Ammonium Ion Enhanced V$_2$O$_5$-WO$_3$/TiO$_2$ Catalysts for Selective Catalytic Reduction with Ammonia

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Abstract: Selective catalytic reduction (SCR) is the most efficient NO$_X$ removal technology, and the vanadium-based catalyst is mainly used in SCR technology. The vanadium-based catalyst showed higher NO$_X$ removal performance in the high-temperature range but catalytic efficiency decreased at lower temperatures, following exposure to SO$_X$ because of the generation of ammonium sulfate on the catalyst surface. To overcome these limitations, we coated an NH$_4^+$ layer on a vanadium-based catalyst. After silane coating the V$_2$O$_5$-WO$_3$/TiO$_2$ catalyst by vapor evaporation, the silanized catalyst was heat treated under NH$_3$ gas. By decomposing the silane on the surface, an NH$_4^+$ layer was formed on the catalyst surface through a substitution reaction. We observed high NO$_X$ removal efficiency over a wide temperature range by coating an NH$_4^+$ layer on a vanadium-based catalyst. This layer shows high proton conductivity, which leads to the reduction of vanadium oxides and tungsten oxide; additionally, the NO$_X$ removal performance was improved over a wide temperature range. These findings provide a new mothed to develop SCR catalyst with high efficiency at a wide temperature range.

Keywords: selective catalytic reduction; V-based catalyst; NO$_X$ removal efficiency; silane; ammonium

1. Introduction

Most energy is generated through the combustion of fossil fuels, which causes air pollution by emitting toxic pollutants, such as NO$_X$, particulate matter, SO$_X$, and CO [1,2]. Nitrogen oxides (NO, NO$_2$, and N$_2$O) are the most representative air pollutants because they are major causes of acid rain, photochemical smog, ozone depletion, and global warming [3–5]. NO$_X$ is emitted by automobiles, power stations, industrial heaters, and non-road vehicles. To reduce this form of pollution, NO$_X$ removal technologies must be developed. Many technologies have been developed to control NO$_X$ emissions, such as selective catalytic reduction (SCR), non-selective catalytic reduction (NSCR), and selective non-catalytic reduction (SNCR). Selective catalytic reduction (SCR), the most efficient NO$_X$ removal technology, selectively converts NO$_X$ in fuel gas into N$_2$ and H$_2$O. Compared with other technologies, such as non-selective catalytic reduction (NSCR) and selective non-catalytic reduction (SNCR), SCR shows a high NO$_X$ removal efficiency and no secondary pollutant emission and can be operated in the temperature range of 100–300 °C [4].

The V$_2$O$_5$-WO$_3$/TiO$_2$ catalyst has been commercially applied for SCR of NO$_X$ with NH$_3$ because of its good thermal stability, N$_2$ selectivity, and low SO$_2$ oxidation activity.
for conversion to SO$_2$ [6]. However, this catalyst shows high NO$_x$ removal performance only in the temperature range of 300–400 °C, and performance decreases at temperatures below 300 °C [7,8]. Therefore, many studies have been conducted to develop catalysts that function over a wide temperature range such as 200–420 °C. Djerad et al. increased the loading of V$_2$O$_5$ in WO$_3$/TiO$_2$ catalysts to improve NO$_x$ removal efficiency at lower temperatures [9,10]. A higher V$_2$O$_5$ content leads to increased catalytic activity but decreased N$_2$ selectivity and a narrow activation temperature range. Other researchers modified catalysts using transition metal oxides (Co, Mn, Ce, Cu, etc.) and rare-earth oxides (Eu, Sm, Nd, and Ho) [3,11–19]. For example, Wang et al. investigated the effect of adding Cu to a V$_2$O$_5$-WO$_3$/TiO$_2$ catalyst on low-temperature NH$_3$-SCR performance [20]. The added Cu oxides improved the catalytic activity of V$_2$O$_5$ by increasing the redox property of V$_2$O$_5$ (Cu$^{2+}$ + V$^{4+}$ ⇌ V$^{5+}$ + Cu$^+$), leading to a fast SCR reaction. GuO et al. modified Nd on MnOx catalysts to improve NH$_3$ SCR performance [21]. The catalytic activity and N$_2$ selectivity were enhanced by doping MnOx with a Nd catalyst. Although catalytic activity was improved at low temperatures (>300 °C), the catalytic performance decreased at temperatures above 400 °C. Therefore, covering a wide window temperature by modifying only the catalyst remains challenging. Another method for improving NO$_x$ removal technology at wide temperature ranges (200–420 °C) involves applying ammonium nitrate (NH$_4$NO$_3$) on the catalysts [22–24]. Chae et al. enhanced the catalytic performance of SCR of NO$_x$ at temperatures below 300 °C by injecting liquid ammonium nitrate on a V$_2$O$_5$-Sb$_2$O$_5$/TiO$_2$ catalyst. The injected ammonium nitrate led to a fast SCR and prevented the formation of ammonia bisulfate on the catalyst surface and catalytic deactivation by SO$_2$ at temperatures below 300 °C.

In this study, we enhanced the NO$_x$ removal efficiency and N$_2$ selectivity over a wide temperature range of 200–420 °C by improving the catalytic activity at temperatures below 300 °C. The catalyst surface was coated with a silane layer, and the silane molecules evaporated with heat treatment at 500 °C in NH$_3$ environment. The resulting catalyst surface was substituted with NH$_4^+$ layers present, and the NH$_4^+$ layers formed on the surface of the V$_2$O$_5$-WO$_3$/TiO$_2$ catalyst increased NO$_x$ removal efficiency at low temperatures (200–250 °C).

2. Materials and Methods

2.1. Catalyst Preparation

The NH$_4^+$-coated V$_2$O$_5$-WO$_3$/TiO$_2$ catalyst was prepared in three steps: first, V$_2$O$_5$-WO$_3$/TiO$_2$ was synthesized by the impregnation method, and then, the catalyst underwent vapor phase silane treatment at 180 °C for 1h. Finally, the silanized V$_2$O$_5$-WO$_3$/TiO$_2$ catalysts were heat treated under NH$_3$ gas with N$_2$ gas.

To synthesize 2 wt.% V$_2$O$_5$–10 wt.% WO$_3$/TiO$_2$, 8.800 g of TiO$_2$ powder (8.800 g, NANO Co., Ltd., Seoul, Korea, NT-01), 0.256 g of NH$_4$VO$_3$ (Sigma-Aldrich, St. Louis, MO, USA, 99.99%), 1.062 g of (NH$_4$)$_6$H$_2$W$_{12}$O$_{40}$ × H$_2$O (Sigma-Aldrich, St. Louis, MO, USA, 99.99%), and 0.386 g of oxalic acid were mixed with 100 mL of deionized water and stirred for 2 h. The solution in the mixture was evaporated at 85 °C in an oil bath for impregnation of V and W atoms followed by drying in an oven at 110 °C for 12 h. The dried powder was placed in a furnace and calcinated at 500 °C under atmospheric pressure.

Vapor phase silanization was conducted. First, the catalyst was cleaned by ozone treatment to remove any impurities and to increase hydroxyl species on the surface. The catalyst was placed in a sealed Teflon jar with 1.0 mL of Trichloro (1H, 1H, 2H, 2H-perfluorooctyl) silane (Sigma-Aldrich, 97%). The jar was subjected to 180 °C to vary the time. To coat the NH$_4^+$ on the catalyst, the silanized V$_2$O$_5$-WO$_3$/TiO$_2$ catalyst underwent heat treatment at 500 °C for 2 h upon purging a of NH$_3$ gas (300 ppm) for 2 h.

To observe the effect of the NH$_4^+$ layer on the commercial catalyst, we prepared commercial plate-type monoliths. The catalyst, consisting of V$_2$O$_5$, MoO$_3$, and TiO$_2$, was pasted on the wall of the plate, which had dimensions of 1 mm × 34 mm × 187 mm, and an
NH$_4^+$ layer coating was performed. After silane coating by vapor deposition, the catalysts were heat treated at 500 °C under 300 ppm NH$_3$ gas with N$_2$ gas for 2 h.

2.2. Catalyst Characterization

The effect of each preparation step on the catalyst morphology was investigated by field emission scanning electron microscopy (Hitachi, Tokyo, Japan, SU8020) at an accelerating voltage of 15.0 kV. The surface properties were determined by measuring the water contact angle using the static sessile drop method with a Contact angle analyzer (Phoenix 300, SEO, Suwon, Korea). The contact angle of the prepared catalysts (thickness = about 0.2 cm) was measured within 10 s after dropping water.

The crystallinity of and impurities in the catalysts were analyzed using X-ray diffraction (XRD, Rigaku, Tokyo, Japan, Ultima IV) with Cu K$_\alpha$ ($\lambda = 0.15406$ nm) radiation in the 2θ range of 10° to 80° at a scan rate of 1°/min. The Si and N elements in the catalysts were measured by X-ray photoelectron spectroscopy (XPS; Thermo VG Scientific, Waltham, MA, USA, K Alpha+) with Al K$_\alpha$ radiation; the binding energy of C1s was normalized to 284.8 eV. Fourier transform infrared spectroscopy (FT-IR, Varian Medical Systems, Palo Alto, CA, USA, 670 FTIR) was carried out over a wavelength range of 400–4000 cm$^{-1}$.

H$_2$-temperature-programmed reduction was carried out using an AutoChem II 2920 (Micromeritics Instrument Corp., Norcross, GA, USA). The samples were exposed to a current of 10% H$_2$/Ar and measured in the 200–900 °C temperature range.

2.3. Catalytic Activity Measurement

The NO$_X$ removal efficiency of the catalysts was evaluated in a fixed-bed reactor under high atmospheric pressure, with the sample placed on a stainless-steel tube and analyzed using a powder catalyst. The analysis temperature was varied from 150 °C to 420 °C, and the reactive gas was composed of 300 ppm NO$_X$, 300 ppm NH$_3$ (NH$_3$/NO$_X$ = 1.0), 300 ppm SO$_2$, and 5 vol.% of O$_2$, with a N$_2$ balance under a total flow rate of 500 sccm. The powder catalyst (0.35 g) was tested, and the gas hourly space velocity was set at 60,000 h$^{-1}$.

Plate-type commercial catalysts were evaluated in a microreactor. The analysis temperature was varied from 200 °C to 450 °C, and the reactive gas was composed of 240 ppm NO$_X$, 288 ppm NH$_3$ (NH$_3$/NO$_X$ = 1.2), 600 ppm SO$_2$, and 3 vol.% of O$_2$, with a N$_2$ balance under a total flow rate of 1.2 m$^3$/h; the area velocity was set to 25 m/h. The reactive gas concentration was determined by FT-IR (Gasmet, Vantaa, Finland, CX-4000) and gas analysis spectrometry (DSMXT, Heidelberg, Germany). NO$_X$ removal efficiency and N$_2$ selectivity were calculated according to Equations (1) and (2), respectively.

\[
\text{NO}_X \text{ removal efficiency (\%)} = \frac{\text{NO}_X \text{ inlet} - \text{NO}_X \text{ outlet}}{\text{NO}_X \text{ inlet}} \times 100, \tag{1}
\]

\[
\text{N}_2 \text{ selectivity (\%)} = \frac{\text{NO} \text{ inlet} - \text{NO} \text{ outlet} - \text{NO}_2 \text{ outlet} - \text{N}_2\text{O} \text{ outlet}}{\text{NO} \text{ inlet} - \text{NO} \text{ outlet}} \times 100, \tag{2}
\]

3. Results

Figure 1 illustrates the process of producing the NH$_4^+$ layer on the V$_2$O$_5$-WO$_3$/TiO$_2$ catalysts. The surface of the synthesized V$_2$O$_5$-WO$_3$/TiO$_2$ catalysts is hydrophilic because of the presence of numerous oxygen groups. After the catalysts were silanized at 180 °C for 1 h, the surface properties became hydrophobic because of the hydrophobic agent in silane [25]. When the catalysts were heat treated at 500 °C under 300 ppm NH$_3$ gas with N$_2$ gas for 2h, the silane molecules underwent thermal decomposition. Subsequently, the catalyst surface acquired NH$_4^+$ on their active sites. As a result, the V$_2$O$_5$-WO$_3$/TiO$_2$ catalysts were covered with NH$_4^+$ layers, generating hydrophilic surface properties.
Figure 1. Schematic illustration of V\textsubscript{2}O\textsubscript{5}-WO\textsubscript{3}/TiO\textsubscript{2}, silanized V\textsubscript{2}O\textsubscript{5}-WO\textsubscript{3}/TiO\textsubscript{2}, and heat-treated V\textsubscript{2}O\textsubscript{5}-WO\textsubscript{3}/TiO\textsubscript{2} with NH\textsubscript{4}\textsuperscript{+} layer coating.

The surface properties and morphology of the prepared catalysts were investigated using a scanning electron microscopy, and contact angle measurements. Figure 2a,d show the V\textsubscript{2}O\textsubscript{5}-WO\textsubscript{3}/TiO\textsubscript{2} catalysts without treatment. Figure 2b,c,e,f show the results obtained for the catalyst after silane treatment and the following heat treatment, respectively. To observe the surface properties, we dropped water on the surface of the prepared SCR catalyst powders; the microscope observation results are shown in Figure 2a–c. Water that dropped on the surface was immediately absorbed into the original V\textsubscript{2}O\textsubscript{5}-WO\textsubscript{3}/TiO\textsubscript{2} catalyst. The inset image shows the results of static contact angle measurement. The observed contact angle was approximately 2°, indicating that the catalysts were hydrophilic. After silane treatment of the V\textsubscript{2}O\textsubscript{5}-WO\textsubscript{3}/TiO\textsubscript{2} catalyst, the water did not spread on the surface but rather formed a drop on the surface with a contact angle of approximately 160°. As the hydrophobic agent in silane covered the catalyst, the surface became hydrophobic [26]. However, the surface properties became hydrophilic after heat treating the catalyst at 500 °C for 2 h under NH\textsubscript{3} gas. This is because the silane molecules are thermally decomposed at a high temperature (e.g., 500 °C). Subsequently, NH\textsubscript{3} can react to the active sites of catalyst and form NH\textsubscript{4}\textsuperscript{+} on the surface as a monolayer. Although the surface properties were changed by each process, the catalyst morphologies (Figure 2d–f), catalyst contents, and the textural properties (Table 1) were not changed because the prepared silane and NH\textsubscript{4}\textsuperscript{+} layers are quite thin.

Figure 2. Microscope images of V\textsubscript{2}O\textsubscript{5}-WO\textsubscript{3}/TiO\textsubscript{2} (a), silanized V\textsubscript{2}O\textsubscript{5}-WO\textsubscript{3}/TiO\textsubscript{2} (b), and heat-treated V\textsubscript{2}O\textsubscript{5}-WO\textsubscript{3}/TiO\textsubscript{2} (c) (insets are contact angle measurement). The red circle marks the location where the water is absorbed on the catalyst. SEM images of V\textsubscript{2}O\textsubscript{5}-WO\textsubscript{3}/TiO\textsubscript{2} (d), silanized V\textsubscript{2}O\textsubscript{5}-WO\textsubscript{3}/TiO\textsubscript{2} (e), and heat-treated V\textsubscript{2}O\textsubscript{5}-WO\textsubscript{3}/TiO\textsubscript{2} (f).
Table 1. X-ray fluorescence analysis and Brunauer-Emmet-Teller (BET) results of the V$_2$O$_5$-WO$_3$/TiO$_2$, silanized V$_2$O$_5$-WO$_3$/TiO$_2$, and heat-treated V$_2$O$_5$-WO$_3$/TiO$_2$ catalyst.

| Sample                  | Chemical Composition (wt.%) | $S_{BET}$ (m$^2$/g) | Pore Volume (cm$^3$/g) | Pore Size (nm) |
|-------------------------|----------------------------|---------------------|------------------------|---------------|
| V$_2$O$_5$/TiO$_2$      | 87.53 2.03 10.04 0.40      | 68.86               | 0.28                   | 15.94         |
| Silanized V$_2$O$_5$/TiO$_2$ | 87.32 2.05 10.02 0.61    | 65.54               | 0.21                   | 12.95         |
| Heat-treated V$_2$O$_5$/TiO$_2$ | 87.53 1.98 9.99 0.50 | 66.39               | 0.24                   | 14.17         |

The crystalline structures of the prepared catalysts were determined using XRD (Figure 3a), which clearly showed anatase TiO$_2$, whereas peaks for V$_2$O$_5$ and WO$_3$ were not observed in any samples. This is because the V$_2$O$_5$ and WO$_3$ catalysts with small nanoparticle sizes were uniformly coated on the TiO$_2$ support, and the peaks of the V$_2$O$_5$ and WO$_3$ catalysts were hard to detect using XRD [27]. Furthermore, the peak intensities and positions were similar for all catalysts, indicating that silane and heat treatments under NH$_3$ gas did not affect the crystallinity of the V$_2$O$_5$-WO$_3$/TiO$_2$ catalyst.

To observe the silane layer and difference in chemical bonding in the catalyst after the heat-treatment process, XPS analysis was conducted (Figure 3b–d). Figure 3b shows the survey peaks in the XPS spectra. The XPS spectra of the Si 2p peak of the V$_2$O$_5$-WO$_3$/TiO$_2$ catalyst (black line), silanized V$_2$O$_5$-WO$_3$/TiO$_2$ catalyst (blue line), and following catalyst after heat treatment (red and green lines) are shown in Figure 3c. In the V$_2$O$_5$-WO$_3$/TiO$_2$ catalyst, no Si 2p peak was observed. After silane treatment, silicon atoms appeared at low binding energy (102 eV), indicating that silane was coated on the V$_2$O$_5$-WO$_3$/TiO$_2$ catalyst. However, the peaks at 102 eV disappeared after heat treatment of the silanized V$_2$O$_5$-WO$_3$/TiO$_2$ catalyst, indicating that the coated silane had decomposed at temperatures over 500 °C. By contrast, binding energies near 401 and 399 eV were observed for the heat-treated V$_2$O$_5$-WO$_3$/TiO$_2$ catalyst. The intensity of V$_2$O$_5$-WO$_3$/TiO$_2$ catalyst and silanized V$_2$O$_5$-WO$_3$/TiO$_2$ catalyst were lower, but the intensity was larger for the heat-treated V$_2$O$_5$-WO$_3$/TiO$_2$ catalyst. The binding energies were attributed to the neutral amine’s residual on the surface and NH$_4^+$, respectively, from the flowing NH$_3$ gas during the heat-treatment process [28,29]. The NH$_2$ peak at around 399 eV came from the use of ammonium-based precursors of V and W, and the NH$_2$ peak is observed in all samples.

Table 2. Atomic percent of element obtained from XPS spectra of the V$_2$O$_5$-WO$_3$/TiO$_2$, silanized V$_2$O$_5$-WO$_3$/TiO$_2$, heat-treated V$_2$O$_5$-WO$_3$/TiO$_2$ catalyst.

| Sample                  | Element (at.%) |
|-------------------------|----------------|
|                         | N  | O  | Si | F  | C  | S  | V  | W  | Ti |
| VW/TiO$_2$              | 0.40 | 52.47 | -  | -  | 18.28 | 0.53 | 1.55 | 1.82 | 24.95|
| Silanized VW/TiO$_2$    | 0.31 | 45.90 | 0.24 | 12.89 | 19.91 | 0.24 | 1.28 | 1.36 | 17.89|
| Heat-treated VW/TiO$_2$ | 0.79 | 56.44 | -  | -  | 18.06 | 0.61 | 1.34 | 1.80 | 20.96|
Figure 3. (a) XRD patterns and XPS spectra for (b) survey, (c) Si 2p, and (d) N 1s of V2O5-WO3/TiO2 (black line), silanized V2O5-WO3/TiO2 (blue line), and heat-treated V2O5-WO3/TiO2 (red line).

The NOx removal efficiency and N2 selectivity following the formation of the NH4+ layer on the surface of the V2O5-WO3/TiO2 catalyst were measured in a fixed bed (Figure 4). Figure 4a shows the NOx removal efficiency of the prepared samples, which were higher for the silanized catalyst and heated silanized catalyst than for the original V2O5-WO3/TiO2 catalyst below 300 °C. The catalytic performance of the silanized V2O5-WO3/TiO2 catalyst improved from 45% to 60%, particularly at 200 °C. Figure 4b shows the N2 selectivity; a trace amount of N2O in the prepared catalyst was produced at 300 °C. The trend in N2 selectivity was similar to the NOx removal efficiency, and the heat-treated V2O5-WO3/TiO2 catalyst showed a higher N2 selectivity at 420 °C. Sulfur in the fuel deactivated the catalyst through the poisoning effect, specifically in the low-temperature range (below 300 °C). When vanadium catalysts are exposed to SOx, ammonium bisulfate (NH4HSO4) and ammonium sulfate ((NH4)2SO4) are formed on the catalyst surface, decreasing efficiency [24]. The hydrophobic properties of the coated silane prevent the formation of ammonium sulfate on the V2O5-WO3/TiO2 catalyst surface, enhancing the NOx removal efficiency at low temperatures. Interestingly, the NOx removal efficiency of the silanized catalyst after heat treatment was higher than that of the silanized and original catalysts. The NH4+ intermediates in the catalyst exhibit high catalytic activity and proton conductivity in NH3 SCR, particularly in the low-temperature range. Therefore, the NH4+ layer on the catalyst produced by silane and heat treatments leads to enhanced NOx removal efficiency at low temperatures, specifically at 250 °C, because of the higher proton conductivity and reactivity [30], whereas silane is decomposed and reacts with NH3 at over 300 °C in the reaction gas during fixed bed evaluation, and some NH4+ is produced on the catalyst surface. Therefore, the silanized and heat-treated V2O5-WO3/TiO2 catalysts show similar catalytic performances at high temperatures (>300 °C). Note that there was no significant difference in the NOx removal efficiency and N2 selectivity between V2O5-WO3/TiO2 and heat-treated V2O5-WO3/TiO2 without a silane coating process in the temperature range of 150–420 °C (Figure S1). This results demonstrate that silane coating is a key process to prepare ammonium ion enhanced V2O5-WO3/TiO2 catalysts.
The formed NH$_4^+$ layer and acid sites were analyzed using FT-IR spectra, as shown in Figure 5a–c. Si-CH$_2$ and Si-O-Si bond peaks only appeared at 1250 and 1216 cm$^{-1}$, respectively, in the silanized V$_2$O$_5$-WO$_3$/TiO$_2$ catalyst (Figure 5b). After heat treatment, the peaks related to Si (e.g., 1250 and 1216 cm$^{-1}$) disappeared while various peaks related to NH$_4^+$ started to appear in the range of 1400 to 1600 cm$^{-1}$. Furthermore, the peak near 3300 cm$^{-1}$ corresponds to N–H stretching (Figure 5c). According to these results, the coated silane layer disappeared during heat treatment, and a new NH$_4^+$ layer was generated after the decomposition of Si atoms on the surface. To investigate the redox properties of the prepared catalysts depending on the silane treatment and formation of the NH$_4^+$ layer, we analyzed the H$_2$-temperature-programmed reduction profiles (Figure 5d). V$_2$O$_5$-WO$_3$/TiO$_2$ exhibited three reduction peaks at 397.1 °C, 480.2 °C, and 800.8 °C, which were assigned to the reduction of V$^{5+}$ to V$^{3+}$ in the vanadium oxides, the reduction of W$^{6+}$ to W$^{4+}$, and the reduction of W$^{4+}$ to W$^0$ in the tungsten oxide, respectively [31–33]. After coating the NH$_4^+$ layer on the V$_2$O$_5$-WO$_3$/TiO$_2$ catalyst surface, the reduction peaks shifted to lower temperatures of 385.6 °C, 461.2 °C, and 778.7 °C, respectively. As the NH$_4^+$ layer on the surface has high proton conductivity and activity, the active materials reduced a larger amount of NOX.

To investigate the effect of the NH$_4^+$ layer under actual conditions, we applied the NH$_4^+$ layer on the commercial catalyst (Figure 6). Figure 6a shows a plate-type commercial catalyst containing V$_2$O$_5$, MoO$_3$, TiO$_2$, etc. (Table S2), which is used in electric power stations to reduce NOX gas emissions. The catalyst surface was hydrophilic, similar to the power type of the catalyst (Figure 6b). Silane treatment was conducted by the vapor evaporation method, and the surface became hydrophobic (Figure 6c). Finally, after heat treating the silanized catalysts at 500 °C for 2h under NH$_3$ gas with N$_2$ gas, the surface properties were hydrophilic because of decomposition of the silane layer and because of coating the NH$_4^+$ layer on the catalyst surface (Figure 6d).
Figure 5. Fourier transform infrared spectra (a–c) and H2-temperature-programmed reduction (d) of V2O5-WO3/TiO2 (black line), silanized V2O5-WO3/TiO2 (blue line), and heat-treated V2O5-WO3/TiO2 (red line).

Figure 6. Microscope image of plate-type commercial catalyst (a), commercial catalyst surface (b), silanized commercial catalyst surface (c), and heat-treated commercial catalyst surface (d) after dropping water.
The prepared plate-type commercial catalysts were evaluated in a microreactor from 200 °C to 450 °C, as shown in Figure 7. The commercial catalysts exhibited a lower NOX removal efficiency at 200 °C, which gradually increased to 400 °C. The commercial catalyst specialized in high temperature range over 300 °C because it used an electric power plant. Therefore, the NOX removal efficiency is not largely changed at high temperature. After forming the NH4+ layer on the catalyst, the NOX removal efficiency was enhanced over a wide window range from 200 °C to 450 °C, particularly at 200 °C. Usually, the catalytic efficiency deteriorated at lower temperature due to generating ammonium sulfate on the catalyst surface. However, the formed NH4+ layer has high proton conductivity, which leads to the reduction of vanadium oxides and tungsten oxide, and improved the NOX removal efficiency.

![Image of NOx removal efficiency](https://www.mdpi.com/article/10.3390/nano11102677/s1, Figure S1: NOx removal efficiency (a) and N2 selectivity (b) of V2O5-WO3/TiO2 without the silane coating process (red line). Reaction conditions: [NO] = 300 ppm, [NH3] = 288 ppm, [SO2] = 600 ppm, [O2] = 3 vol.%, [area velocity] = 25 m/h.

**Figure 7.** NOx removal efficiency of V2O5-WO3/TiO2 (black line) and heat-treated V2O5-WO3/TiO2 (red line). Reaction conditions: [NO] = 240 ppm, [NH3] = 288 ppm, [SO2] = 600 ppm, [O2] = 3 vol.%, [area velocity] = 25 m/h.

**4. Conclusions**

We investigated the effect of coating of V2O5-WO3/TiO2 catalysts with an NH4+ layer through heat treatment of silanized catalysts at 500 °C under NH3 gas with N2 gas. The silane molecules were substituted with NH4+ by decomposing the silane layer on the surface. V2O5-WO3/TiO2 catalysts with an NH4+ layer showed an increased NOX removal efficiency over a wide temperature range (150–420 °C) compared with the V2O5-WO3/TiO2 catalysts. Particularly, the performance was improved at low temperatures (<300 °C). The coated NH4+ layer led to enhanced proton conductivity and promoted further reduction of vanadium oxides and tungsten oxide. The V2O5-WO3/TiO2 catalysts with an NH4+ layer exhibited improved SCR performance. These results may contribute to future studies on SCR catalysts and other catalyst systems.

**Supplementary Materials:** The following are available online at https://www.mdpi.com/article/10.3390/nano11102677/s1, Figure S1: NOX removal efficiency (a) and N2 selectivity (b) of V2O5-WO3/TiO2 without the silane coating process (red line). Reaction conditions: [NO] = 300 ppm, [NH3] = 300 ppm, [SO2] = 600 ppm, [O2] = 5 vol.%, and GHSV = 60,000 h⁻¹. Table S1: Atomic percent of elements obtained from the XPS spectra of the heat-treated V2O5-WO3/TiO2 catalyst without silane coating process. Table S2: X-ray fluorescence analysis of the commercial plate-type monoliths.

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