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Photo-oxidation of NH_3 over various TiO_2

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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

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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

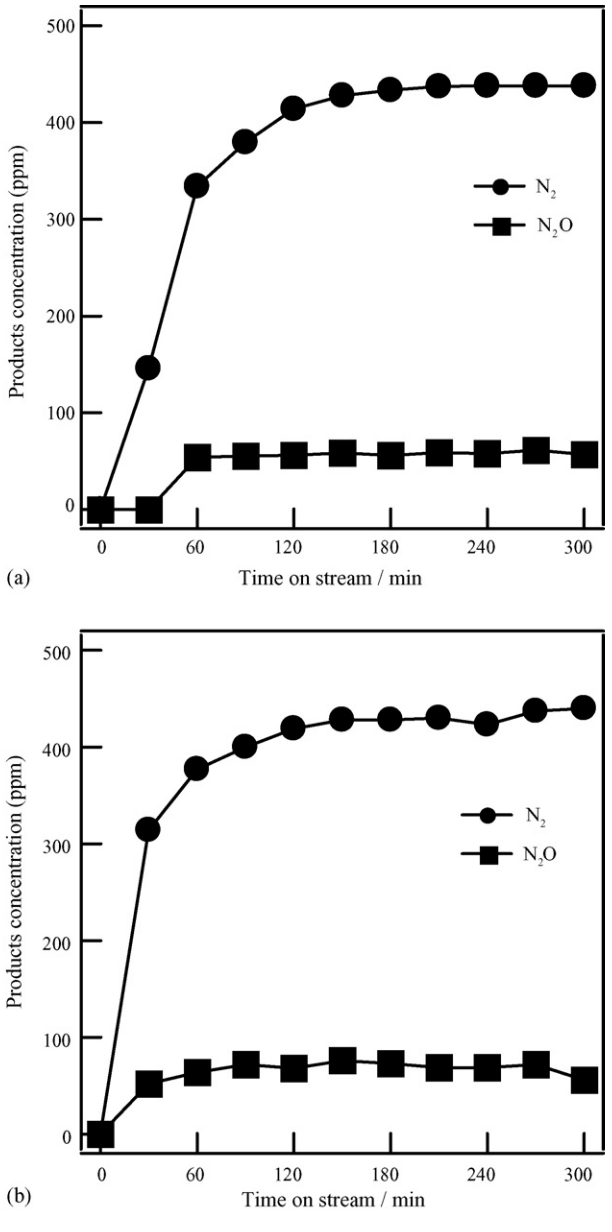

Fig. 1. The time course of photo-SCO: (a) over JRC-TIO-11 at GHSV = 8000 h^{-1} and (b) over JRC-TIO-8 at GHSV = 25,000 h^{-1}; NH_3: 1000 ppm; O_2: 2%. (●) N_2; (■) N_2O.