

A study of the increase in selective catalytic reduction (SCR) activity of the V/TiO₂ catalyst due to the addition of monoethanolamine (MEA)

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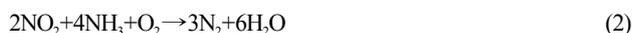
(Received 11 November 2009 • accepted 16 February 2010)

Abstract—Experiments were conducted to evaluate the effect of adding ethanol amine during the preparation of a V/TiO₂ catalyst to remove nitrogen oxide (NO_x) by selective catalytic reduction (SCR). The catalyst added monoethanolamine (MEA) had the highest NO_x conversion among all the neutralization reagents tested, and the optimum MEA concentration was determined to be 10%. The catalyst-added MEA had a large amount of lattice oxygen, which was determined in the O₂ on/off experiment. In addition, it also displayed a high reoxidation rate in the O₂ reoxidation experiment. In the XPS analysis, the superior redox properties of the catalyst-added MEA were shown to be caused by the presence of Ti⁺³, a non-stoichiometric species.

Key words: SCR, Monoethanolamine, Non-stoichiometric, V/TiO₂, Redox

INTRODUCTION

NO_x, along with sulfur oxides, is the cause of acid rain, which leads to corrosion processes and the pollution of soil and water. Moreover, it reacts with moisture and hydrocarbons in the atmosphere to create a photochemical smog and depletes the ozone layer, ultimately having a great damaging effect on the human body [1]. Among the methods developed for removing NO_x emitted from such stationary sources of pollution, SCR using NH₃ is the most promising. The major SCR reactions are as follows.



The SCR reaction is a process that removes NO_x through the chemical reactions (1)-(2), whereby the catalyst is installed within the passageway through which the emitted gases pass through, and NH₃ is sprayed in front of the catalyst [2].

The core technology involved in the SCR process using NH₃ is based on catalyst technology. In preparation of the V/TiO₂ catalyst, ammonium metavanadate (AMV, NH₄VO₃), is commonly used as vanadium source, and oxalic acid (OA, (COOH)₂) is added to increase the solubility of AMV [3-5]. Solutions of AMV with OA become acidic in the atmosphere, and its pH is around 2.1-2.5. Among the other additives included during the production of the catalyst, ethanol amine functions to elevate the pH, thereby limiting corrosion of the equipment by OA and changes in the surface properties of the catalyst [6,7].

Economidis et al. [8] reported that, when producing catalysts for

the NH₃-SCR through the impregnation method, outstanding response activation was obtained with complete dissolution of NH₄VO₃ and reduction of V⁵⁺ to the V⁴⁺ state under acidic conditions where the pH was approximately 2.5. Lee [9] reported that in catalysts impregnated with vanadium, a higher level of activation was observed in catalyst that did not contain OA relative to catalysts containing OA, and that the response activation differed in accordance with the pH established at the time the catalyst was prepared. Also, Roozeboom et al. [10] prepared V₂O₅ based catalysts by ion exchange, passing a NH₄VO₃ solution at pH 4 through a bed of support material. Ciambelli et al. [11] examined methods of removing NO_x from V₂O₅/TiO₂ catalysts by varying the pH in the range of 2.86-10 using HNO₃ and NH₄OH. According to the results of this study, the rate of NO_x conversion improved markedly with an increase in pH. Therefore, it can be concluded that pH influences the activation of the catalysts at the time the catalyst is prepared.

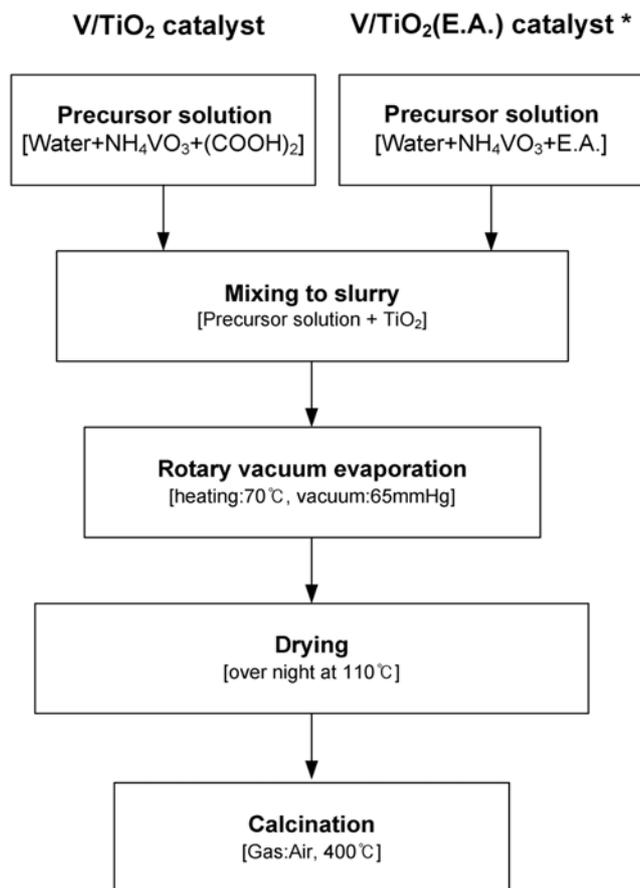
Therefore, in this study, we investigated the impact that acidic and alkaline conditions have on SCR activity during the production of the V/TiO₂ catalyst for SCR by preparing catalysts in which OA and other neutralization reagents such as NH₄OH, MEA, diethanolamine (DEA) and triethanolamine (TEA) have been added. We determined the optimum quantity of the neutralization reagents that resulted in catalysts with superior activity. In addition, through O₂ on/off experiments, reoxidation experiments and XPS analysis, we also examined the causes for the activation of the prepared catalyst.

EXPERIMENTAL

1. Catalyst Preparation

The TiO₂ used in this study was a commercial TiO₂ precursor that was calcined at 500 °C. The TiO₂ precursor phase was amorphous, which was calcined to the crystalline phase. Precursor TiO₂

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* E.A. : MEA, DEA, TEA

Fig. 1. Flow diagram of the procedures used to fabricate the V/TiO₂ catalysts.

consisted of a pure anatase structure with a specific surface area of 95 m²/g. Vanadium was the active material used, and for all catalysts, an equal quantity of 2% was added.

The catalyst used in the present study was prepared by the wet impregnation method, and this process is illustrated in Fig. 1. First, the vanadium content in relation to TiO₂ was calculated according to the desired composition ratio, and the calculated quantity of AMV (Aldrich Chemical Co.) was dissolved in distilled water that was heated to 60 °C. At this time, OA (Aldrich Chemical Co.) and neutralization reagents such as MEA, DEA, TEA were added according to the ratio of weight. The calculated amount of TiO₂ was gradually added to the solution while stirring and sufficiently mixing. The mixed slurry was agitated for 1 hour or more and then the moisture was evaporated using a rotary vacuum evaporator at 70 °C. The catalyst was then further dried in dry oven at 110 °C for 24 hours. The dried catalyst was calcined in a tubular furnace at 400 °C for 4 hours under air conditions.

2. Catalytic Activity Measurement

The fixed bed reactor used for the SCR reaction experiment was composed of the gas injection section, the reactor section, and the section that analyzed the reacted gas. The gases supplied into the reactor were injected using an MFC (mass flow controller, MKS Co.) from each of the cylinders for NO, N₂, O₂, NH₃.

Also, moisture was supplied to the SCR reaction system by using

Table 1. Experimental condition in a fixed bed reactor

Particle size (μm)	297-400	
Temperature (°C)	150-400	
Inlet gas conc. (N ₂ balance)	NO _x (ppm)	800
	NH ₃ (ppm)	860 (NH ₃ /NO _x =1)
	O ₂ (%)	3
	H ₂ O (%)	6
Space velocity (hr ⁻¹)	60,000	
Total flow (mL/min)	500	

a water bubbler that was maintained at constant temperature. The gas pipe was made of a stainless steel tube. To prevent the formation of salts such as NH₄NO₃, NH₄NO₂, which are formed through the reaction between NO and NH₃, and also to prevent the condensation of moisture in the stainless steel tube, a heating band was wrapped around the tube to maintain a constant temperature of 180 °C.

The reactor was a continuous-flow type fixed bed reacting device made with a quartz tube that had an interior diameter of 8 mm and a height of 60 cm. Quartz wool was used to fix the catalyst powder.

For measuring the concentration of the reactant and the product, a non-dispersive infra red gas analyzer (Uras10E, Hartman & Braun Co.) was used for NO while NO₂ was analyzed using the detector tube (9L, Gas Tec. Co.) located in the exit area of the main reactor.

3. Experimental Procedure and Characterization

To maintain the consistency of the filling catalyst, the prepared powder catalyst was made into pallets using 5,000 pounds of powder in a hydraulic press, and then catalyst powder that had a size of 297-400 μm was selected.

The experimental conditions are shown in Table 1. The methods used in these experiments were as follows. First, a certain quantity of the catalyst was placed in the reactor, and 3% O₂/N₂ gas was injected into the reactor and maintained at 120 °C for 30 minutes so as to remove moisture and impurities from the catalyst surface. When the temperature reached a steady state, other gases were injected into the reactor. The reaction was continued until the concentration of the product became consistent, at which time the concentration was recorded.

To examine the reoxidation of the catalyst, the catalyst was filled in the reactor and reduced at 400 °C with 0.5% NH₃/N₂ for 30 minutes. The SCR reaction was then conducted at the respective temperature under conditions without oxygen and with NO+NH₃ in order to reach stabilization. When the reaction was stabilized, 200 ppm O₂/N₂ was continuously supplied, while the concentration of NO was monitored.

The O₂ on/off experiment was conducted by supplying NO+NH₃+O₂ at a fixed temperature and stably executing the SCR reaction. During the middle of the reaction the O₂ supply was momentarily cut off. One hour after the cut-off, O₂ was again supplied while the concentration of the NO was monitored.

XPS analysis was conducted with an ESCALAB 210 from VG Scientific, and Al Kα monochromate (1,486.6 eV) was used as an excitation source. After moisture contained in the catalysts was completely removed. The catalysts were analyzed without surface sputtering and etching in order to maintain the degree of vacuum of the

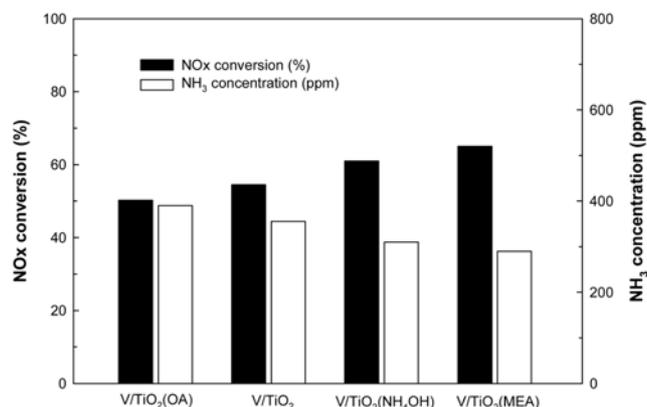


Fig. 2. The effect of the additives in the preparation of V/TiO₂ catalyst on NO_x conversion and NH₃ concentration at 200 °C.

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.

RESULT AND DISCUSSION

1. The Influence of pH when Preparation of the Catalyst

In this study, we investigated the influence of acidic and alkaline conditions during the preparation of the same TiO₂ catalysts on the SCR reaction. Also, in the alkaline environment, the pH of each added neutralization reagent was maintained at 10.4 in order to exclude the effect of pH.

Fig. 2 compares the reaction activity at 200 °C of four different catalysts: a catalyst containing OA under acidic pH conditions, a catalyst containing NH₄OH and MEA of under alkaline pH conditions, and a catalyst produced under neutral conditions (pH 7-8) without any additives. As shown in the figure, the catalyst prepared with the addition of OA has the lowest SCR activity at 200 °C. The catalyst made under alkaline conditions was the highest, followed by the NH₄OH added catalyst and the MEA added catalyst.

In the SCR reaction, unreacted NH₃ is toxic, and at low temperature it forms NH₄NO₃ by reacting with NO_x or salts such as NH₄HSO₄ by reacting with SO₂ in the exhaust gas, which consequently lowers the activity of the catalyst [12]. The MEA-added catalyst had the lowest NH₃ slip and the OA-added catalyst had the highest NH₃ slip at 200 °C.

Lee [9] conducted an experiment using V/NMO and NMO as low-temperature SCR catalysts, and reported that when preparing the catalyst, OA increased the solubility of the V/NMO and NMO, but when OA was added, the SCR reaction activity was diminished.

Similarly, the V/TiO₂ catalyst in our study showed a superior SCR activity and small amount of NH₃ slip when the catalyst was prepared under alkaline conditions. In addition, the catalytic activities were found to be different according to the neutralization reagent even at the same pH.

2. The Effect of the Addition of Ethanol Amine

In the experiment described above, the catalyst made under alkaline conditions had superior activity. Also, the activity of the catalyst containing MEA was higher than the catalyst containing NH₄OH even though the solution pH was same. Therefore, the effect of etha-

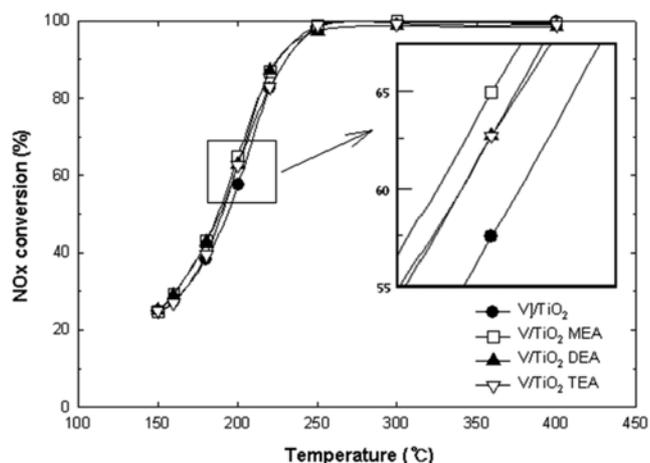


Fig. 3. The effect of the ethanolamine in the preparation of V/TiO₂ catalyst on NO_x conversion.

molamine such as MEA, DEA and TEA, which are in the same ethanolamine family, was investigated.

Fig. 3 compares the catalytic activities of the V/TiO₂ catalysts containing different added ethanolamines. As indicated in the figure, at high temperatures of 250 °C or more, no difference in the activity among the catalysts was observed; however, a difference in the activity was observed at temperatures below 220 °C. In addition, the catalyst containing amine was superior to V/TiO₂ at 200 °C, and the activity increased in the order of MEA, DEA and TEA. The catalytic activity at 200 °C decreased as the number of ethanol groups increased.

To increase the catalytic activity, the optimum amount of added MEA was determined. The catalytic activity at different MEA quantities is shown in Fig. 4. As indicated in the figure, all catalysts demonstrated high activity at 300 °C. This was due to the high temperature, which supplies a sufficiently amount of activation energy to drive the SCR reaction for the V/TiO₂ catalyst. At 200 °C, the activity increased with an increase in the quantity of MEA up to 10%. However, the activity decreased at an MEA concentration of 20% or more.

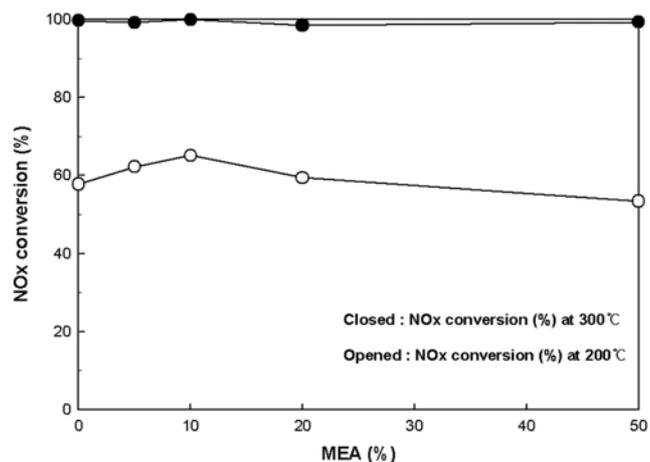


Fig. 4. The effect of the MEA quantity in the preparation of V/TiO₂ catalyst on NO_x conversion.

Therefore, it is possible to conclude that the addition of the ethanalamine catalyst at the time of production can increase the SCR activity, and that there is an optimal quantity of added MEA.

3. The Redox Property of the Catalyst, and Non-stoichiometric Species

In the standard SCR reaction, oxygen is one of the most important reacting substances, as shown in the chemical reaction (1). Wu et al. [13] conducted an O₂ on/off experiment using MnOx/TiO₂, and reported that oxygen was an important oxidation agent in the catalyst. Also, according to our previous study [14], the reoxidation of the catalyst by oxygen was shown to have a decisive influence on the SCR reaction activity. Moreover, when there was no oxygen in the atmosphere, the lattice oxygen and adsorbed oxygen of the catalyst caused the SCR reaction to continue, and the quantity of this oxygen influenced the reaction activity and durability against SO₂.

Therefore, the redox property of the catalyst containing MEA was examined in O₂ on/off experiments and the O₂ reoxidation experiment at 200 °C. Fig. 5(a) shows the results of the O₂ on/off experiments for the V/TiO₂ (MEA 10%) catalyst. Under the condition of NO+NH₃+O₂, the NO_x conversion is 100%. However, when the injection of oxygen was discontinued, NO_x conversion rapidly decreased, and then remained at around 65% after decreasing again to 30%. A NO_x conversion of 65% in the SCR reaction was maintained for a several minutes after the O₂ supply was shut off because

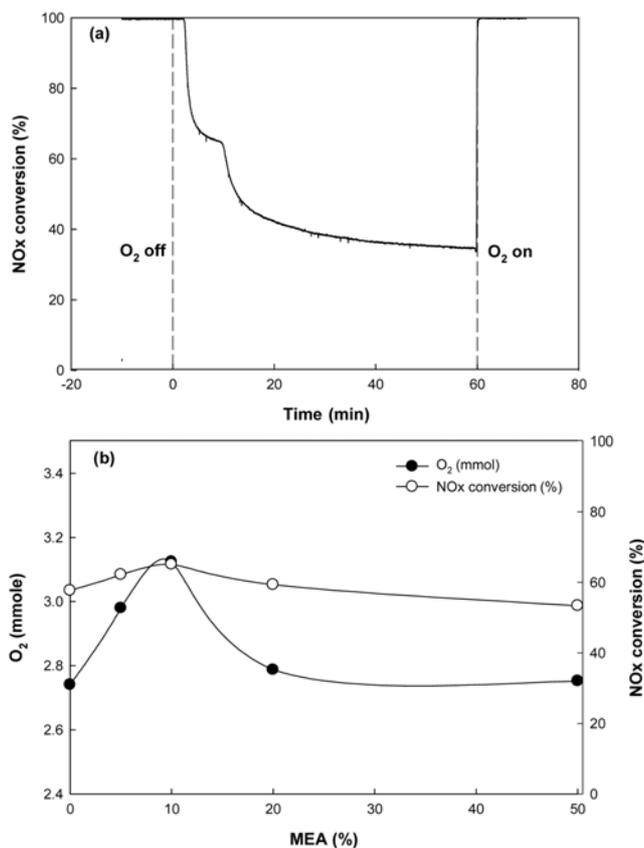


Fig. 5. The characteristics of reduction of V/TiO₂ catalyst added MEA (a) the decline of NO_x conversion with time after shut-off O₂, and (b) the relationship of NO_x conversion and reacted lattice oxygen at 200 °C.

of the presence of lattice oxygen [14]. For all the catalysts, the amount of lattice oxygen that participated in the reaction after the supply of O₂ was shut off was quantified. In the standard SCR reaction, 1 mole of NO molecules reacts with 0.25 moles of O₂. The quantity of oxygen participating in the reaction can be obtained by calculating the quantity of NO_x removed by the SCR reaction following oxygen shut-off and conversion into O₂.

The consumption of lattice oxygen after the supply of O₂ was shut-off is shown in Fig. 5(b). As indicated in the figure, the V/TiO₂ (MEA 10%) catalyst, which was the most efficient, contained the greatest amount of lattice oxygen. Therefore, it can be concluded that the quantity of lattice oxygen and the NO_x conversion were closely related.

Fig. 6(a) shows the results of the O₂ reoxidation experiment for the V/TiO₂ (MEA 10%) catalyst. Before injecting O₂, the SCR reaction was conducted under the condition of NH₃+NO_x. After the NO_x conversion stabilized, oxygen was injected. Upon injection of O₂, the NO_x conversion dramatically increased. The O₂ reoxidation experiments were conducted for all catalysts, and the reoxidation rates of the catalysts were calculated and presented in Fig. 6(b). As shown in Fig. 6(b), the rate of reoxidation differed according to the catalysts, and the catalyst containing 10% MEA had the highest reoxi-

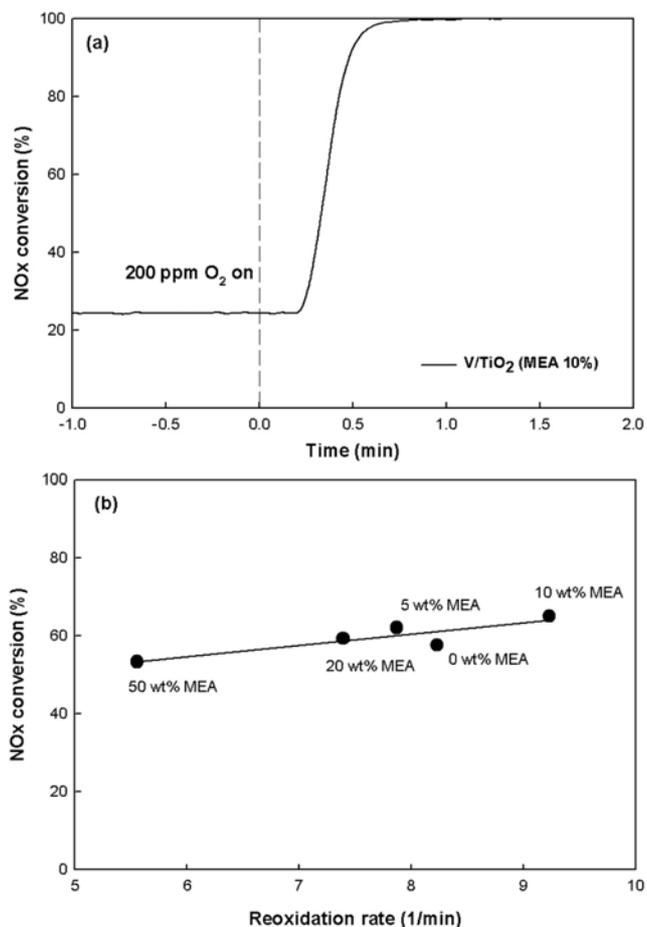


Fig. 6. The characteristics of reoxidation of V/TiO₂ catalyst added MEA (a) the change of NO_x conversion by the reoxidation, and (b) the relationship of NO_x conversion and reoxidation rate.

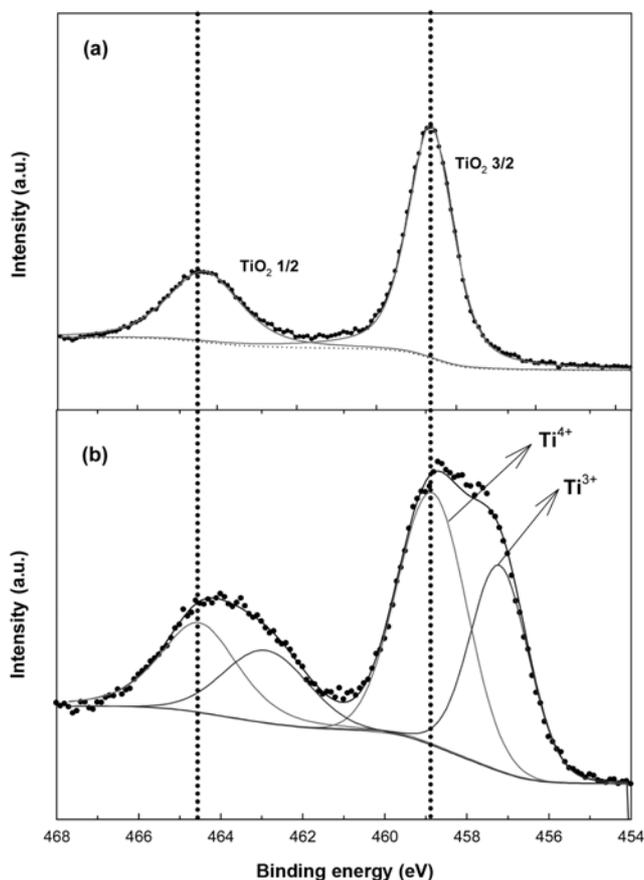


Fig. 7. Ti 2p spectra measured for different catalysts by XPS (a) TiO_2 and (b) V/TiO_2 .

ation rates.

Based on the above results, it was demonstrated that the catalyst containing the optimal quantity of MEA had the highest reoxidation ability due to the oxygen in the atmosphere and the abundant amount of lattice and absorbed oxygen within the catalyst itself. To determine the relationship between this redox characteristic and the oxidation state of the catalyst, XPS analysis was conducted. In the XPS analysis, the Ti 2p spectra were divided into Ti 2p_{3/2} and Ti 2p_{1/2} by the spin-orbit interaction [15]. The peaks that appeared around 458.8 eV and 464.5 eV were the Ti 2p_{3/2} peak and Ti 2p_{1/2} peak, respectively, which corresponded to a Ti^{4+} value.

In pure TiO_2 , not containing a vanadium deposit, the typical Ti peak can be observed, as shown in Fig. 7(a). In other words, at 458.8 eV, a Ti 2p_{3/2} peak was observed, and only the Ti^{4+} existed. However, as shown in Fig. 7(b), when vanadium was added to TiO_2 , low oxidation state such as Ti^{3+} was observed. This result is in agreement with a previous study conducted by Price et al. [16]. Therefore, TiO_2 can be reduced differently from its original surface properties through the addition of vanadium, and the oxidation states can be changed. In the case of V2p, it was difficult to divide because the peak was too small. Accordingly, the results were omitted from this study.

Fig. 8 shows the Ti peak of the catalyst-added MEA. As was the case for the V/TiO_2 catalyst, non-stoichiometric Ti species such as Ti^{3+} were observed. Moreover, as shown in Fig. 8(b), the V/TiO_2

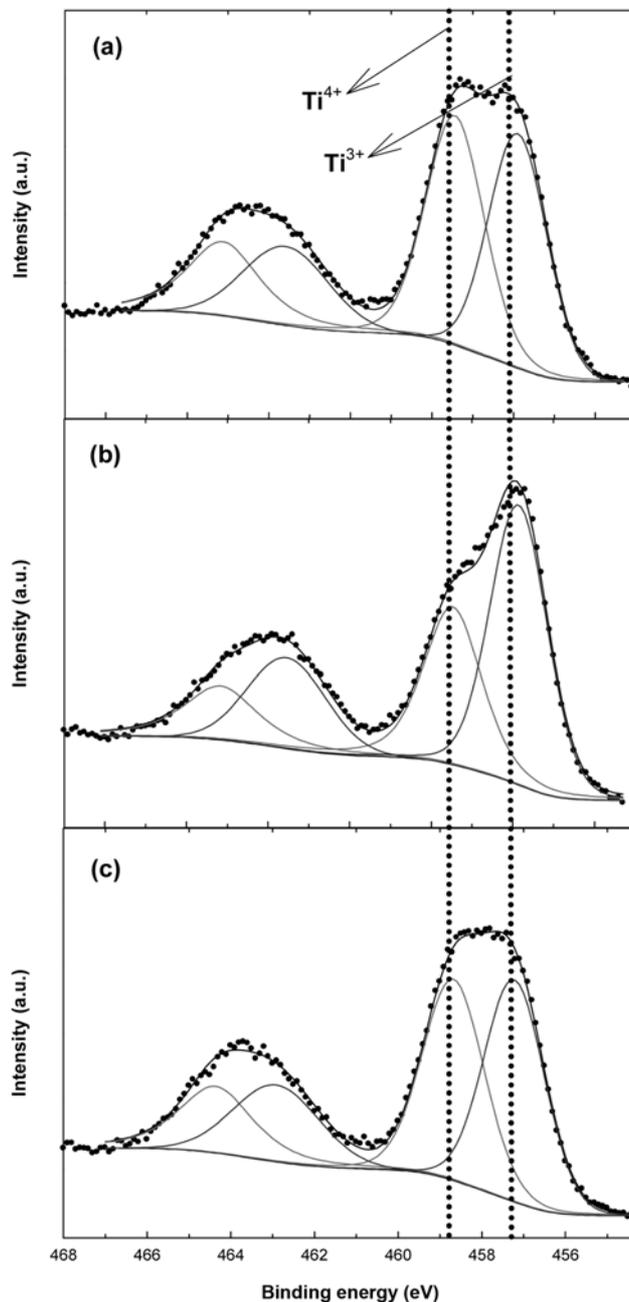


Fig. 8. Ti 2p spectra measured for different catalysts by XPS (a) V/TiO_2 (5% MEA), and (b) V/TiO_2 (10% MEA) and (c) V/TiO_2 (20% MEA).

(MEA 10%) catalyst had the greatest amount of non-stoichiometric species. To determine the quantities of these non-stoichiometric species, the following method was used to calculate the number of atoms per volume unit in all catalysts.

$$n=I/S \quad (3)$$

Where n is the number of electrons per unit volume (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 the atomic sensitivity constant, which can be deter-

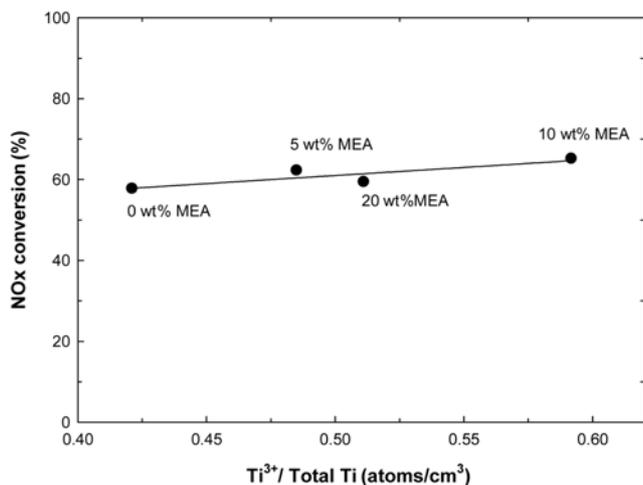


Fig. 9. The correlation between non-stoichiometric Ti species and NO_x conversion.

mined experimentally.

The number of atoms was compared with the NO_x conversion and the results are presented in Fig. 9. As shown in this figure, there was a close relationship between the formed non-stoichiometric species and the reaction activity. According to Choi et al. [17], the non-stoichiometric V and Ti species in the V/TiO₂ catalyst increase with an increase in the NO_x conversion, which agrees with the results of the present study.

Therefore, the enhanced redox characteristics demonstrated by the increase in the redox rate and the increase in the lattice oxygen, etc., was caused by the formation of non-stoichiometric species (Ti³⁺) in the catalyst, and this characteristic can lead to an increase in the reaction activity of the catalyst.

CONCLUSION

When preparing the V/TiO₂ catalyst, the catalyst produced with the addition of MEA had a higher SCR reaction activity than the catalyst produced with the addition OA. Also, each added neutralization reagent led to different activity levels, demonstrating that when producing the catalysts, both the pH and the added neutralization reagent influence the reaction activity of the catalyst. The optimal quantity of added MEA was shown to be 10 wt%, and the V/TiO₂ (MEA 10%) catalyst, which had the highest activity, also had the highest level of lattice oxygen and the fastest reoxidation rate. These improved redox properties were caused by the non-stoichi-

ometric Ti species, which resulted from the addition of MEA.

ACKNOWLEDGEMENTS

This research was supported by a grant (code #: 08K1501-01411) from the Center for Nanostructured Materials Technology under the 21st Century Frontier R&D Programs of the Ministry of Science and Technology, Korea.

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