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The control of valence state: How V/TiO_2 catalyst is hindering the deactivation using the mechanochemical method

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ABSTRACT

Various experiments were conducted to improve durability against SO_2 by impregnating the same amount of vanadium in TiO_2 which had the various physical properties. According to those catalysts, the degree of deactivation by SO_2 had various results, and it was found that the production of unreacted NH_3 in selective catalytic reduction reaction should be low. Based on X-ray photoelectron spectroscopy analysis, O_2 on–off test, O_2 reoxidation test and H_2-temperature programmed reduction experiment, the redox capacity of catalyst was improved due to increasing of non-stoichiometric compounds. Such a non-stoichiometric oxide and redox capacity of catalyst can be enhanced by the ball-milling process, and the production of ammonium sulfate salt can be more easily inhibited by the superior oxidation–reduction capacity of catalyst. We found that this result is caused by producing and increasing of V^{x+} $(x \leq 4)$, Ti^{y+} $(y \leq 3)$ which are non-stoichiometric chemical species of catalyst.

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1. Introduction

Among several technologies proposed for removing nitrogen oxide emitted from stationary sources, the selective catalytic reduction (SCR) process in flue gas treatment (FGT) is recognized to be most desirable in the technological and economic aspect. The keys of this technology are the composition of catalyst, the form of the reactor, operation conditions, etc., but most of researches have been focused on the development of catalyst. Until now, hundreds of catalysts have been proposed from noble metal catalysts to basic metal catalysts, and most of developed catalysts are V_2O_5–WO_3/TiO_2 and zeolite, iron oxide, copper oxide, manganese oxide, etc. [1–3], which are manufactured in the form of honeycomb and plate and operated at high temperature of 300–500 °C.

Particularly because of the durability of catalyst against SO_2 in the SCR process, research has been conducted on various supports, and durability against SO_2 is different according to supports as titania = silica > α-alumina > η-alumina > γ-alumina [4].

Active elements were mostly noble metals in early researches, but according to the results of studies on transition metals such as Co_3O_4, Cu_2O, Fe_2O_3, MnO, NiO, CrO_3 and V_2O_5, activity and selectivity were similar but resistance to SO_x was highest in V_2O_5 [5].

In general, the SCR process in power plants is installed before or after the desulfurization facility. If it is installed before, it causes problems such as the thermal fatigue of catalyst, abrasion by dust and shortening of life by SO_2 poisoning. In most cases, accordingly, a wet or semi-dry flue gas desulfurization process is used in connection to a denitrification process using catalyst for simultaneous treatment of SO_x/NO_x [6]. However, if the SCR process is installed after the desulfurization facility, because the desulfurization process is of wet type, the temperature of exhaust gas decreases rapidly after desulfurization, and in order to obtain the optimal efficiency, an additional source of heat is necessary, which in turn consumes a large amount of energy. In addition, salt such as NH_4NO_3 and NH_4HSO_4 is produced by unreacted NH_3 from the low-temperature region and it corrodes the equipment, shortens the life of catalyst, and lowers the efficiency of denitrification.

In order to prevent this, several attempts have been made to develop low-temperature denitrification catalyst, but few researches have been made on the poisoning of catalyst by SO_2 and catalysts durable against SO_2.

Thus, for an efficient process in the thermodynamic and economic aspect, the present study purposed to explain the SCR reaction characteristic of high-activity denitrification catalyst resistant to SO_2 poisoning at temperature of 250 °C, focused on power plants among stationary sources of emission.

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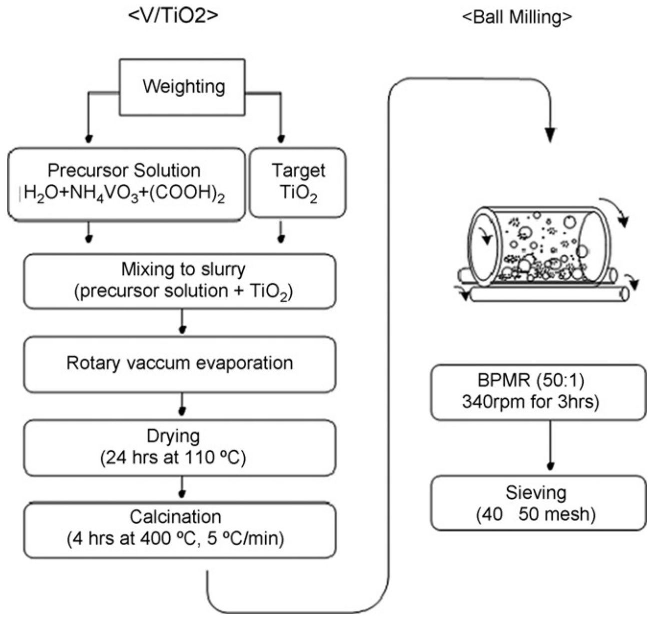

Fig. 1. Flow diagram for the preparation of the catalysts.

For this, based on the results of researches [7] for determining differences in the redox characteristic caused by the existence of non-stoichiometric chemical species $\{V^{x+}$ $(x \leq 4)$, Ti^{y+} $(y \leq 3)\}$ as a method of improving durability against SO_2 in V/TiO_2 catalyst, we inhibited the production of ammonium sulfate salt by improving the oxidation/reduction characteristic of catalyst through non-stoichiometric improvement using ball milling, one of high-energy metal dissolution methods, and by doing so, enhanced the durability of the catalyst against SO_2.

In addition, for examining how denitrification catalyst prepared by this method has increased durability against SO_2 and the reaction characteristic of the catalyst, we conducted reactivity experiments and several physicochemical characteristic analysis using a fixed bed reactor fit for the composition of the actual process.

2. Materials and catalyst preparation

2.1. Wet impregnation method

The catalyst used in this study is one of V_2O_5/TiO_2 line, which was prepared by impregnating vanadium with several commercial TiO_2 supports with different specific surface area and crystal structure. The used TiO_2 supports are largely divided into anatase supports, rutile supports, and supports of the mixture of the two phases. The BET area (m^2/g) alphabetically 92(A), 94(B), 106(C) and 80(D). Each sample that contains W and SO_3 with TiO_2. TiO_2(A) and TiO_2(B) contain 1.2% and 0.4% of SO_3 respectively. TiO_2(B) and TiO_2(C) contain 7.47% and 6.68% of W and 1.9% and 0.4% of SO_3 respectively. Also, TiO_2(C) 4.3% of Si respectively.

The active metal contents impregnated in this study were presented in the form of [ ]. V_2O_5/TiO_2 catalyst can be prepared by the method obtaining from $VOCl_3$ non-aqueous solution, the method dissolving NH_3VO_3 in NH_4OH aqueous solution or hydrochloric acid, or the method dissolving it in distilled water or oxalic acid. The catalyst preparation method used in this study was the last one in particular the wet impregnation method among infiltration methods, and the process is as in Fig. 1.

First, calculate the vanadium content in TiO_2 according to desired composition, and dissolve the calculated amount of ammonium metavanadate [NH_4VO_3; Aldrich Chemical Co.] in distilled water heated up to 60 °C. Because the solubility of NH_4VO_3 is very low, add oxalic acid [$(COOH)_2$; Aldrich Chemical Co.] into the ammonium metavanadate aqueous solution little by little while stirring until pH becomes 2.5. Then the color of the solution turns into bright orange. Then add the calculated amount of TiO_2 to the solution little by little while stirring. Agitate the resultant mixed solution in the slurry state for over 1 h, and evaporate moisture at 70 °C using a rotary vacuum evaporator (Eyela Co. N-N series). After the evaporation of moisture, dry the specimen additionally for 24 h in a 110 °C dry oven, and then heat the specimen in a tubular furnace up to 400 °C at a heating rate of 10 °C/min, and calcine at the temperature in air atmosphere for 4 h.

In case of dry V/TiO_2(D) catalyst, TiO_2 was first heated up to 500 °C at a heating rate of 10 °C/min and calcined at the temperature for 8 h in air atmosphere, and the remain procedure was the same as above.

2.2. Ball-milling method

For enhancing low-temperature SCR activity, this study introduced ball milling in preparing high-activity denitrification catalyst.

In this study, we used 20 mm, 10 mm and 5 mm large balls made of zirconia and 2-L jars through a two-stage ball-milling machine of Samhwajedo Company. The ball power mass ratio (BPMR) was fixed at 50:1 for maximum milling efficiency and the milling speed was 340 rpm.

Dry milling was used for both of the two types above, and the catalyst supporting vanadium was milled and calcined, and the obtained powder was sieved and used in the experiments. The preparation process is as in Fig. 1.

2.3. Catalytic activity measurement

Fig. 2 shows the schematic diagram of the fixed bed reactor used for on–off experiments on the characteristic of denitrification reaction and the effects of moisture and oxygen. The experimental apparatus was composed largely of gas inlet, reactor and reaction gas analyzer. Gas was supplied to the reactor from the cylinders of NO, N_2, O_2 and NH_3, and the flow was controlled using MFC (Mass Flow Controller, MKS Co.). In addition, moisture was supplied through injecting N_2 containing moisture using a bubbler, and in order to maintain the supply rate constant, we circulated water at constant temperature (50 °C) using a circulator outside the bubbler in the form of a double jacket. The gas supply pipe was all stainless steel pipe, and was kept at 180 °C using a heating band in order to prevent the production of salt such as NH_4NO_3 and NH_4NO_2, which may happen from reaction between NO and NH_3, and the condensation of moisture in the reaction gas.

The reactor was continuous-flow-type fixed bed reaction equipment made of a quartz tube 8 mm in inner diameter and 60 cm in height, and the catalytic bed was fixed using quartz wool. The temperature of the reactor was controlled by a PID temperature controller using a K-type thermocouple fixed on the bottom of the fixed bed. In order to measure temperature at the gas inlet, a thermocouple of the same type was installed on the top of the catalytic bed and the difference of temperature before and after the catalytic bed was measured.

The concentration of reactants and products was measured as follows. The concentration of NO was measured with a non-dispersive infrared gas analyzer (Uras 10E, Hartman & Braun Co. and ZKJ-2, Fuji Electric Co.) and the concentration of SO_2 was measured with a chemiluminescent analyzer (43C HL, Thermo Ins.) and a detector tube (5L, 5La, 5M, Gas Tec. Co.). In addition, the

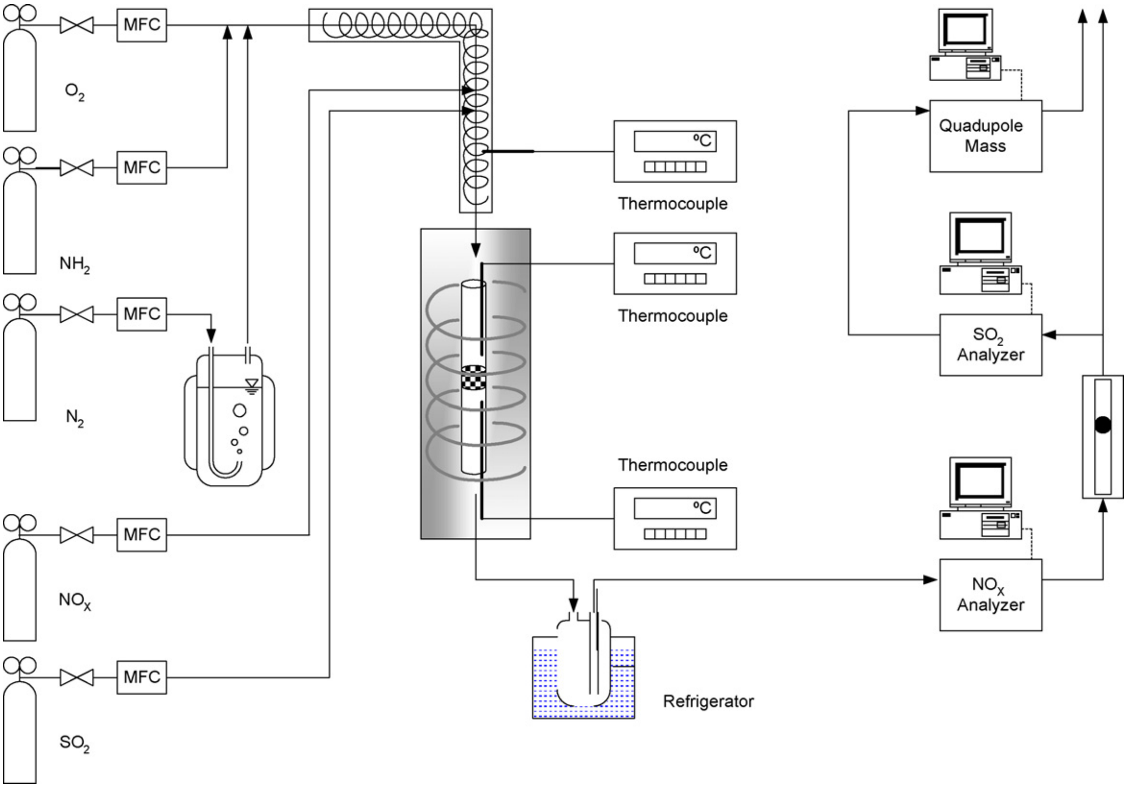

Fig. 2. Schematic diagram of a fixed bed SCR reaction system.

concentration of NO_2 was measured with a detector tube (9L, Gas Tec. Co.) and that of ammonia with a detector tube (3M, 3La, 3L, Gas Tec. Co.). For all gases, moisture was removed using a moisture trap in the chiller before they were supplied to the analyzers.

The reactivity of each catalyst was represented in NO_x conversion rate, and was defined as follows:

$$NO_x\ (\text{conversion, }\%) = \frac{C_{\text{before reaction}}NO_x - C_{\text{after reaction}}NO_x}{C_{\text{before reaction}}NO_x} \times 100 \quad (1)$$

H_2-TPR was performed in order to evaluate the reduction power of the catalysts and TiO_2 supports. After 50 mg of catalyst powdered at particle size below 150 μm was filled, it was heated up to 300 °C at a heating rate of 10 °C/min while 2% O_2/Ar was being dripped at 150 cm^3/min, and then after 3 min maintenance of the temperature for removing moisture from the surface of the catalyst, the catalyst was activated. Then, the specimen was cooled down to 300 °C and absorbed oxygen was removed while N_2 was being dripped at 30 cm^3/min. After the specimen was cooled down to normal temperature (around 30 °C), adsorption/desorption of the catalyst surface was stabilized while 5% H_2/Ar was being dripped at 300 cm^3/min. Then, it was heated up to 900 °C at a heating rate of 10 °C/min while 5% H_2/Ar was being dripped at 300 cm^3/min, and the concentration of H_2 was monitored with TCD. The reference gas of TCD was Ar. In order to prevent moisture from getting into TCD, we supplied the gas after reaction to TCD through a molecular sieve (4A) trap.

In order to analyze the effect of lattice oxygen in the catalysts on activity, we conducted an O_2 on/off experiment. While SCR reaction was going on stably by supplying $NO + NH_3 + O_2$ at constant temperature, the supply of O_2 was stopped, and an hour's stoppage, it was resumed fully and the concentration of NO was monitored. The concentration of NO was measured with URAS 10E, and signals were collected through 812PG A/D converter board.

In order to evaluate the reoxidation power of the catalysts, we conducted an O_2 reoxidation experiment. The filled catalyst was activated with air at 500 cm^3/min at 400 °C for 3 min. The catalyst was reduced with 0.5% NH_3/N_2 at 400 °C for 90 min and then purged with N_2 at 500 cm^3/min. Then, SCR reaction was made at the corresponding temperature under the condition of $NO + NH_3$ without oxygen, and when the reaction was stabilized, 200 ppm O_2/N_2 was supplied continuously from a certain point of time and data on the concentration of NO was collected through URAS 10E.

The specific surface area of the catalysts was measured with ASAP 2010C of Micromeritics Co., and specific surface area was calculated using the BET (Brunauer–Emmett–Teller) equation. Here, each specimen was analyzed after degassed into a vacuum state at 110 °C or 3–5 h.

In order to observe the crystal structure of TiO_2 supports and V/TiO_2 catalysts, we performed XRD analysis, and XRD patterns were analyzed with D/Max-III (3 kW) diffractometer of Rigaku Co. Cu Kα ($\lambda = 0.1506$ nm) was used as a radiation source, and measurement was made in the range of $2\theta = 10$–$90°$ at a scanning rate of 4°/min.

XPS analysis used ESCALAB 210 of VG Scientific, and Al Kα monochromate (1486.6 eV) was used as an excitation source. After moisture contained in the catalysts was removed completely through drying at around 100 °C for 24 h, the catalysts were analyzed without surface sputtering and etching in order to maintain the degree of vacuum of the XPS equipment at 10–12 mmHg. The binding energy and intensity of Ti, V, O and C existing in the specimens were analyzed through wide scanning spectrum.

True density was measured with Pycnometer (Accupyc 2375 model) of Micromeritics Co. True density was calculated by displacing analysis gas He in two chambers of known volume, namely, V sample cell and V expansion cell, based on the ideal gas phase equation and measuring the volume of the specimen using the change of pressure caused by the displacement. After an adequate amount of specimen in the cells, it was preprocessed for 1 h at 105 °C in air atmosphere, and He was applied at around 3–4 psi.

Ion chromatography (IC) was analyzed using DIONEX-120 Automated Dual Column IC. The column was AS4A SC 4 mm, the flow rate was 1 mL/min, the eluent was 1.8 mM Na_2CO_3/1.7 mM $NaHCO_3$, and the anion self-regenerating suppressor was ASRS-I 4 mm.

Inductive Coupled Plasma-Atomic Emission Spectrometer (ICP-AES) was Perkin-Elmer Optima 3000XL. RF power was 1300 W, plasma flow was 15 L/min, coolant flow was 0.5 L/min, and nebulizer flow was 0.8 L/min. In a Teflon bottle, 0.1 g of specimen was decomposed with 2 mL of reagent that mixed HF, HNO_3 and $HClO_4$ at a ratio of 4:4:1, and then diluted with distilled water and analyzed through ICP analysis.

In denitrification experiment, the concentrations of injected gas were 800 ppm/N_2, 500 ppm/N_2 on catalyst which size was 359 μm at 250 °C. NH_3/NO_x ratio was 0.8–1.0, O_2 and H_2O were respectively 3% and 6%, space velocity was 60,000 h^{-1} and total flow was 600 cm^3/min.

3. Result and discussion

3.1. Characteristics of SCR reaction in the presence of SO_2

Catalyst applicable to the SCR process in the presence of SO_2 should be low in SO_2 adsorption power, and should not produce unreacted ammonia by maintaining its reactivity even after SO_2 has reached adsorption/desorption equilibrium in the catalyst.

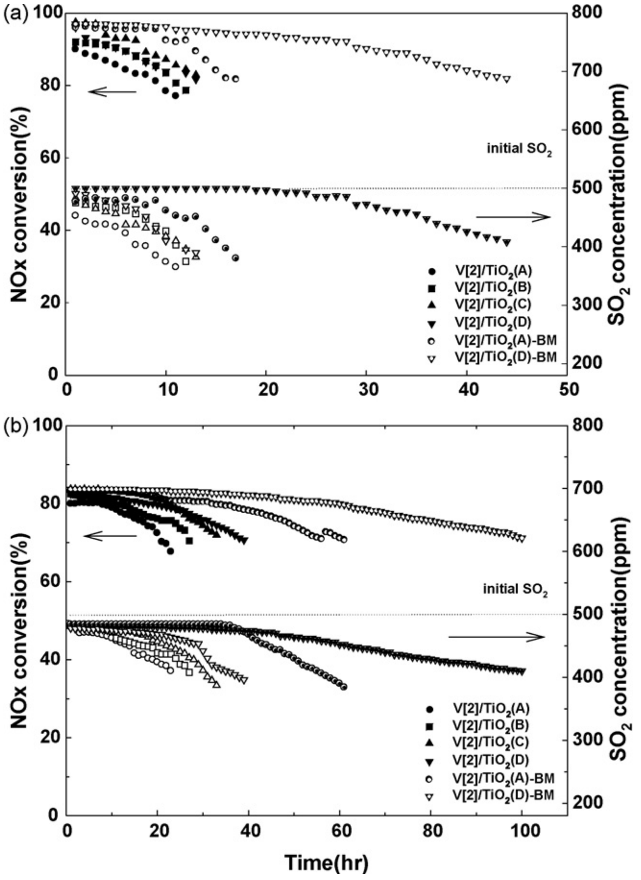

Fig. 3. The effect of SO_2 on NO_x conversion and SO_2 concentration over V[2]/TiO_2 at 250 °C. (a) NH_3/NO_x: 1.0 and (b)NH_3/NO_x: 0.8 (NO: 730 ppm; NO_2: 68 ppm; O_2: 3%, H_2O: 6%; SO_2: 500 ppm; S.V: 60,000 h^{-1}).

Fig. 3(a) shows a SCR long-run test using commercial catalysts at reaction temperature of 250 °C by putting 500 ppm of SO_2 when SCR reaction reached the normal state at space velocity 60,000 h^{-1}, NO_x 800 ppm, NH_3/NO_x mole ratio 1.0, O_2 3% and H_2O 6%.

In case of V[2]/TiO_2(A) catalyst, when SCR reaction reached the normal state at 250 °C, around 50 ppm of NH_3 slip took place, and by the effect of the NH_3 slip, the concentration of SO_2 and NO_x conversion rate showed a rapid decrease after the input of SO_2.

In case of V[2]/TiO_2(B), V[2]/TiO_2(C) and V[2]/TiO_2(D) catalysts, when SCR reaction reached the normal state at 250 °C, around 5–10 ppm of NH_3 slip took place, and the concentration of SO_2 and NO_x conversion rate decreased slowly after 5 h.

In V[2]/TiO_2(D)-BM, however, despite the initial occurrence of 5 ppm of NH_3 slip, durability against SO_2 was superior probably because of the effect of Ball Mill process added to TiO_2(D).

In Fig. 3(b), in order to ignore the effect of NH_3 slip at the beginning of SCR reaction, a SCR long-run experiment was conducted at NH_3/NO_x mole ratio 0.8, a condition where NH_3 slip does not happen in SCR reaction at 250 °C in all the catalysts above.

In all the catalysts, the early NO_x conversion rate decreased to around 80% due to the shortage of NH_3 and durability against SO_2 increased substantially compared to that when NH_3/NO_x mole ratio was 1.0. In the actual process as well, the production of ammonium sulfate salt is inhibited by minimizing NH_3 slip through setting NH_3/NO_x mole ratio to 0.8–0.9.

When NH_3/NO_x mole ratio was 1.0, it was difficult to compare durability against SO_2 among the catalysts because of the effect of NH_3 slip, but when it was 0.8, the catalysts showed different durability against SO_2.

In SCR reaction, unreacted NH_3 is a toxic substance, and at low temperature it forms NH_4NO_3 by being combined with NO_x or forms salt such as NH_4HSO_4 by reacting with SO_2 in exhaust gas, and consequently lowers the activity of the catalyst [8].

Accordingly, in order to achieve durability against SO_2 by inhibiting the formation of ammonium sulfate salt or ammonium bisulfate from unreacted NH_3, most of all, the production of NH_3 slip should be minimized by high NO_x conversion rate at the beginning of SCR reaction.

It was confirmed that durability against SO_2 is different among catalysts, and in order to compare durability against SO_2 among the catalysts, we quantified the degree of deactivation by SO_2 and used it as an index of durability against SO_2.

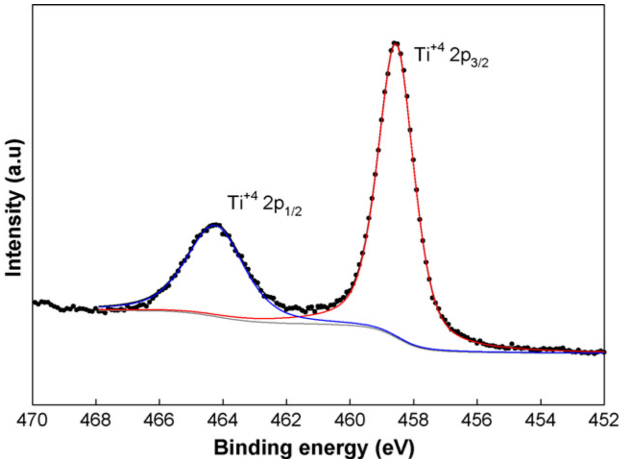

Fig. 4. Ti 2p spectra of TiO_2(B) by XPS spectrum of TiO_2.

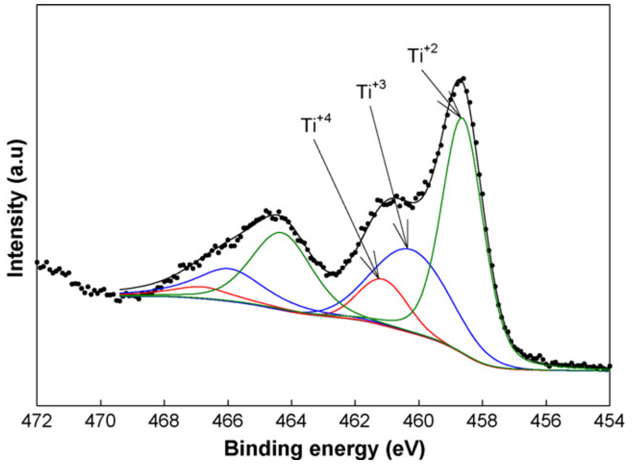

Fig. 5. Ti 2p spectra of V[2]/TiO_2(B) catalyst by XPS spectrum of V/TiO_2.

First, when K_0 was the initial NO_x conversion rate in SCR reaction at 250 °C and K_f was the NO_x conversion rate decreased after the deactivation of catalyst by the input of 500 ppm of SO_2, the SO_2 deactivation index (SDI) was set by calculating time taken until $K_f/K_0 = 0.85$.

That is, catalysts with high durability against SO_2 have a large SDI.

Using the calculated SDI, we compared durability against SO_2 among the catalysts. According to the values which were correlated by SDI, the durability against SO_2 on each catalyst result that 23(SDI) on V[2]/TiO_2[A] catalyst, 27(SDI) on V[2]/TiO_2(B) catalyst, 33(SDI) on V[2]/TiO_2(C) and 39(SDI) on V[2]/TiO_2(D) catalyst, and the experiments condition was of 0.8 NH_3/NO_x ratio.

Compare SDI values with those results were dramatically increased as 56(SDI) on V[2]/TiO_2(A)-BM catalyst and 100(SDI) on V[2]/TiO_2(D)-BM catalyst which were applied by ball-milling treatment.

3.2. Non-stoichiometric oxides and durability against SO_2 of catalysts

To understanding the relation of non-stoichiometric oxide and against SO_2 about catalysts, XPS analysis was applied.

Fig. 4 is Ti 2p peak of TiO_2 B. In XPS analysis, Ti 2p spectra are divided into Ti $2p_{3/2}$ and Ti $2p_{1/2}$ by spin–obit interaction, and this is the same for V 2p.

The peak appearing at around 458.8 eV is quadrivalent Ti $2p_{3/2}$ peak, and the peak appearing at around 464.5 eV is quadrivalent Ti $2p_{1/2}$ peak. As in the figure, TiO_2 support has only Ti^{4+}, and other TiO_2 also have only Ti^{4+}.

Fig. 5 is the Ti 2p peak of catalyst that impregnated vanadium 2 wt% with TiO_2(B), it is totally different from the Ti 2p peak of TiO_2 alone, meaning that there is a different kind of titanium besides Ti^{4+}. That is, the peak appearing at binding energy lower than Ti^{4+} is an atom with high oxidation value such as Ti^{3+} and Ti^{2+}. By Gaussian–Lorentzian curve fitting, it was applied to the peak of Ti^{3+} and Ti^{2+} besides Ti^{4+}.

When the peak of non-stoichiometric Ti such as Ti^{3+} and Ti^{2+} is applied, it is almost coincident with the original value (dot line) obtained from XPS analysis. Accordingly, as vanadium is impregnated with TiO_2 support, TiO_2 is reduced differently from its original surface characteristic, showing that there are various oxidation values.

Fig. 6 shows the result of XPS analysis for vanadium impregnated with TiO_2. The peak of V 2p appears adjacent to O 1s peak. For this reason, the satellite line, which is an auxiliary peak of O 1s, appears at around 519.77 eV. V 2p peak appears adjacent to the satellite line, and in general, V^{5+} is known to appear at 516.4–517.0 eV, V^{4+} at 515.7–516.2 eV, and V^{3+} at 515.2–515.7 eV [9].

Because the shift of the central point of the V 2p line toward high binding energy means the oxidation of vanadium [10], non-stoichiometric vanadium shows lower binding energy like titanium above. As to the existence of high oxidation value, when the V $2p_{3/2}$ peak is not symmetric but has lower binding energy the vanadium is considered to contain trivalent or quadrivalent vanadium [11]. When curve fitting was applied to results of XPS analysis by the same method as Ti 2p, the results were almost coincident. The V 2p peak of V[2]/TiO_2(B) catalyst is a typical form observed in other catalysts as well.

According to previous research, V/TiO_2-line catalysts are known to be in the form that V_2O_5 is impregnated with TiO_2 support. However, V 2p peak in this study showed the existence of V^{4+} and V^{3+} besides V^{5+}. This supports Lee et al.'s [12] opinion that when vanadium is impregnated with TiO_2 support TiO_2 and vanadium are formed non-stoichiometrically. That is, vanadium has a stable pentavalent oxidation value, but it forms V^{3+} through oxygen combination, and it is known that activation energy was much lower in vanadia containing V^{3+} than vanadia where V^{5+} is dominant [13]. Paganini et al. [14] reported that V^{4+} was confirmed by EPR and V^{4+} was formed first in the first layer of TiO_2 surface.

Non-stoichiometric V^{4+} or V^{3+} can be expressed in V^{x+} ($x \leq 4$). V^{x+} ($x \leq 4$) is unstable and highly active compared to stoichiometrically stabilized V^{5+}. That is, V^{x+} ($x \leq 4$) is in a reduced state compared to V^{5+}, and therefore V^{4+} has one extra electron and V^{3+} two extra electrons. As these extra electrons do not have a constraint in the atom, they can work as free electrons with high activity. At low temperature, these free electrons exist at a delocalized orbital and have high reactivity, and therefore they can be easily transferred by low activation energy. That is, vanadium oxide fills a part of d-orbital, the outermost orbital, and depending on d-orbital, its electromagnetic, magnetic and catalyst properties are different. After all, electros in the catalyst of non-stoichiometric vanadium can be actuated by low activation energy. That is, if the form of catalyst surface is incomplete, the incomplete sites function as donors or acceptors locally on the surface [13], and activity goes up for stabilization. Accordingly, we can say that activity is high in catalysts containing V^{x+} ($x \leq 4$) with free electrons [15]. As this tendency is applicable to SO_2 oxidation, the high oxidation value of active sites is advantageous to the oxidation reaction [16].

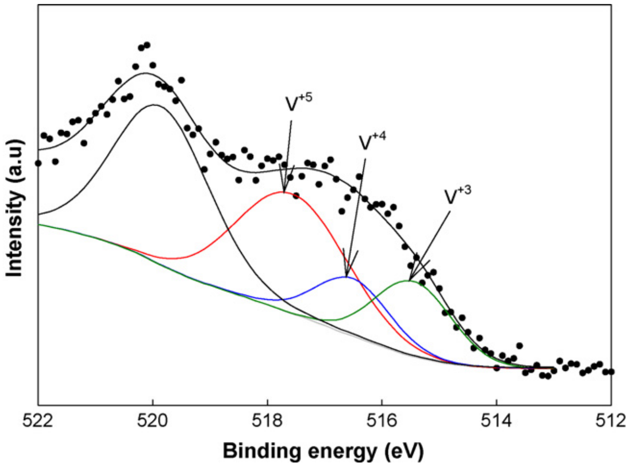

Fig. 6. V 2p spectra of V[2]/TiO_2(B) catalyst by XPS spectrum of V/TiO_2.

In addition, as in XPS analysis, binding energy is lower in V^{4+} than in V^{5+} and in V^{3+} than in V^{4+}. This also means the possibility of actuation by low activation energy.

In all the catalysts applied in this study, V^{4+} and V^{3+} were found, and even V^{2+} was found in some of them. Thus, we calculated the number of electrons per unit volume in V^{4+} and V^{3+} by the equation as $n = I/S$ and compared it with durability against SO_2 where n is the number of electrons per unit volume and its unit is atoms/cm^3, and I is the number of characteristic photoelectrons obtained per second for a photoelectron peak from an atom and is the area of the photoelectron peak of elements obtained from XPS analysis. In addition, S is an atomic sensitivity constant that can be determined experimentally.

According to Cho [7], the existence of non-stoichiometric vanadium makes the flow of electrons in catalyst very active, and the activated electrons facilitate oxidation/reduction in SCR reaction. As a result, the catalyst can have electron exchange reaction with reactants smoothly. The reaction appears as the reduction and oxidation of oxygen in the catalyst. That is, the catalyst repeats oxidation and reduction by oxygen, and this process facilitates the flow of internal electrons of the catalyst by non-stoichiometric vanadium.

Because the decomposition of ammonium sulfate salt such as ammonium sulfate ($(NH_4)_2SO_4$) and ammonium bisulfate (NH_4HSO_4) is also oxidation, it is believed that the increase of non-stoichiometric oxide facilitates oxidation in SCR reaction and can inhibit the production of ammonium sulfate salt.

The graph in Fig. 7(a) shows the relation between the number of atoms of V^{4+} and V^{3+} and durability against SO_2. With the increase of non-stoichiometric vanadium such as V^{4+} and V^{3+}, durability against SO_2 increased linearly.

Durability against SO_2 is affected not just by the number of atoms of non-stoichiometric vanadium. The composition of non-stoichiometric compounds in catalyst is found also in Ti. Fig. 7(b) shows the number of electrons per unit volume in non-stoichiometric Ti of Ti^{3+} and Ti^{2+}. With the increase of non-stoichiometric oxide such as Ti^{3+} and Ti^{2+}, durability against SO_2 also increased exponentially.

This tendency is more obvious when it is compared with durability against SO_2 at NH_3/NO_x mole ratio = 0.8 without the effect of NH_3 slip as in Fig. 8.

3.3. *Lattice oxygen of catalysts and durability against SO_2*

It has been reported that oxygen linking the support and vanadium in SCR reaction is the active species of SCR, and because oxygen is directly linked to the support, further research is necessary for this. Thus, in order to examine the behavior of lattice oxygen in catalysts, we performed O_2 on–off experiment with each catalyst at 250 °C and presented the results in Fig. 9. In the experiment, we measured the NO_x conversion rate over time when oxygen supply was stopped suddenly during normal SCR reaction at space velocity 20,000 h^{-1} and O_2 3%, and observed the restoration of the NO_x conversion rate when oxygen supply was resumed after an hour. Before the stoppage of oxygen supply at reaction temperature of 250 °C, the NO_x conversion rate was close to 100%, but with the stoppage of oxygen supply the rate decreased rapidly. Then, the NO_x conversion rate became constant for around 3–10 min depending on catalyst and again decreased exponentially. When atmospheric oxygen was supplied again after an hour, the NO_x conversion rate restored the original efficiency rapidly.

Accordingly, the segment in the middle after O_2 off that maintained activity is considered that the activity was maintained temporarily by lattice oxygen participating in the reaction of the catalysts, and the segment was longest in V[2]/TiO_2(D)-BM catalyst, which showed the highest durability against SO_2, and shortest in V[2]/TiO_2(A) catalyst, which showed the lowest durability against SO_2.

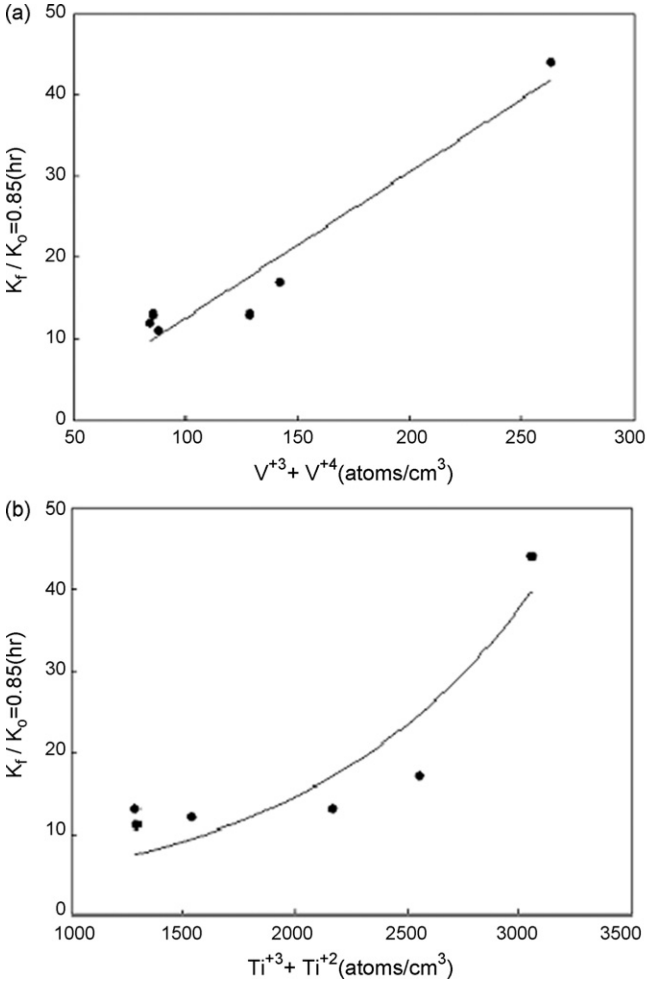

Fig. 7. The effect of the amount of non-stoichiometric vanadium and titanium atoms in unit volume on $K_f/K_0 = 0.85$ over V[2]/titania catalysts at 250 °C. (a) Vanadium species and (b)titanium species (NH_3/NO_x: 1.0; NO: 730 ppm; NO_2: 68 ppm; O_2: 3%; H_2O: 6%; SO_2: 500 ppm; S.V: 60,000 h^{-1}).

Fig. 10 compares the relation between the quantity of lattice oxygen and durability against SO_2. With the increase of the quantity of lattice oxygen participating in reaction, durability against SO_2 also increased, and the increase of the quantity of lattice oxygen increased non-stoichiometric oxide through the BM process, and consequently activated the flow of electrons in the catalyst and increased the oxidation/reduction characteristic. Thus, it is believed that the superior redox capacity facilitates the oxidative decomposition of ammonium sulfate salt and consequently inhibits the production of ammonium sulfate salt.

Because the participation of lattice oxygen in catalyst means the reduction power of the catalyst, in order to examine the effect, we performed an H_2-TPR experiment on the catalysts above.

Fig. 11 shows the results of H_2-TPR experiment on TiO_2(A) support and crystallite V_2O_5 not impregnated with catalyst. Crystallite V_2O_5 began to be reduced from around 500 °C and showed the maximum reduction power at 600–750 °C.

According to Kim et al. [17], the peaks of V_2O_5 appearing at 650 °C are sharp peaks showing the reduction of $V_2O_5 \rightarrow V_6O_{13}$ and the reduction of $V_6O_{13} \rightarrow V_2O_4$. On the contrary, as in Fig. 11(b),

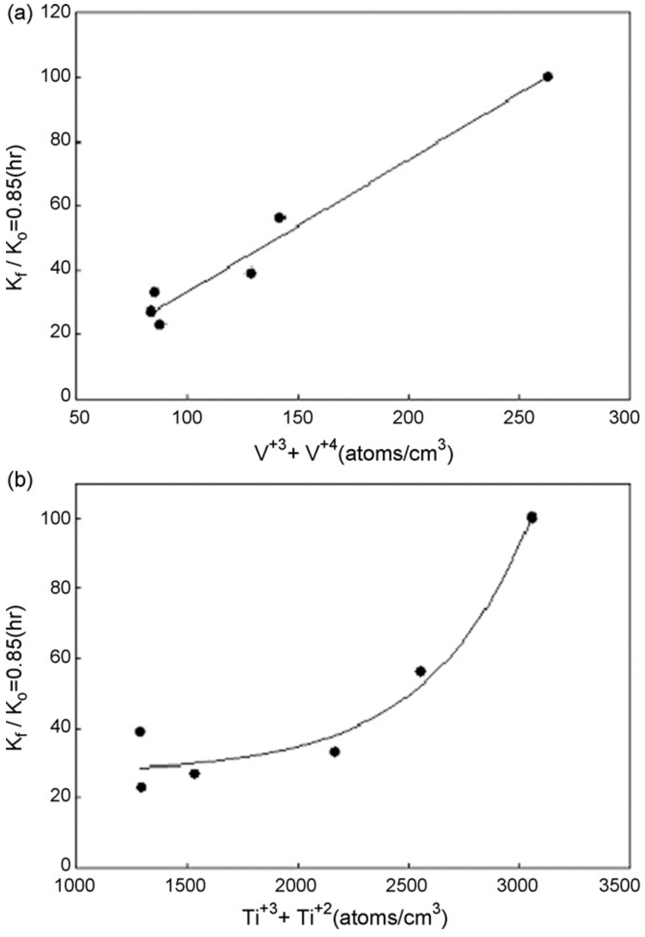

Fig. 8. The effect of the amount of non-stoichiometric vanadium atoms in unit volume on $K_f/K_0 = 0.85$ over V[2]/titania catalysts at 250 °C. (a) Vanadium species and (b)titanium species (NH_3/NO_x: 0.8; NO: 730 ppm; NO_2: 68 ppm; O_2: 3%; H_2O: 6%; SO_2: 500 ppm; S.V: 60,000 h^{-1}).

TiO_2(A) began to be reduced at around 400 °C and showed the maximum reduction power at 550–650 °C. That is, V_2O_5 and TiO_2 support have a different reduction characteristic depending on the bonding structure of oxygen, and the temperature at which the catalyst is reduced by hydrogen and the maximum reduction temperature indicate the reduction power of the catalyst. Accordingly, considering that the temperature at when TiO_2 support begins to be reduced and the maximum reduction temperature are lower than crystallite V_2O_5, we can say that reduction power is increased because the existence of oxygen by the covalent bond with vanadium and titanium enhances the affinity of oxygen to hydrogen rather than because of the bonding structure of vanadium and

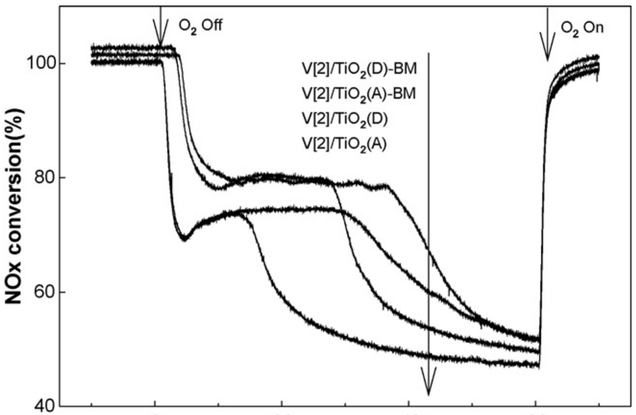

Fig. 9. The decline of NO_x conversion with time after shut-off O_2 over V[2]/TiO_2 (NH_3/NO_x: 1.0; NO: 730 ppm; NO_2: 68 ppm; O_2: 3%; S.V: 60,000 h^{-1}).

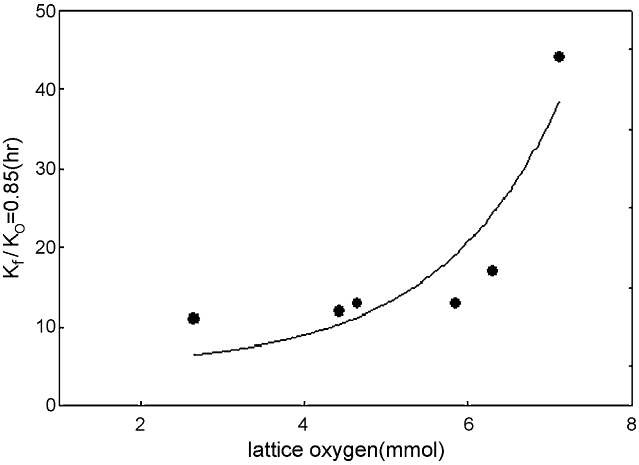

Fig. 10. The effect of the amount of lattice oxygen in unit volume on $K_f/K_0 = 0.85$ over V[2]/titania catalysts at 250 °C (NH_3/NO_x: 1.0; NO: 730 ppm; NO_2: 68 ppm; O_2: 3%; H_2O: 6%; SO_2: 500 ppm; S.V: 60,000 h^{-1}).

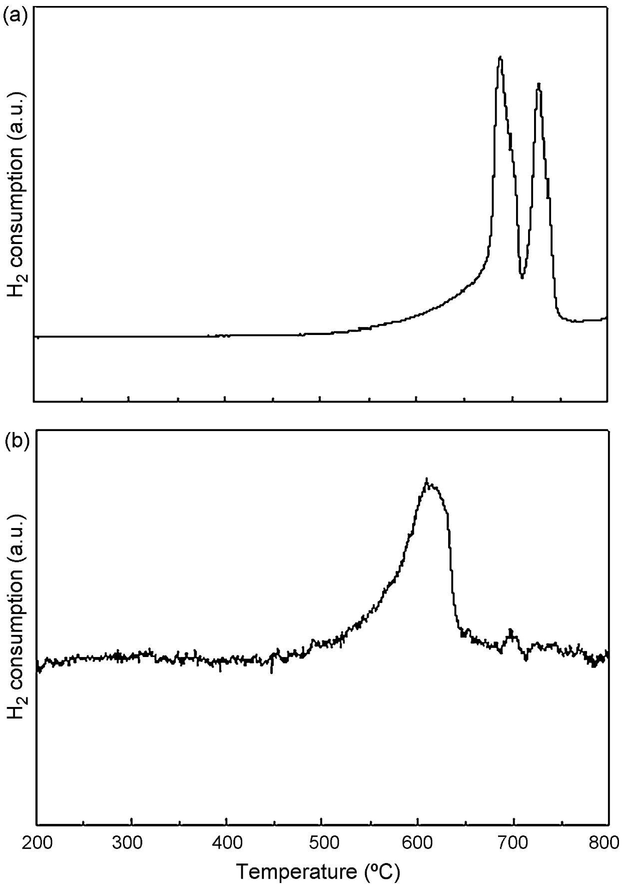

Fig. 11. H_2-TPR profiles of the (a) crystallite V_2O_5 and (b) TiO_2(A) support. Experimental conditions: 50 mg cat, pretreatment at 300 °C for 30 min with 2% O_2/Ar 150 cm^3/min, 5% H_2/Ar 300 cm^3/min reduction with heating rate 10 °C/min, total flow rate 150 cm^3/min.

oxygen. For this reason, SCR activity is higher in catalysts of vanadium impregnated with support than with TiO_2.

Fig. 12 shows the results of H_2-TPR experiment on V[2]/TiO_2(A) catalyst and ball-milled V[2]/TiO_2(A) catalyst. Due to the reduction characteristic of TiO_2 support, the catalysts showed the maximum reduction with the start of reduction at low temperature, and when the TPR peaks of the raw catalyst and BM catalyst were compared, the BM catalyst showed the lower maximum reduction temperature, which means the increase of reduction power in the BM catalyst. The increase of the reduction power of catalyst means the participation of lattice oxygen in reaction, and the increase of lattice oxygen is believed to work as a cause increasing durability against SO_2.

3.4. Reoxidation characteristic of catalysts and durability against SO_2

SCR reaction in catalyst is a composite reactive system involving not only the adsorption, desorption and reduction of reactants but also their oxidation. The oxidation of catalyst is a process that the reduced catalyst receives atmospheric oxygen. In the dual ERLH model, it is the stage that reduced vanadium is restored to Lewis acid sites by receiving atmospheric oxygen or lattice oxygen of TiO_2. Moreover, in this stage, TiO_2, which provided lattice oxygen to vanadium, forms lattice oxygen by receiving atmospheric oxygen.

In order to measure the oxidizing power of catalyst by atmospheric oxygen, we conducted O_2 reoxidation experiment on V[2]/TiO_2(A) and V[2]/TiO_2(D) catalysts and ball-milled V[2]/TiO_2(A) and V[2]/TiO_2(D) catalysts, and presented the results in Fig. 13. In the experiment, we reduced catalyst using NH_3, supplied 200 ppm of O_2, and measured the degree of reoxidation of the catalyst. To distinguish the change of redox capacity, this experiment was performed at space velocity of 120,000 h^{-1}. In Fig. 13, the activity is low before the supply of atmospheric oxygen, but all the catalysts maintain reactivity of around 20–30%. This means that, for the same reason as that in the results of the O_2 on/off experiment, SCR reaction is being made in the state without atmospheric oxygen and lattice oxygen. In the condition, the degree of restoration of the initial activity is different according to the oxidizing power of the catalyst, namely, the exhaustion of lattice oxygen by the reduction of the catalyst, which determines the degree of receiving atmospheric oxygen supplied. This can be explained by Lee's [8] report that SCR reaction has the cycle that the lattice oxygen of vanadia participates in the reaction and is reduced and then the vanadia is reoxidized by receiving oxygen from TiO_2, and the reoxidation power is highly affected by the characteristic of TiO_2 support.

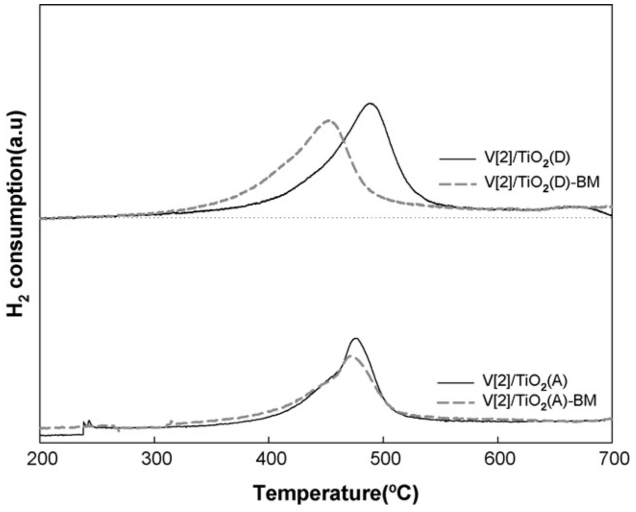

Fig. 12. H_2-TPR profiles of the V[2]/TiO_2(A) and V[2]/TiO_2(A)-BM catalysts. Experimental conditions: 50 mg cat, pretreatment at 300 °C for 30 min with 2% O_2/Ar 150 cm^3/min, 5% H_2/Ar 300 cm^3/min reduction with heating rate 10 °C/min, total flow rate 150 cm^3/min.

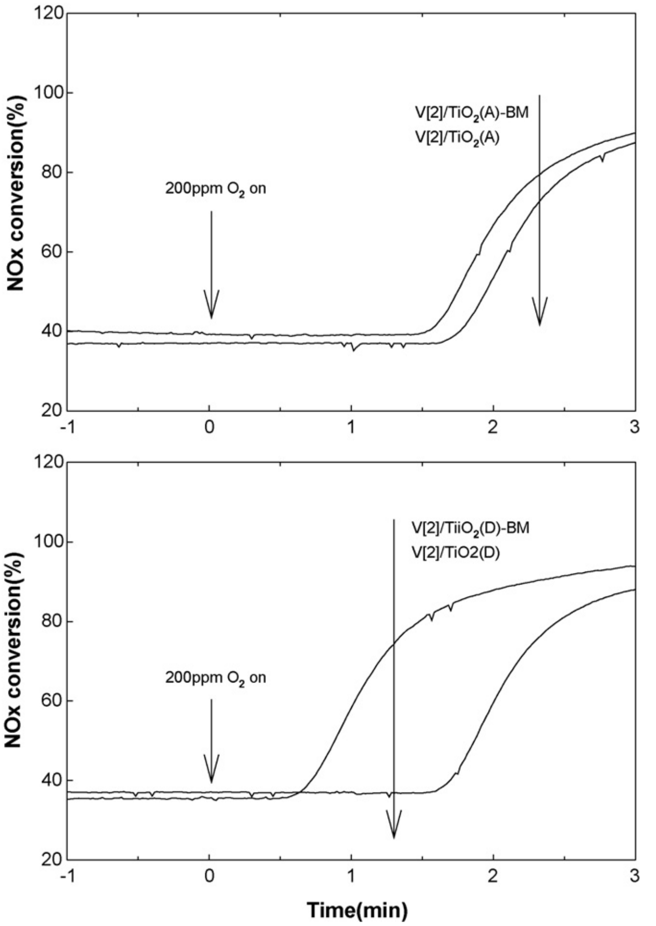

Fig. 13. The change of NO_x conversion by the reoxidation of V[2]/TiO_2 catalysts at 250 °C (NH_3/NO_x: 1.0; NO: 730 ppm; NO_2: 68 ppm; O_2: 200 ppm; S.V: 120,000 h^{-1}).

For both V[2]/TiO_2(A) and V[2]/TiO_2(D) catalysts, ball milled ones received oxygen more promptly, so they were superior in reoxidation power. V[2]/TiO_2(D)-BM, which was most durable against SO_2, was far superior to other catalysts in reoxidation power. As explained in the previous section, this increases non-stoichiometric oxide through the BM process, which in turn activate the flow of electrons in the catalyst and increases the oxidation/reduction characteristic. Thus, it is believed that the superior redox capacity facilitates the oxidative decomposition of ammonium sulfate salt and consequently inhibits the production of ammonium sulfate salt.

4. Conclusions

The present study conducted reactivity experiments and several physicochemical property analysis using a fixed bed reactor fit for the actual process in order to improve durability against SO_2 based on the properties of V/TiO_2 catalyst by the high-energy metal dissolution method using ball milling and to explain the causes of the improvement, and drew conclusions as follows:

(1) The decrease of durability against SO_2 resulting from the deactivation of catalyst by SO_2 is different according to catalyst, and for high durability against SO_2, most of all, the production of NH_3 slip should be minimized through a high NO_x conversion rate at the beginning of SCR reaction.
(2) Through XPS analysis, it was found that non-stoichiometric oxide of impregnated vanadium catalyst increases, and the increase of non-stoichiometric oxide can inhibit the production of ammonium sulfate salt by facilitating oxidation in SCR reaction.
(3) It was confirmed that with the increase of the quantity of lattice oxygen and reduction power of catalyst durability against SO_2 is improved. This shows that the durability of catalyst increases by the redox capacity of the catalyst.
(4) Non-stoichiometric oxide in catalyst and the redox capacity of the catalyst can be enhanced by the ball-milling process. As to the cause of the increase in durability against SO_2, the dissolution of active elements through high-energy treatment of catalyst produces free electrons with high reactivity and activates the flow of electrons in the catalyst and consequently the activated electrons increase the oxidation/reduction characteristic on the surface of the catalyst. The superior redox capacity oxidizes ammonium sulfate salt more easily and inhibits the production of ammonium sulfate salt. We found that this was caused by the formation and increase of non-stoichiometric chemical species V^{x+} ($x \leq 4$) and Ti^{y+} ($y \leq 3$).

Acknowledgement

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