



The influence of non-stoichiometric species of V/TiO₂ catalysts on selective catalytic reduction at low temperature

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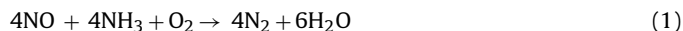
ABSTRACT

The removal efficiency of nitrogen oxides (NO_x) at low temperature depends on the titania support. This phenomenon was found in laboratory scale experiments using various catalysts which have different properties of titania supports. In order to identify the factors that affect the selective catalytic reduction (SCR) activity at low temperature, the physicochemical properties of titania support such as surface area, particle size, crystal phase, crystallinity, impurities and the vanadium compound structures of catalysts were analyzed and compared with NO_x removal efficiency at low temperature. Although those properties could be important in catalytic activity, no direct relationship between those properties and NO_x removal efficiencies at low temperature could be revealed. Because SCR depends on a redox reaction, electron transfer can participate in the reaction. Using X-ray photoelectron spectroscopy (XPS) method to analyze the electronic state of the catalysts, it was found that V/TiO₂ catalysts contain not only Ti⁴⁺ but also Ti³⁺ and Ti²⁺ called non-stoichiometric Ti^{y+} ($y \leq 3$), while the vanadium-free titania support consists of only Ti⁴⁺. Moreover V has various valence states such as V⁵⁺ and V^{x+} ($x \leq 4$), which contains V⁴⁺, V³⁺, etc. The SCR catalytic activity increases with increasing the amount of non-stoichiometric species per unit volume. Those non-stoichiometric species are more active than the stoichiometric species such as V⁵⁺ and Ti⁴⁺ due to their metastable properties. Therefore, the main factor affecting the low temperature SCR is the presence of non-stoichiometric species of catalysts and their amount per unit volume.

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1. Introduction

Stationary facilities like thermal power plants and mobile sources like automobiles use energy from burning fossil fuel with air and at the same time produce various pollutants including carbon dioxide (CO₂), nitrogen oxides (NO_x) and sulfur oxide. Of them, NO_x is known to have fatal impacts not only on the environment but also on human health. The most common method of removing NO_x is selective catalytic reduction (SCR) using ammonia (NH₃) as reductant over V/TiO₂ as catalyst. The main reactions of the method are as follows:



In general, the optimal activation temperature of V/TiO₂ catalyst is relatively high being around 300–400 °C. However, the temperature of the exhaust gas passing the system where SCR facility can be

installed in processing pollutants from thermal power plants, incinerators, etc. is often lower than the optimal temperature region. Some incinerators require SCR at 180–250 °C, but if a SCR unit with a high optimal operating temperature is operated in a low temperature region, NO_x removal efficiency will be low. In addition, SCR is sometimes installed upstream of flue gas desulfurization (FGD) in consideration of the poisoning of V/TiO₂ catalyst by SO₂ and the life time of the catalyst, but as FGD is usually a wet type process, the temperature of exhaust gas drops sharply through the process. In such a case, a reheating system is required to raise NO_x removal efficiency. To raise the temperature of exhaust gas by 100 °C through reheating, a huge amount of energy is required, which would consume 2–5% of power generated by the thermal power plant. In order to solve this problem, an SCR catalyst with high reactivity at low temperature, preferably below 250 °C, is needed.

Research has been continued in various aspects to increase the activity of V/TiO₂ catalyst both at low and high temperature regions. It is already known that the activity is affected by the structure of vanadium oxide (polymeric/monomeric/crystallite) on TiO₂ support [1], the V layer [2], the crystal phase of TiO₂ [3–5], secondary metals [6], etc., and it has been reported that the electric conductivity of V/TiO₂ catalyst affects the SCR activity [7]. That is,

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Table 1
Physicochemical properties of 15 kinds of TiO₂ supports.

TiO ₂ support	NOx conversion at 200 °C of V/TiO ₂ catalyst (%)	Specific surface area (m ² /g)	Particle size (nm)	W (wt.%)	Ratio of anatase:rutile
TiO ₂ (A)	65.6	73	23	4.48	100:0
TiO ₂ (B)	49.9	94	22	8.65	100:0
TiO ₂ (C)	49.4	54	34	0.21	100:0
TiO ₂ (D)	48.4	51	33	0.00	74:26
TiO ₂ (E)	40.4	63	27	0.20	100:0
TiO ₂ (F)	37.7	84	29	0.00	100:0
TiO ₂ (G)	37.2	92	24	0.10	100:0
TiO ₂ (H)	35.2	95	16	0.00	100:0
TiO ₂ (I)	33.9	97	21	0.00	100:0
TiO ₂ (J)	25.7	66	15	0.00	0:100
TiO ₂ (K)	24.0	10	63	4.46	100:0
TiO ₂ (L)	22.7	193	15	0.00	100:0
TiO ₂ (M)	22.4	4	55	0.00	4:96
TiO ₂ (N)	21.9	13	54	0.00	98:2
TiO ₂ (O)	16.2	134	15	0.00	100:0

SCR reaction can be explained with electron transfer. The present study attempted to explain SCR reaction with oxidation/reduction through electron transfer. The increase of SCR activity can be related to the redox properties. Arfaoui et al. [8] reported that a good balance between redox and acidic sites led to an excellent catalyst for SCR [8]. According to Lee et al. [9], NOx removal efficiency is high at low temperature when the oxidation state of V in V/TiO₂ catalyst includes non-stoichiometric valence states in addition to 5+. This study examines the formation, main properties and roles of non-stoichiometric species as well as their relation with NOx removal rate at low temperature.

2. Experimental method and analysis

2.1. Catalyst preparation and characterization

Various catalysts supported on TiO₂ with different physical properties were prepared. The 15 kinds of commercially available TiO₂ were used. Their physical properties are listed in Table 1.

The preparation of V/TiO₂ catalysts was as follows: the required amount of ammonium metavanadate (AMV) corresponding to 2 wt.% V on TiO₂ was dissolved in heated distilled water. In order to increase the solubility of AMV, oxalic acid was added little by little while stirring until pH became 2.5. A slurry was made by adding TiO₂ to the solution little by little while stirring. After 1 h, water was evaporated under vacuum of 65 cm Hg at 70 °C using a rotary evaporator. The material was further dried at 110 °C in an oven for 24 h, and then air calcined in a tubular furnace at 400 °C. The temperature was raised at a rate of 10 °C/min, and kept at 400 °C for 4 h.

2.2. Experimental set-up

The experimental set-up was composed of gas injection port, reactor, and reaction gas analyzer. Gases supplied to the reactor were NO, N₂, O₂ and NH₃, and their flow rate was controlled using mass flow controllers. In order to supply moisture to the reactor, we made N₂-containing moisture through a bubbler, and in order to maintain the supply constant we circulated water at specific temperature outside the double-jacket-type bubbler using a circulator. The gas pipe was made of stainless steel, and its temperature was kept at 180 °C constantly to prevent the formation of salt such as NH₄NO₃ and NH₄NO₂ from reaction between NO and NH₃ and to prevent the condensation of moisture contained in the reaction gas. The reactor was a continuous-flow type fixed-bed reactor made of a quartz tube 8 mm in inner diameter and 60 cm in height, and quartz wool was used to fix the catalytic bed. The temperature of the reac-

tor was controlled with a PID temperature controller using a K-type thermocouple fixed on the upper part of the fixed bed, and a thermocouple of the same type was fixed on the bottom of the catalytic bed to measure the temperature of the gas injection port and to examine difference in temperature between that before and after the catalytic bed. To measure the concentration of the reactants and products, we used a NDIR type gas analyzer for NO, and used a detector tube at the outlet port of the main reactor for NO₂ and NH₃.

2.3. Experimental procedures

To avoid the impact of pressure drop, the catalyst was crushed into 300–425 μm granules, and filled 0.5 mL of it in a quartz tube. The catalyst was activated at 400 °C in air atmosphere for 1 h, then cooled down to the desired experiment temperature. When the experiment temperature has reached the stationary state, a flow of simulated gas was supplied to the reactor, and reaction took place until the concentration of the product has become constant.

The SCR experiment was conducted at space velocity (SV) of 60,000 h⁻¹, NO and NO₂ concentrations of 766 and 36 ppm, respectively, O₂ concentration of 3%, moisture concentration of 6% and NH₃/NOx mole ratio of 1.0. The experiment temperature was 150–450 °C.

3. Results and discussions

3.1. SCR activity in the low temperature region

TiO₂ as a support of SCR catalyst may have different physical properties depending on manufacturing method and the contents of impurities and additives. Thus, even if V/TiO₂ catalysts are prepared by the same method, SCR activity may appear different. Thus, in order to examine such characteristics, we prepared catalysts using 15 kinds of TiO₂ with different physical properties by the same method, and conducted SCR experiment. To compare the effect of TiO₂ support, we also used unsupported V₂O₅.

As in Fig. 1, all the catalysts except V/TiO₂(K), V/TiO₂(L), V/TiO₂(M), V/TiO₂(N) and V/TiO₂(O) showed high NOx removal efficiency at high temperature over 300 °C. V/TiO₂(A) to V/TiO₂(I) catalysts showed relatively high performance not only at high temperature but also at low temperature below 250 °C. This means that, at low temperature, catalyst activity depends on TiO₂ supports. It is believed that TiO₂ of catalysts showing lower activity than bulk V₂O₅ play a role only as a support. On the contrary, in catalysts with higher activity than bulk V₂O₅, V oxide is considered to interact with TiO₂. That is, monolayer vanadia formed on TiO₂ support is

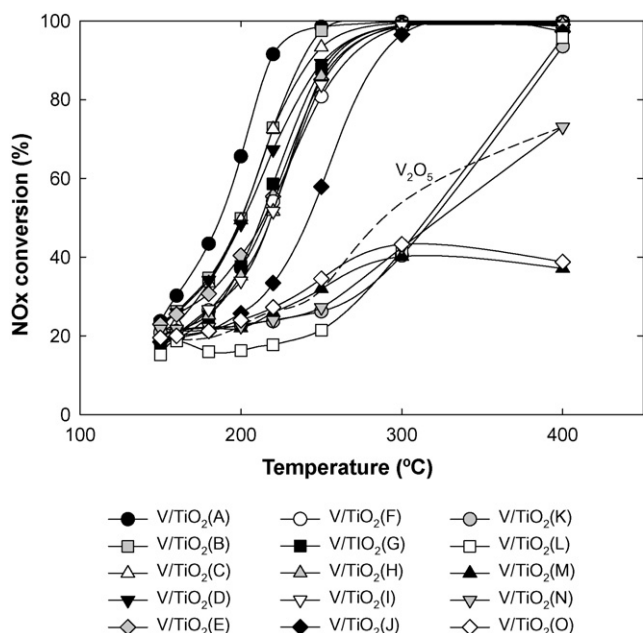


Fig. 1. Effect of temperature on NOx conversion over various vanadia/titania catalysts. Inlet NO 766 ppm; NO₂ 36 ppm; O₂ 3%; H₂O 6%; NH₃/NOx mole ratio 1.0; SV 60,000 h⁻¹.

known to be superior to bulk V₂O₅ in activity [10]. Monolayer vanadia species is different from bulk V₂O₅ in structure, so its activity and selectivity are higher than unsupported oxide [11]. Accordingly, TiO₂ should be regarded not only as a support but also as a component initiating chemical reactions by interacting with vanadium oxide.

Most of the catalysts showed relatively high activity at high temperature over 300 °C. This is because the increased rate of both the ammonia adsorption–desorption processes and SCR surface reaction at high temperature [12]. But those rate and SCR surface reaction are lower at low temperature below 250 °C. Because SCR surface reaction is different depending on catalyst, NOx removal efficiency at 250 °C or less is also different. After all, SCR surface reaction can be determined by TiO₂ support. In order to identify the factor that differentiates NOx removal efficiency at low temperature, we examined the physical properties of TiO₂ support, and the activity of V/TiO₂ catalysts in SCR was compared with the physical properties of TiO₂ supports.

3.2. Physicochemical properties of catalysts

Physical properties that may affect the activity of catalyst are specific surface area, W (tungsten) concentration, particle size, the distribution of pore size, etc. In general, a larger specific surface area is more advantageous to catalytic reaction. With the increase in specific surface area, the number of active sites also increases and this enhances activity. Păarvulescu et al. [13] reported that a large specific surface area raises the degree of dispersion of vanadium and it induces the chemical adsorption of ammonia at Lewis acid sites. As in Table 1, however, NOx conversion at 200 °C was not affected by specific surface area.

The particle size of catalyst affects the specific surface area and pore volume and size. Particle size can be obtained using Sherrer's equation. The particle size of TiO₂ in Table 1 is not significantly related to NOx conversion at 200 °C. However, TiO₂ of pigment grade has relatively large particles due to high calcination temperature, and this is consistent with the tendency of specific surface area.

Additives contained in TiO₂ can change not only the structure of TiO₂ but also various physicochemical properties. Representative metals affecting SCR reaction are W and Mo. In particular, W is contained in commercial V/TiO₂ SCR catalysts in order to increase resistance to deactivation and the sulfur oxides in exhaust gas and to inhibit the transition of crystal phase. As shown in Table 1, however, the effect does not depend on the W content. The most active V/TiO₂(A) contains W around 4.4 wt.%, so its effect is not negligible, but because V/TiO₂(K) with very low activity also contains W around 4.4 wt.%, we cannot conclude that the W content determines activity. V/TiO₂(B) also contained W around 8 wt.%, showing high activity. Mo is known to play a role similar to that of W in SCR catalyst. Thus, we cannot exclude the possibility that W or Mo increases activity. What is more, because their positive effect on activity was proved in previous research [14] it should be considered. Rather than their effect, however, there is more dominant factor to determine SCR activity.

TiO₂ has three crystal phases – anatase, rutile and brookite – and metastable anatase is known to be more active than rutile. Fig. 2 shows the results of XRD analysis without activation. The ratios of crystal phases in Table 1 were calculated by the formula proposed by Spurr and Myer [15] using the peak area of (0 1 0) at 25.2° for anatase and the peak area of (1 1 0) at 27.4° for rutile.

TiO₂(A), the support of the most active catalyst, is 100% anatase. TiO₂(D) contains rutile around 25% but its activity is relatively high, but TiO₂(J) is 100% rutile but more active than TiO₂(L), which is 100% anatase. However, TiO₂(M) and TiO₂(N), though both representing rutile and anatase, respectively, show low activity. Accordingly, it is not believed that the crystal phase of support affects activity. In XRD of catalyst deposited with vanadium, the peaks of V₂O₅ appeared at 2θ of 26.18°, 20.31° and 31.06° but it is hard to confirm the peaks because the loading is small. The XRD pattern of V/TiO₂ catalyst is almost identical with that of TiO₂ and they show little difference in anatase and rutile.

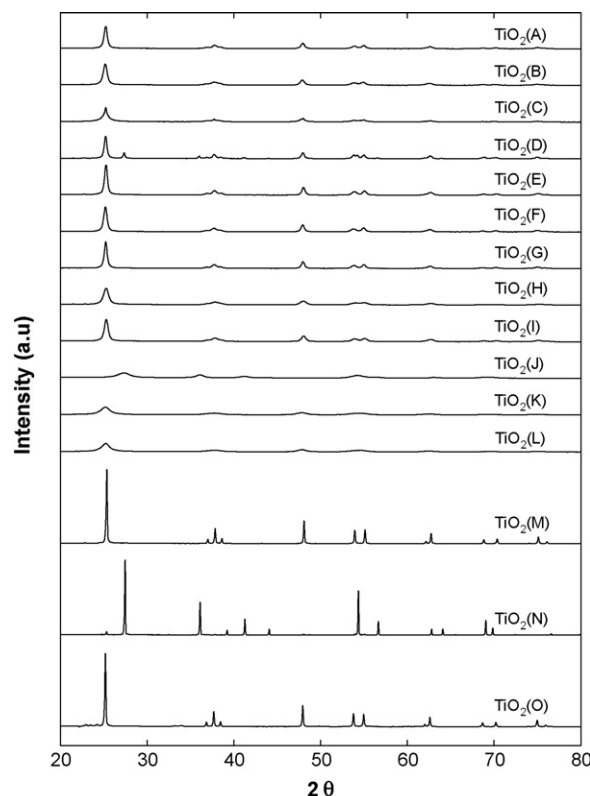


Fig. 2. X-ray diffractograms of the various titania supports.

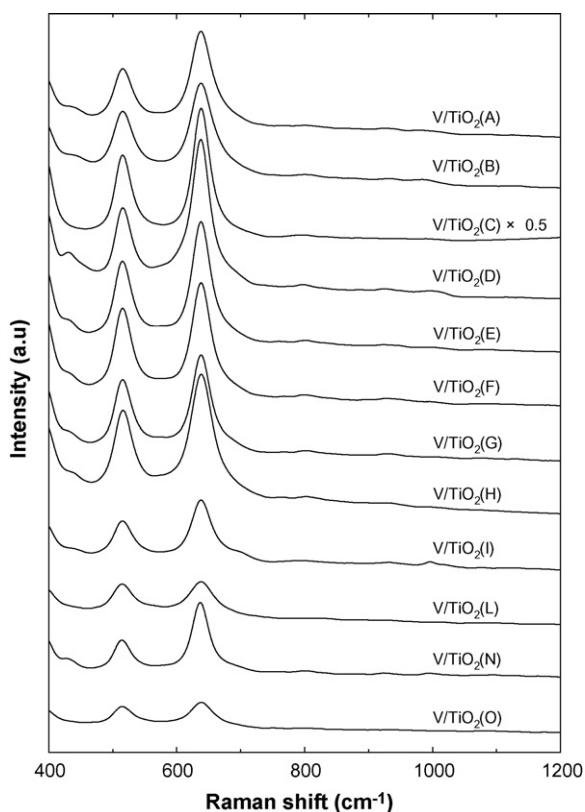


Fig. 3. Raman spectra of vanadia/titania catalysts. Power 300 mW, resolution 10 cm^{-1} , 100 scan.

According to XRD results, however, the crystallinity of TiO_2 of catalyst having relatively high activity is neither very high nor very low. Thus, the XRD pattern of TiO_2 may be used to estimate activity roughly but is not a direct indicator of activity. Thus, we can conclude from the results that SCR activity is related to the crystallinity of TiO_2 .

In V/TiO_2 catalyst, vanadium exists generally in three forms. The forms of dry V/Ti -oxide are monomeric and, polymeric species and bulk V_2O_5 . Polymeric and monomeric vanadates can be distinguished through Raman analysis under ambient conditions. We conducted Raman analysis of V/TiO_2 above and presented the results in Fig. 3.

The Raman bands are the V=O stretching band at 994 cm^{-1} and the Ti-O stretching band at $634\text{--}638\text{ cm}^{-1}$. The 1033 cm^{-1} band corresponds to the V=O vibration in tetrahedrally coordinated vanadia species (monomeric species) and $920\text{--}930\text{ cm}^{-1}$ corresponds to the V=O vibration in polymeric species. The V in bulk V_2O_5 and the content of V strongly interacting with titania surface can be estimated by the ratio of the intensities of those Raman bands [16]. We calculated the ratio of the intensity at 994 cm^{-1} (bulk V_2O_5) to $634\text{--}638\text{ cm}^{-1}$ (TiO_2), the intensity at 1033 cm^{-1} (monomeric species) to $634\text{--}638\text{ cm}^{-1}$ and the intensity at $920\text{--}930\text{ cm}^{-1}$ (polymeric species) to $634\text{--}638\text{ cm}^{-1}$. Calculation results are given in Table 2. As shown in Table 2, it is difficult to find the correlation between NO_x conversion at low temperature and the ratio of intensity of vanadium species. The reason that the general correlation of polymeric and monomeric vanadate is not found in this study may be associated with the various titania supports used. When same titania supports are used, the structure of vanadium compounds can affect the SCR activity. When titania supports with different physicochemical properties are used there may be more dominant factor to affect the SCR activity at low temperature.

Table 2

The intensity ratio of vanadium compounds over TiO_2 supports by Raman analysis.

Catalyst	$994\text{ cm}^{-1}/634\text{--}638\text{ cm}^{-1} (\times 10^{-2})$	$1033\text{ cm}^{-1}/634\text{--}638\text{ cm}^{-1} (\times 10^{-2})$	$920\text{--}930\text{ cm}^{-1}/634\text{--}638\text{ cm}^{-1} (\times 10^{-2})$
V/TiO ₂ (A)	8.31	5.65	10.63
V/TiO ₂ (B)	12.38	7.98	13.68
V/TiO ₂ (C)	6.39	5.16	6.71
V/TiO ₂ (D)	6.77	3.66	7.99
V/TiO ₂ (E)	6.44	4.83	8.19
V/TiO ₂ (F)	6.37	4.53	8.92
V/TiO ₂ (G)	6.94	5.95	9.75
V/TiO ₂ (H)	8.02	6.52	10.78
V/TiO ₂ (I)	14.18	8.71	13.93
V/TiO ₂ (J)	16.16	11.79	20.09
V/TiO ₂ (L)	9.27	8.06	13.71
V/TiO ₂ (N)	9.30	6.98	9.53
V/TiO ₂ (O)	11.24	10.67	14.61

3.3. Valence states of catalysts

SCR reaction is one of oxidation/reduction. Casagrande et al. [17] found that ternary catalyst $\text{V}_2\text{O}_5\text{--MoO}_3/\text{TiO}_2$ is more active in the SCR reaction than the corresponding binary $\text{V}_2\text{O}_5/\text{TiO}_2$ and $\text{MoO}_3/\text{TiO}_2$ catalysts because it is more easily reduced and reoxidized. That is, the higher reactivity of the catalyst at low temperature is related to its superior redox properties. Oxidation and reduction reactions occur by electron transfer. The fact that electric conductivity changes during SCR reaction provides evidence that electron transfer is involved in SCR [7]. Accordingly, in order to understand electron transfer in catalyst, we need to investigate the atomic state of the catalysts surface by XPS.

Fig. 4 shows $\text{Ti } 2p$ peak of $\text{TiO}_2(\text{B})$. The peak appearing at around 458.8 eV is a tetravalent $\text{Ti } 2p_{3/2}$ peak, and the peak at around 464.5 eV is a quadrivalent $\text{Ti } 2p_{1/2}$ peak. If the chemical binding state of atoms is different, the binding energy is different. Using the change, we can see chemical binding state and the valence state of surface species. As shown in the figure, only Ti^{4+} exists in $\text{TiO}_2(\text{B})$ as well as in different TiO_2 . Accordingly, we could not find any difference in TiO_2 with no deposited V .

Fig. 5(a) shows the $\text{Ti } 2p$ peak where vanadium is deposited on $\text{TiO}_2(\text{B})$. It is clearly different from $\text{Ti } 2p$ peak of vanadium-free TiO_2 support, suggesting the presence of a different kind of titanium besides Ti^{4+} . That is, peaks with binding energy lower than Ti^{4+} correspond to species with high oxidation states such as Ti^{3+} and Ti^{2+} . The peaks of Ti^{3+} and Ti^{2+} in addition to Ti^{4+} are identified through Gaussian–Lorentzian curve fitting. Compared to Ti^{4+} , Ti^{3+} shows low binding energy of around 1.8 eV [18]. Accordingly, Ti^{3+} and Ti^{2+} appear at around 457.9 and 456.3 eV , respectively. When

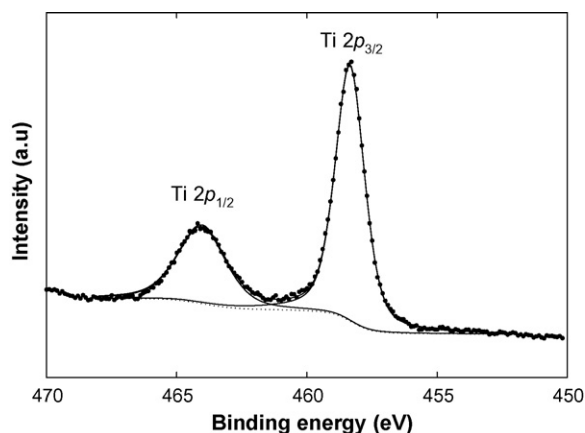


Fig. 4. $\text{Ti } 2p$ XPS spectrum of vanadium-free $\text{TiO}_2(\text{B})$ deconvoluted using the Gaussian–Lorentzian curve-fitting method.

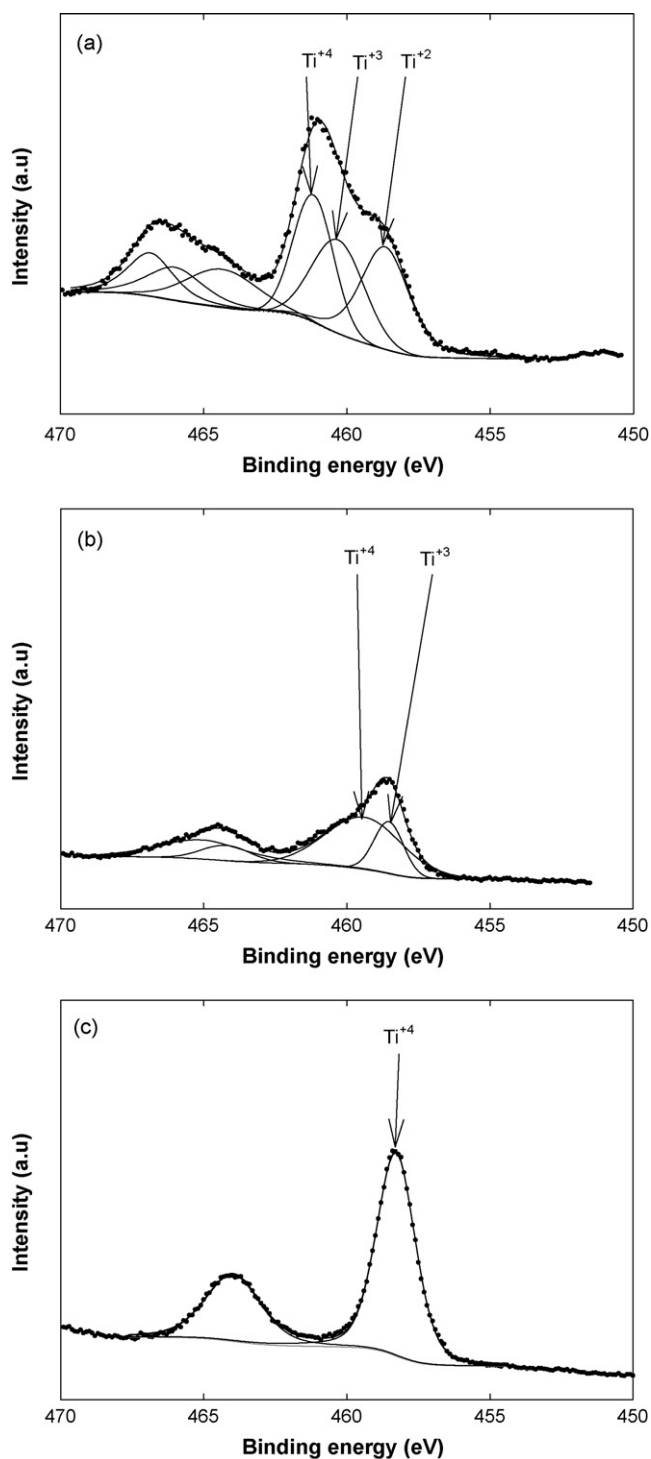


Fig. 5. Ti 2p XPS spectra of V/TiO₂ catalysts deconvoluted using the Gaussian–Lorentzian curve-fitting method. (a) V/TiO₂(B), (b) V/TiO₂(H) and (c) V/TiO₂(L).

these peaks of non-stoichiometric titanium (Ti^{y+} ($y \leq 3$)) such as Ti³⁺ and Ti²⁺ are combined, the results are almost the same as the original XPS spectrum. This shows that due to the deposition of vanadium on TiO₂ support, TiO₂ is reduced differently resulting in various oxidation states. Wong and Vohs [19] reported that CeO₂ or TiO₂ has a number of stable oxidation states, and TiO₂ is more easily reduced than CeO₂. This report supports the figure above.

The Ti 2p of different catalysts also shows various Ti oxidation states after the deposition of V. Similar results are obtained for

V/TiO₂(A) to V/TiO₂(I) catalysts having high SCR activity at relatively low temperature. Fig. 5(b) shows the Ti 2p peak of V/TiO₂(H) having moderate SCR activity at low temperature. Compared to Fig. 5(a), non-stoichiometric Ti is less, and oxidation state is also less various. Fig. 5(c) shows the Ti 2p peak of V/TiO₂(L) having very low SCR activity at low temperature. As in the figure, non-stoichiometric Ti is not found. Thus, it is concluded that catalysts having high SCR activity at low temperature should contain various kinds of non-stoichiometric Ti.

Fig. 6(a) shows V 2p obtained from XPS analysis of V/TiO₂(B) catalyst. The peak of V 2p appears near the satellite line of O 1s peak (binding energy 519.8 eV). V 2p peak is asymmetric as a whole and, like titanium, this means the presence of non-stoichiometric forms (V^{x+} ($x \leq 4$)) such as V³⁺ and V⁴⁺. The V 2p peak of V/TiO₂(B) catalyst has a typical form, and the V 2p of different catalysts has a peak of similar form. Fig. 6(b) and (c) are the results of analyzing the V 2p of V/TiO₂(H) and V/TiO₂(L). V/TiO₂(L) has relatively low SCR activity at low temperature, and does not show various non-stoichiometric vanadium atoms. This is different from Fig. 6(a). The trend of the V 2p peak of V/TiO₂(H) catalyst graphed in Fig. 6(b) is similar to Fig. 6(a) as a whole.

Vanadium has a stable oxidation state of 5+, but V³⁺ is formed by oxygen vacancy, and it is known that vanadia containing V³⁺ is more active than V⁵⁺ [20]. V^{x+} ($x \leq 4$) is in unstable state, having very high activity compared to stoichiometrically stable V⁵⁺. Because V^{x+} ($x \leq 4$) is in reduced state compared to V⁵⁺, V⁴⁺ has one extra electron while V³⁺ has two extra electrons. These extra electrons can work as free electrons because there is no constraint in the atom, and the activity is very high. At low temperature, these free electrons are positioned at a delocalized orbit, and have very high reactivity, so they can be transferred easily. In all catalysts used in this study, V⁴⁺ and V³⁺ were observed, and even V²⁺ was found in some catalysts. Accordingly, it is believed that the presence of non-stoichiometric vanadium is not always crucial factor to affect SCR activity. Thus, we calculated the number of atoms in non-stoichiometric Ti and V and compared the results with NOx conversion at each reaction temperature.

3.4. Effect of the amount of non-stoichiometric species

As in Fig. 7(a), the amount of V^{x+} ($x \leq 4$) atoms is closely related to NOx conversion. In particular, the amount of V^{x+} ($x \leq 4$) atoms is in nearly a linear relation with NOx conversion at low temperature of 200 or 220 °C. Accordingly, it is concluded that SCR activity at low temperature increases with the rise of the contents of non-stoichiometric vanadium. NOx conversion at 300 °C is almost constant and very high in case the amount of V^{x+} ($x \leq 4$) atoms is over around 70 atoms/cm³. Because 300 °C is high temperature, high activation energy is supplied and as a result core electrons in the catalyst can participate in oxidation/reduction without the participation of non-stoichiometric vanadium in the reaction. Thus, at high temperature, the presence of V^{x+} ($x \leq 4$) or the amount of V^{x+} ($x \leq 4$) atoms does not have a significant effect. However, if the amount of V^{x+} ($x \leq 4$) atoms is below a specific level, SCR activity can be low even at 300 °C. The sharp decrease suggests that, in addition to the amount of non-stoichiometric vanadium atoms in catalyst, the driving force of electrons is also an important factor.

Not only the amount of non-stoichiometric vanadium atoms affects SCR reaction activity, but also non-stoichiometric Ti species. Fig. 7(b) shows the effect of the number of non-stoichiometric Ti expressed as Ti^{y+} ($y \leq 3$) per unit volume on NOx conversion. The figure shows that NOx conversion is in a linear relation with Ti^{y+} ($y \leq 3$) at low temperature of 200 and 220 °C. Like V^{x+} ($x \leq 4$), Ti^{y+} ($y \leq 3$) also has high activity at low temperature. Compared to conversion at 300 °C, however, the same phenomenon as that of vanadium was observed. Ti^{y+} ($y \leq 3$) is more active than stoichiometric Ti⁴⁺. It is

difficult for Ti^{y+} ($y \leq 3$) to provide sites for SCR reaction directly but they induce oxidation/reduction through supplying lattice oxygen through vanadium.

3.5. Electronic properties of the catalyst

The electrochemical superiority of non-stoichiometric compounds comes from the well-mobile electrons of catalysts. Thus,

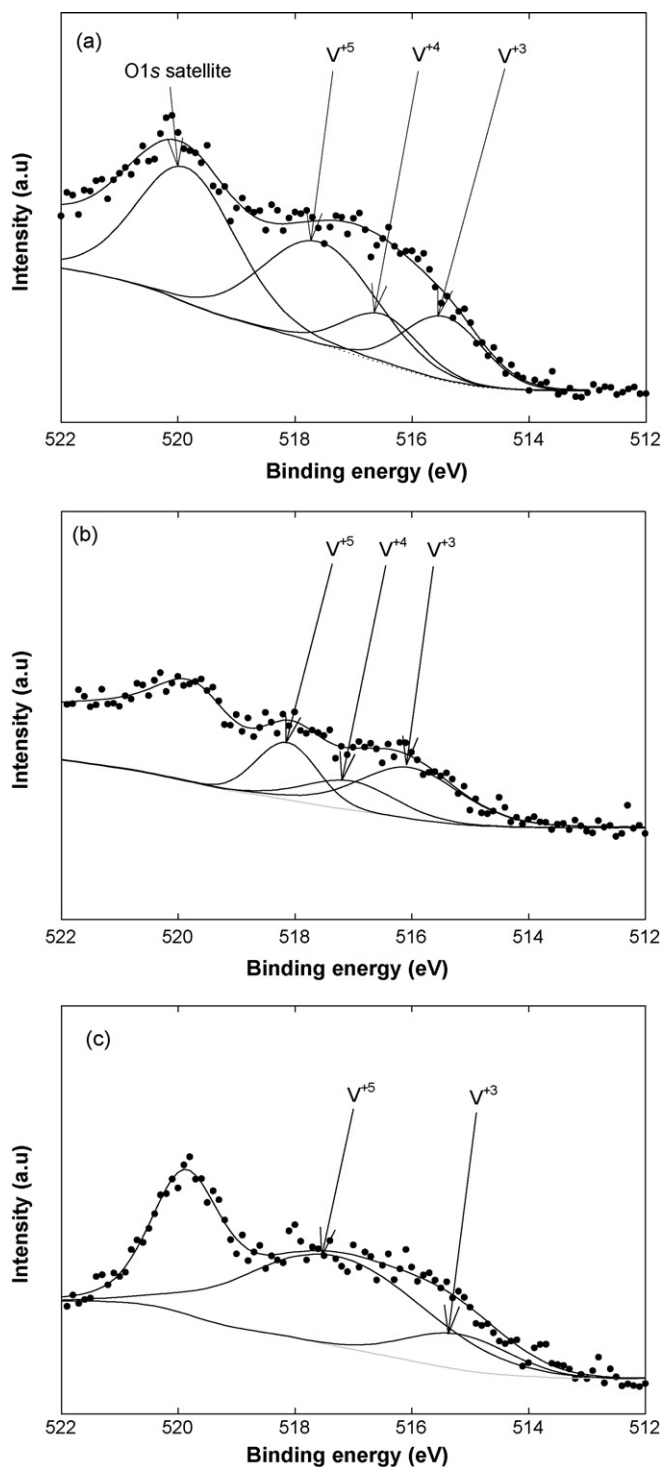


Fig. 6. V 2p XPS spectra of V/TiO₂ catalysts deconvoluted using the Gaussian-Lorentzian curve-fitting method. (a) V/TiO₂(B), (b) V/TiO₂(H) and (c) V/TiO₂(L).

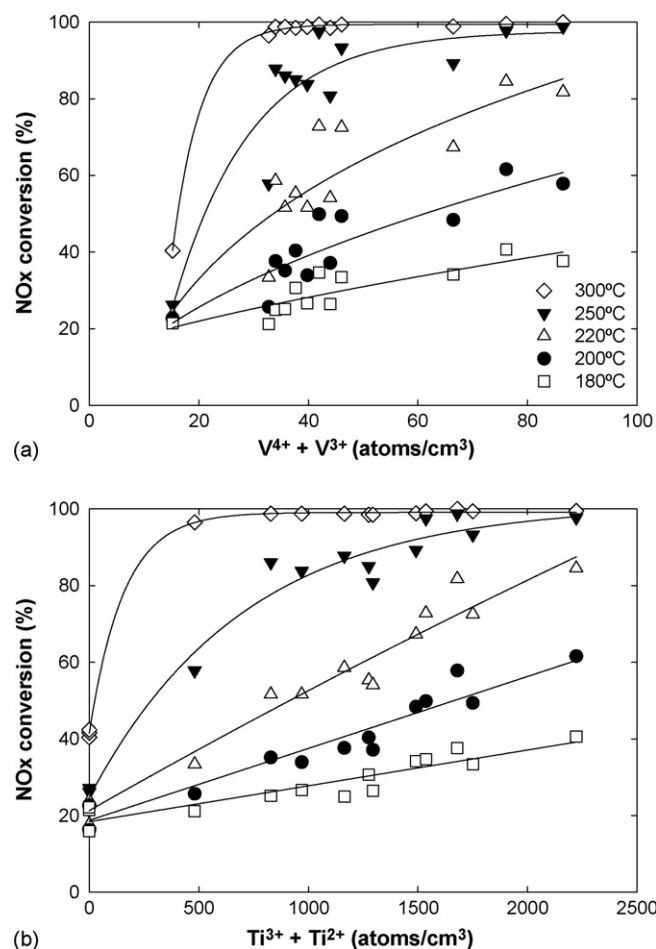


Fig. 7. Effect of non-stoichiometric atoms per unit volume of vanadia/titania catalysts on NO_x conversions at various operation temperatures (a) vanadium and (b) titanium.

we need to study the electronic structure of catalysts, that can be implemented by parameters such as atomic charge, bond order, total energy and density of states (DOS) [20]. Thus, we simulated DOS for catalysts and supports.

Fig. 8(a) is the results of simulation for TiO₂. If TiO₂ is used for simulation, the results may be different from the real situation because the number of variables is small. Thus, we conducted simulation with Ti₄O₈, which is equivalent to TiO₂. As to the electron transfer of TiO₂, if energy higher than the band gap energy of TiO₂ is applied from outside, stable electrons filling the valance band (VB) transfer to the conduction band (CB), and as a result the reduction of the external matter takes place in CB and oxidation occurs in VB. In the result of simulation with Ti₄O₈, EF on the x-axis indicates the Fermi level. Centering on EF, signals are formed on both sides, and there is a gap between them. Of the two signals, the left one is for VB and the right one for CB. Accordingly, in the signal on the VB side the energy at the rightmost end is the edge of VB, and in the signal on the CB side the energy at the leftmost end is the edge of CB, and the difference between the two points is the band gap energy. For Ti₄O₈, the Fermi level exists between the band edges and closer to VB. EF is located slightly higher than VB and below CB. Thus, in order for electrons in VB of Ti₄O₈ to be excited and transferred to CB, energy of around 2.5 eV is required, and energy for excitation to CB at the Fermi level is nearly as high as that, though slightly lower.

Fig. 8(b) shows the result of simulating a compound reduced to Ti₄O₇. The figure shows that the band gap energy is lower than that of Ti₄O₈. In addition, the Fermi level is higher than CB and the

electron density increases sharply at the Fermi level. Accordingly, as electrons existing at the Fermi level can be transferred easily to CB, in non-stoichiometric compound electron transfer can happen at as a high degree as that of metals.

When vanadium is deposited on TiO_2 support, V^{4+} can be formed as V atom is displaced with Ti atom. To implement the phenomenon, we considered Ti_3VO_8 compound by replacing a Ti atom in Ti_4O_8 with V atom and showed the result in Fig. 9(a). Ti_3VO_8 shows a result quite similar to that of Ti_4O_7 . In Ti_3VO_8 , the difference between CB and VB is smaller than that in Ti_4O_8 and the Fermi level is higher than CB. Thus, very smooth electron transfer between the Fermi level and CB is expected, and because electron density at the Fermi level is higher than that in Ti_4O_7 , there are relatively more electrons having mobility than Ti_4O_7 . Accordingly, doping with vanadium forms non-stoichiometric structure by reducing TiO_2 , and consequently increases electron transfer further, which in turn can increase the catalytic activity.

As reduction changes the electronic properties of catalyst, we conducted computer simulation for Ti_3VO_7 reduced by extracting an oxygen atom from Ti_3VO_8 . As in Fig. 9(b), CB and VB are hardly distinguishable and their electronic characteristic is closer to a conductor than a semiconductor. In addition, the Fermi level is around 3 eV higher compared to that in Ti_3VO_8 , so electrons in Ti_3VO_7 can move freely like free electrons. However, as electron density at the Fermi level appears lower than that in Ti_3VO_8 , it is hard to estimate

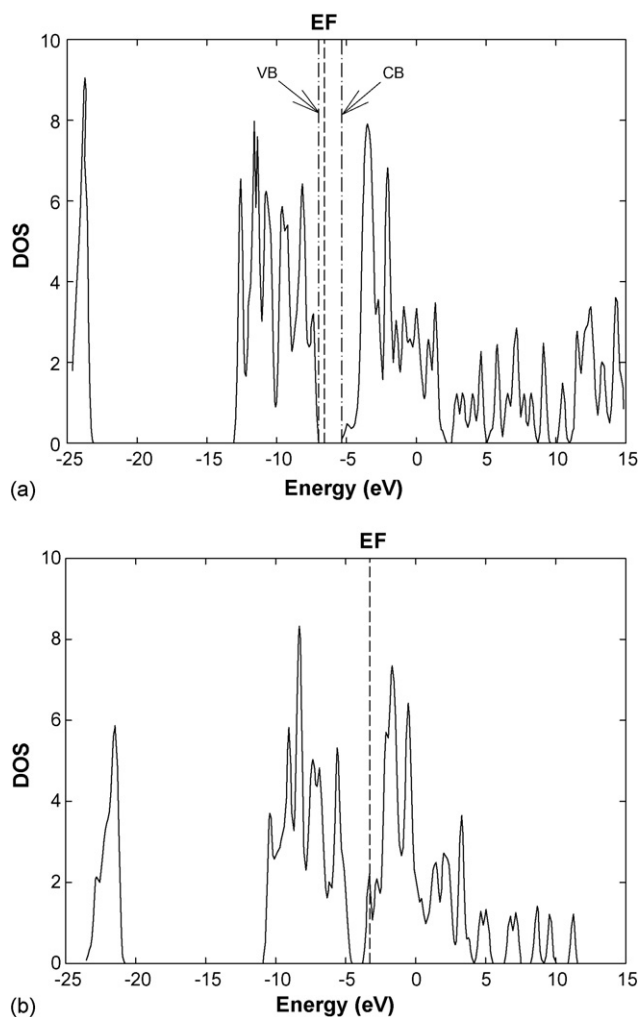


Fig. 8. Energy levels along some symmetry axes and the density of states curves of titanium oxides (a) Ti_4O_8 and (b) Ti_4O_7 .

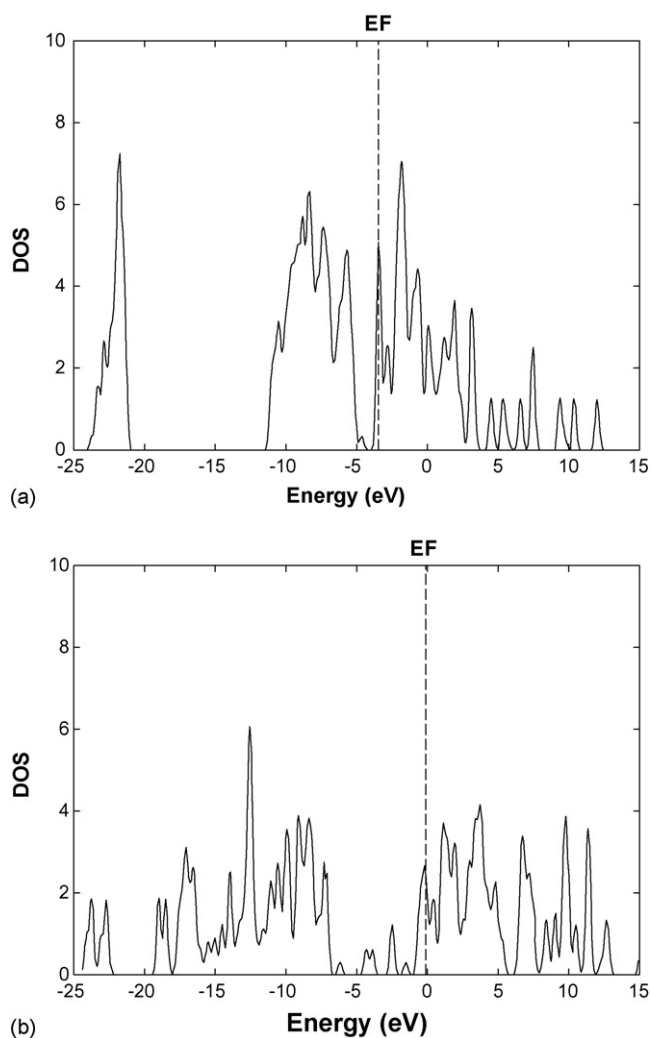


Fig. 9. Energy levels along some symmetry axes and the density of states curves of titanium oxides (a) Ti_3VO_8 and (b) Ti_3VO_7 .

how they affect oxidation/reduction. However, as the Fermi level is located higher than CB, electron transfer is expected to be very smooth as in Ti_3VO_8 .

Summing up the results, as catalysts for SCR forms non-stoichiometric vanadium or titanium, their electronic characteristic is improved compared to stoichiometric one, and as a result it is possible to drive electrons with low energy. What is most remarkable among the electric properties of non-stoichiometric compounds is that the Fermi level is close to or above CB and as a result the catalysts have metal-like properties and electrons in the catalyst work as free electrons. This characteristic causes the catalysts to have activity at low temperature.

4. Conclusions

Catalysts prepared by depositing vanadium on various TiO_2 supports by the same method have different SCR activity at low temperature of 180–250 °C depending on the TiO_2 support. No direct relation was found between NO_x conversion at low temperature with physicochemical properties such as specific surface area, particle size, the crystal phase of TiO_2 , additive contents and the structure of vanadium. XPS analysis showed that Ti^{4+} exists in all pure TiO_2 supports, but if vanadium is deposited, non-stoichiometric titanium (Ti^{y+} ($y \leq 3$)) such as Ti^{3+} and Ti^{2+} as well as Ti^{4+} and non-stoichiometric vanadium (V^{x+} ($x \leq 4$)) such as V^{4+} ,

V^{3+} and V^{2+} as well as V^{5+} are formed. Compared to stoichiometric species, catalysts with non-stoichiometric TiO_2 and vanadium have the Fermi level close to or above the conduction band and as a result electron can transfer with low activation energy. It was found that the amount of non-stoichiometric vanadium and titanium per unit volume is in a linear relation with denitrification efficiency at low temperature.

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