Poels, A. Bliek, J. Catal. 171 (1997) 208.
[8] L. Gang, J. van Grondelle, B. Anderson, R. van Santen, J. Catal. 186 (1999) 100.
[9] T. Curtin, F. O'Regan, C. Deconinck, N. Knuttle, B. Hodnett, Catal. Today 55 (2000) 189.
[10] N. Sazonova, A. Simakov, T. Nikoro, G. Barannik, V. Lyakhova, V. Zheivot, Z. Ismagilov, H. Veringa, React. Kinet. Catal. Lett. 57 (1996) 71.
[11] F. Dannevang, U.S. Patent, 5, 1996, 137.
[12] K.H. Wang, Y.H. Hsieh, M.Y. Chou, C.Y. Chang, Appl. Catal. B: Environ. 21 (1999) 1.
[13] X.Z. Li, F.B. Li, C.L. Yang, W.K. Ge, J. Photochem. Photobiol. A 141 (2001) 209.
[14] S. Farhadi, M. Afshari, M. Maleki, Z. Babazadeh, Terahedron Lett. 46 (2005) 8483.
[15] T. Tanaka, K. Teramura, K. Arakaki, T. Funabiki, Chem. Commun. (2002) 2742.
[16] K. Teramura, T. Tanaka, T. Funabiki, Chem. Lett. 32 (2003) 1184.
[17] K. Teramura, T. Tanaka, T. Funabiki, Langmuir 19 (2003) 1209.
[18] K. Teramura, T. Tanaka, S. Yamazoe, K. Arakaki, T. Funabiki, Appl. Catal. B: Environ. 53 (2004) 29.
[19] S. Yamazoe, T. Okumura, K. Teramura, T. Tanaka, Catal. Today 266 (2006) 111.
[20] P. Meriaudeau, J.C. Vedrine, J. Chem. Soc. Faraday I 72 (1976) 472.
[21] A.R. Gonzalez-Elipe, G. Munuera, J. Soria, J. Chem. Soc. Faraday I 75 (1979) 748.
[22] N. Cant, J.R. Cole, J. Catal. 134 (1992) 317.
[23] Y. Nakaoka, Y. Nosaka, J. Photochem. Photobiol. A 110 (1997) 299.
[24] H. Einaga, A. Ogata, S. Futamura, T. Ibusuki, Chem. Phys. Lett. 338 (2001) 303.
[25] M. Okumura, J.M. Coronado, J. Soria, M. Haruta, J.C. Conesa, J. Catal. 203 (2001) 168.