

Nitration-Promoted Vanadate Catalysts for Low-Temperature Selective Catalytic Reduction of NO_x with NH₃

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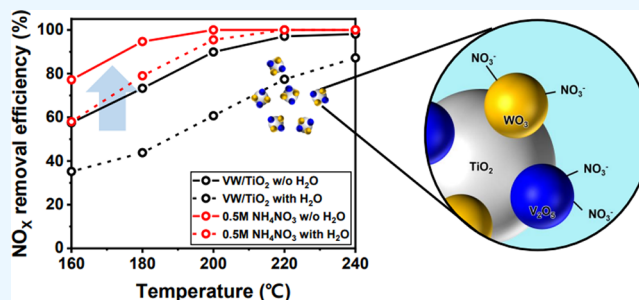


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ABSTRACT: Vanadium-based catalysts have been commercially used in selective catalytic reduction (SCR), owing to their high catalytic activity and effectiveness across a wide temperature range; however, their catalytic efficiency decreases at lower temperatures under exposure to SO_x. This decrease is largely due to ammonium sulfate generation on the catalyst surface. To overcome this limitation, we added ammonium nitrate to the V₂O₅-WO₃/TiO₂ catalyst, producing a V₂O₅-WO₃/TiO₂ catalyst with nitrate functional groups. With this approach, we found that it was possible to adjust the amount of these functional groups by varying the amount of ammonium nitrate. Overall, the resultant nitrate V₂O₅-WO₃/TiO₂ catalyst has large quantities of NO₃⁻ and chemisorbed oxygen, which improves the density of Brønsted and Lewis acid sites on the catalyst surface. Furthermore, the nitrated V₂O₅-WO₃/TiO₂ catalyst has a high NO_x removal efficiency and N₂ selectivity at low temperatures (i.e., 300 °C); this is because NO₃⁻ and chemisorbed oxygen, generated by nitrate treatment, facilitated the occurrence of a fast SCR reaction. The approach outlined in this study can be applied to a wide range of SCR catalysts, allowing for the development of more, low-temperature SCR catalysts.



1. INTRODUCTION

Recently, due to anthropogenic activity, NO_x, SO_x, carbon oxides, volatile organic compounds (VOCs), and particulate matter (PM) emissions have increased.^{1,2} Specifically, nitrogen oxides (i.e., NO, NO₂, and N₂O) are extremely hazardous air pollutants, which have been linked to many environmental issues (e.g., acid rain, smog, and ozone depletion) that can directly impact human health. Thus, many nations and governments have strengthened their emission regulation policies to control nitrogen oxide emissions.³ Several processes have been proposed to either eliminate or control nitrogen oxide emissions: for example, selective catalytic reduction (SCR), selective noncatalytic reduction, and non-selective catalytic reduction.^{4–8} Among these technologies, SCR is the most advanced and efficient; it works by converting NO_x in exhaust gas into N₂ and H₂O, using ammonia (NH₃) as a reducing agent.^{9–11} This technology can reduce up to 60–90% of NO_x in exhaust gas, contain secondary pollutant emission, and can operate at a relatively low temperature (~350 °C).¹² Many transition-metal catalysts have been used for SCR reactions, such as vanadium, tungsten, copper, iron, and manganese oxides. Among these, V-based catalysts (V₂O₅-WO₃ or MoO₃/TiO₂) have been commercially adopted due to their lower ability to oxidize SO₂ to SO₃; additionally, these catalysts exhibit greater catalytic activity, compared to other transition-metal catalysts.^{13–15} However, this catalytic activity is limited to the temperature range of 300–400 °C and decreases at lower temperatures (below 300 °C).¹⁶

Currently, there are methods for enhancing V-based catalyst activity at low temperatures, the first of which entails the use of an Mn-based catalyst. Kapteijn et al. have demonstrated the high catalytic activity of MnO_x at low temperatures. Additionally, MnO₂ can achieve its highest efficiency through MnO_x catalyst synthesis by controlling the oxidation states of manganese.¹⁷ However, this is limited by Mn sulfate formation when in contact with SO₂, owing to its low sulfur resistance. The second method involves adjusting the carbon material. Zhu et al. fabricated activated carbon (AC)-supported vanadium catalysts that achieved high SCR activity and resistance to SO₂ deactivation.¹⁸ Li et al. designed carbon nanotube (CNT)-containing V₂O₅/TiO₂ catalysts, which increased the specific area, pore volume, acidity, and reducibility; the catalyst added with 10 wt % CNT exhibited excellent activity in NO SCR at 100–300 °C.¹⁹ However, the commercialization of these catalysts within the context of industrial settings is difficult. This is because exhaust gas contains large amounts of sulfur and water, which deactivates Mn and causes the carbon material to thermally decompose.²⁰

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Recently, many researchers have attempted to control catalyst surface functional groups to improve their activity at low temperatures.^{21–24} For example, Zhao et al. reported that V₂O₅/TiO₂ catalyst NO_x removal efficiency reached 90% at 210 °C by co-doping with S and N.²⁵ These catalysts cause the formation of O₂ active sites, which drive the SCR reaction. Additionally, these catalysts have been linked to a large surface area and greater quantities of chemisorbed oxygen and NH₃. In addition, S and N inhibit TiO₂ during transformation to the rutile phase. Maqbool et al. prepared CeO₂-added Sb/V₂O₅/TiO₂ catalysts that were pretreated with SO₂ under oxidizing conditions.²⁶ These catalysts formed sulfate species on the surface and had high NH₃-desorption and catalytic performance when containing SO₂ because of the formation of more cerium(III) sulfate. Although many researchers have studied V-based catalysts to improve the catalytic performance at low temperatures by controlling catalyst functional groups, previous studies have not attained results that can be easily applied in a commercial context.

In this study, we introduced a simple method to control the functional groups on a vanadium-based catalyst surface. Specifically, we added ammonium nitrate (NH₄NO₃) to the V₂O₅-WO₃/TiO₂ catalyst and investigated nitrate-treated V₂O₅-WO₃/TiO₂ catalyst effectiveness under SCR conditions. The functional groups on the V₂O₅-WO₃/TiO₂ catalyst were controlled by controlling the amount of ammonium nitrate that was added. These catalytic processes were characterized through X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and Fourier transform infrared spectroscopy (FTIR).

2. MATERIALS AND METHODS

2.1. Catalyst Preparation. V₂O₅-WO₃/TiO₂ catalysts with NH₄NO₃ were prepared using an impregnation method. NH₄VO₃ (0.128 g, Sigma-Aldrich, 99.99%) and (NH₄)₆H₂W₁₂O₄₀ × H₂O (0.531 g, Sigma-Aldrich, 99.99%) were dissolved in 50 mL of deionized water with 0.1959 g of oxalic acid, which acted as a solubility agent. Then, NH₄NO₃ was then added to the prepared mixture at varying concentrations (i.e., 0, 0.03, 0.05, and 0.08 M, respectively); the resultant mixtures were denoted VW/TiO₂, 0.03 M NH₄NO₃, 0.05 M NH₄NO₃, and 0.08 M NH₄NO₃, respectively. TiO₂ powder (4.400 g, NANO Co., Ltd., NT-01) was added to the prepared solution, and the mixture was stirred for 2 h. The solution was evaporated at 85 °C in an oil bath and placed in an oven at 110 °C for 12 h, and the resultant powders were then calcinated at 500 °C in a furnace for 5 h under atmospheric pressure.

2.2. Catalyst Characterization. The sample surface morphologies and elemental compositions were investigated using field-emission scanning electron microscopy (model: SU8020/Hitachi, Tokyo, Japan), transmission electron microscopy (TEM, model: JEM-2100F/JEOL Ltd., Tokyo, Japan), and electron energy loss spectroscopy (EELS) at an accelerating voltage of 10.0 kV. Textural properties were analyzed using the Brunauer–Emmett–Teller method (BET, model: ASAP2020/Micromeritics Instrument Corp., Norcross, USA). Catalyst chemical compositions were determined using X-ray fluorescence spectrometry (XRF; Zetium; Malvern Panalytical, Malvern, UK). We analyzed the extent of crystallinity using X-ray diffraction (XRD, model: Ultima IV/Rigaku, Tokyo, Japan) with Cu K α (λ = 0.15406 nm) radiation in the 2θ range from 20–80° at a 1°/min scan rate. X-ray

photoelectron spectroscopy (XPS, model: K Alpha+/Thermo Scientific, Waltham, USA) was conducted with Al K α radiation to confirm the sample oxidation states, and C 1s binding energy was normalized as 284.8 eV. Catalyst reduction properties were measured by NH₃-temperature-programmed desorption (NH₃-TPD, model: AutoChem II 2920/Micromeritics Instrument Corp., Norcross, USA). The samples were pretreated at 150 °C in a current of N₂ for 4 h to remove physisorbed NH₃ species and organic matter, and NH₃ was then adsorbed with 10% NH₃/He gas at 150 °C for 1 h. The TPD experiment was conducted under 100–900 °C. An H₂-temperature-programmed reduction (H₂-TPR, model: AutoChem II 2920/Micromeritics Instrument Corp., Norcross, USA) experiment was conducted, during which the samples were immersed in a current of 10% H₂/Ar at 150–900 °C.

2.3. Catalytic Activity Evaluation. The catalyst NO_x removal efficiencies were evaluated in a fixed-bed reactor under high atmospheric pressure, with each sample placed in a stainless-steel tube and analyzed using a powder catalyst. The temperatures under which the samples were analyzed varied from 150–350 °C, and the reactive gas consisted of 300 ppm NO_x, 300 ppm NH₃ (NH₃/NO_x = 1.0), 300 ppm SO₂, and 5 vol % of O₂, with N₂ 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. Commercial plate-type catalysts were evaluated in a microreactor. The temperatures under which the catalysts were evaluated varied from 160–240 °C, and the reactive gas consisted of 300 ppm NO_x, 300 ppm NH₃ (NH₃/NO_x = 1.2), 300 ppm SO₂, and 5 vol % of O₂, with N₂ balance under a total flow rate of 1.2 m³/h; the area velocity was set to 10 m/h. The in situ FTIR spectra of all samples were measured using an FTIR spectrometer (VERTEX 70v FTIR; Bruker, Billerica, MA, USA) under operating conditions and 16 scans with a resolution of 4 cm⁻¹ in the 3900–1200 cm⁻¹ range. A mixture of NH₃ (500 ppm), NO (500 ppm), and O₂ (5 vol %) with N₂ was used for in situ FTIR, and the flow rate was 0.3 L/min.

3. RESULTS AND DISCUSSION

To analyze the nitrated surface impact on the V₂O₅-WO₃/TiO₂ catalysts, XRD measurements were performed, and the diffraction patterns are shown in Figure S1. All the prepared catalysts were detected only as anatase TiO₂ signals through XRD. These anatase peaks at around 2θ = 25°, 38°, 48°, 54°, 55°, 63°, 69°, 70°, and 75° were matched to phase (1 0 1), (0 0 4), (2 0 0), (1 0 5), (2 1 1), (2 0 4), (1 1 6), (2 2 0), and (2 1 5) diffractions (JCPDS card no. 21-1272), respectively. However, V₂O₅ and WO₃ signals were not observed in the XRD results because small amounts of V₂O₅ and WO₃ with low concentrations were uniformly dispersed on TiO₂.²⁷ The gross elemental composition (wt %) XRF analyses for the prepared catalyst are shown in Table 1. This table clearly indicates the presence of vanadium and W, as inferred from the XRD results. Moreover, ammonium nitrate did not affect V₂O₅-WO₃/TiO₂ catalyst crystallinity. This is because NH₄NO₃ is not substituted in the V₂O₅-WO₃/TiO₂ crystal but is in the ionic state on the catalyst surface.

The prepared nitrate-treated 0.03, 0.05, and 0.08 M V₂O₅-WO₃/TiO₂ catalyst morphologies were observed via SEM, and the resultant images are shown in Figures 1a and S1a,b. All the catalysts exhibited similar morphologies with similar particle sizes and shapes, ranging from 15–50 nm. Ammonium nitrate treatment did not cause particle agglomeration and sustained

Table 1. X-ray Fluorescence Analysis Results of the V₂O₅-WO₃/TiO₂, 0.03 M NH₄NO₃, 0.05 M NH₄NO₃, and 0.08 M NH₄NO₃ Added V₂O₅-WO₃/TiO₂ Catalysts, Respectively

sample	chemical composition (wt %)			
	TiO ₂	WO ₃	V ₂ O ₅	SO ₃
VW/TiO ₂	87.35	10.04	2.03	0.58
0.03 M NH ₄ NO ₃	87.63	9.83	2.02	0.52
0.05 M NH ₄ NO ₃	87.65	9.87	1.94	0.54
0.08 M NH ₄ NO ₃	87.31	9.98	2.03	0.67

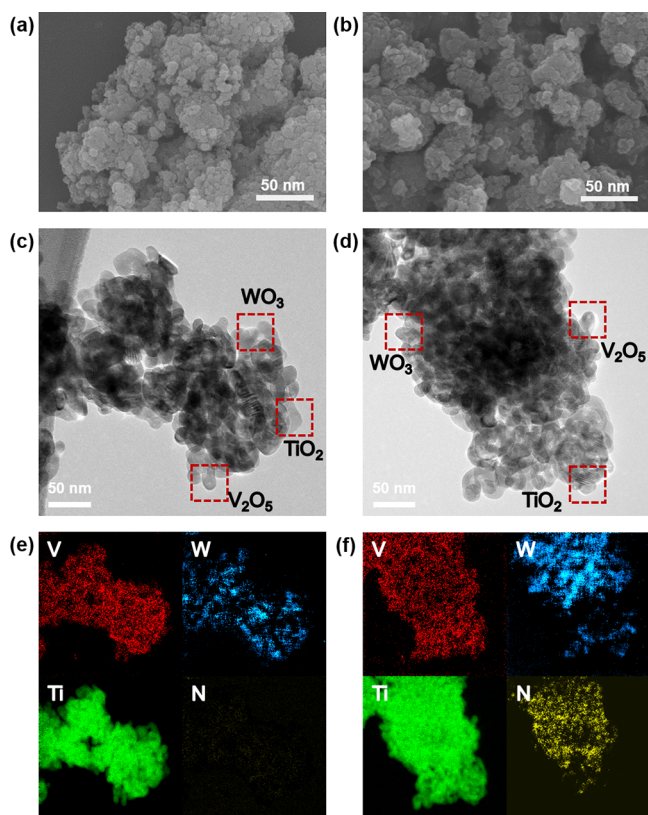


Figure 1. SEM image of (a) V₂O₅-WO₃/TiO₂ and (b) 0.05 M NH₄NO₃ added V₂O₅-WO₃/TiO₂ catalyst. TEM images of (c) V₂O₅-WO₃/TiO₂ and (d) 0.05 M NH₄NO₃ added V₂O₅-WO₃/TiO₂ catalyst. EELS elemental mapping of V, W, Ti, and N of (e) V₂O₅-WO₃/TiO₂ and (f) 0.05 M NH₄NO₃ added V₂O₅-WO₃/TiO₂ catalyst.

the uniform shape of the VW/TiO₂ catalysts. TEM and EELS elemental mapping were conducted to observe the synthesized catalysts in detail (Figure 1c,d). The catalyst particles were composed of V₂O₅ and WO₃ nanoparticles on TiO₂ supports. The nitrate-treated 0.05 M V₂O₅-WO₃/TiO₂ catalysts were uniformly distributed on TiO₂ supports without agglomeration, which was confirmed by EELS mapping. The red and blue lines in the mapping images indicate V and W, respectively, and the elements are evenly distributed on the TiO₂ support. Consequently, the nitrate treatment process was not affected by catalyst morphology. Interestingly, N (yellow color) was only observed in the nitrate-treated 0.05 M V₂O₅-WO₃/TiO₂ catalysts. These results confirm that ammonium nitrate was adsorbed on the surface of the V₂O₅-WO₃/TiO₂ catalysts, as shown in the scheme (Figure S1).

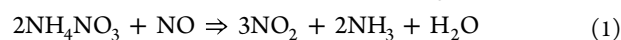
The textural properties, such as specific surface areas, pore volumes, and pore sizes of the prepared catalysts, as well as the

V₂O₅, WO₃, and TiO₂ weight fractions, are shown in Table 2. As ammonium nitrate was added to the V₂O₅-WO₃/TiO₂

Table 2. Brunauer–Emmett–Teller (BET) Results of the V₂O₅-WO₃/TiO₂, 0.03 M NH₄NO₃, 0.05 M NH₄NO₃, and 0.08 M NH₄NO₃ Added V₂O₅-WO₃/TiO₂ Catalysts, Respectively

sample	S _{BET} (m ² /g)	pore volume (cm ³ /g)	pore size (nm)
VW/TiO ₂	66.05	0.24	13.49
0.03 M NH ₄ NO ₃	67.27	0.24	13.16
0.05 M NH ₄ NO ₃	67.46	0.24	12.98
0.08 M NH ₄ NO ₃	65.42	0.19	12.08

catalyst, the surface area and pore properties did not change significantly. However, the properties decreased when adding 0.08 M ammonium nitrate, and we assumed that the ions block the pores of the catalyst surface. To better scrutinize the V₂O₅-WO₃/TiO₂ catalyst nitrated surface chemical state, XPS analysis was conducted (Figure 2). Figure 2 shows the XPS survey peaks. The N 1s spectrum exhibited two main peaks, that is, NH₂ at approximately 399 eV and NO₃⁻ at approximately 402 eV, which were attributed to the neutral amine residual on the surface and NO₃⁻ (Figure 2b).²⁸ The NH₂ peak at approximately 399 eV originated from the ammonium-based precursors of V and W (ammonium metavanadate and ammonium metatungstate hydrate); therefore, the NH₂ peak was observed in all samples. However, the NO₃⁻ peak at approximately 402 eV originates from the V₂O₅-WO₃/TiO₂ catalyst nitrated surface. No signal was observed for the NO₃⁻ peak of the V₂O₅-WO₃/TiO₂ catalysts. However, the intensity of the 0.03 M NH₄NO₃ catalyst increased slightly and 0.05 and 0.08 M NH₄NO₃ catalysts increased remarkably. These results were commonly observed for O 1s in the XPS results (Figure 2c). The O 1s peaks can be fitted to three different peaks, i.e., NO₃⁻ at around 531.2 eV, chemisorbed oxygen (O_α) at around 529.8 eV, and lattice oxygen (O_β) at around 528.4 eV.²⁹ The NO₃⁻, O_α, and O_β ratios are shown in Table 3. When NH₄NO₃ was added, the intensities of the NO₃⁻ and chemisorbed oxygen peaks increased simultaneously, and the 0.08 M NH₄NO₃ catalyst had a higher ratio of O_α (61.18) and NO₃⁻ (22.70). O_α and NO₃⁻ are very important factors in SCR reaction. Surface chemisorbed oxygen plays a crucial role in the oxidation of NH₄⁺ in SCR because it is more movable than lattice oxygen and boosts the oxidation of NO to NO₂.^{30–33} In addition, nitrate species can react with NO to form more NO₂ according to eq 1.²⁷



Therefore, the presence of O_α and NO₃⁻ induces “fast SCR”, and the concentrations of O_α and NO₃⁻ are important for SCR reaction.³² V 2p is mainly composed of V⁵⁺ and V⁴⁺, and the two fitted peaks at approximately 516.8 and 515.3 eV are attributed to V⁵⁺ 2p_{3/2} and V⁴⁺ 2p_{3/2}, respectively.³⁴ According to previous studies, V⁴⁺ can promote oxygen adsorption and form reactive oxygen species on the catalyst surface, leading to fast redox cycles and improved redox properties.³⁵ Figure 2d shows that V⁴⁺ increases as NH₄NO₃ is added, and 0.05 and 0.08 M catalysts had higher ratios of V⁴⁺ at 36.06 and 40.53, respectively. Additionally, the NO₃⁻ + O_α / (NO₃⁻ + O_α + O_β) and V⁴⁺ / (V⁴⁺ + V⁵⁺) concentrations can be confirmed in Table 3.

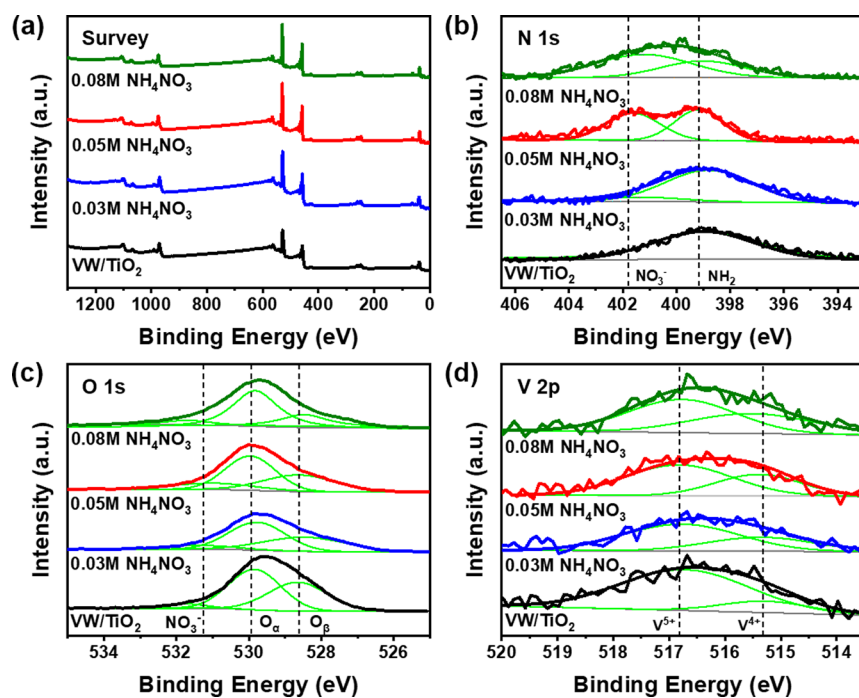


Figure 2. XPS spectra representing (a) survey, (b) N 1s, (c) O 1s, and (d) V 2p of V_2O_5 - WO_3 / TiO_2 , 0.03 M NH_4NO_3 , 0.05 M NH_4NO_3 , and 0.08 M NH_4NO_3 added V_2O_5 - WO_3 / TiO_2 catalysts, respectively.

Table 3. NO_3^- , O_α , V^{4+} Ratio of V_2O_5 - WO_3 / TiO_2 , 0.03 M NH_4NO_3 , 0.05 M NH_4NO_3 , and 0.08 M NH_4NO_3 Added V_2O_5 - WO_3 / TiO_2 Catalysts, Respectively

sample	NO_3^-	O_α	O_β	$NO_3^-/(NO_3^- + O_\alpha + O_\beta)$	$(NO_3^- + O_\alpha)/(NO_3^- + O_\alpha + O_\beta)$	$V^{4+}/(V^{4+} + V^{5+})$
VW/ TiO_2	4.93	52.76	42.31	4.93	57.69	15.81
0.03 M NH_4NO_3	9.30	52.11	38.59	9.30	61.41	32.44
0.05 M NH_4NO_3	15.46	49.94	34.60	15.46	65.40	36.06
0.08 M NH_4NO_3	22.70	61.18	16.12	22.70	83.88	40.53

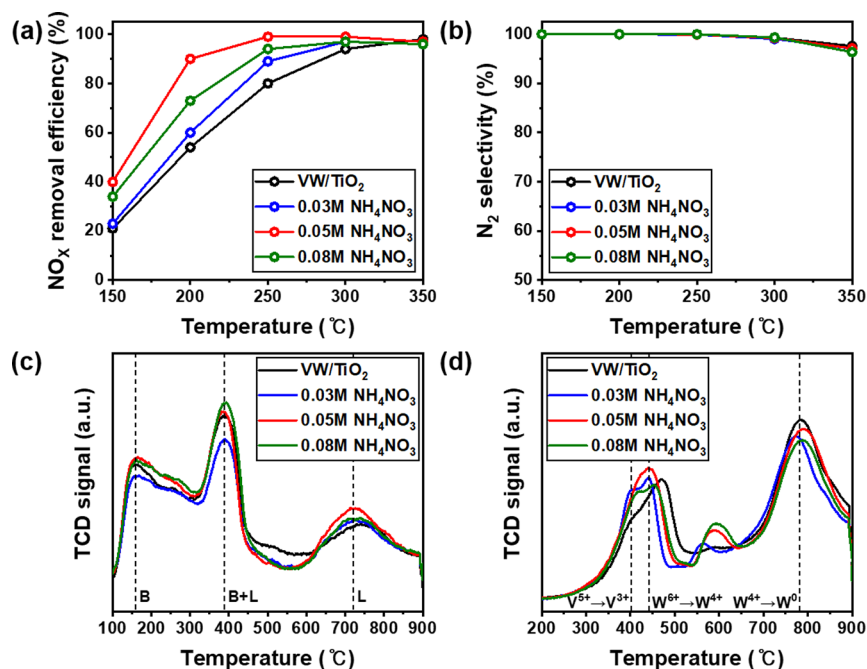


Figure 3. (a) NO_x removal efficiency; (b) N_2 selectivity; (c) NH_3 -TPD profiles; (d) H_2 -TPR profiles of V_2O_5 - WO_3 / TiO_2 , 0.03 M NH_4NO_3 , 0.05 M NH_4NO_3 , and 0.08 M NH_4NO_3 added V_2O_5 - WO_3 / TiO_2 catalysts, respectively. Reaction conditions: $[NO]$ & $[NH_3]$ & $[SO_2] = 300$ ppm, $[O_2] = 5$ vol %, $[GHSV] = 60,000$ h^{-1} .

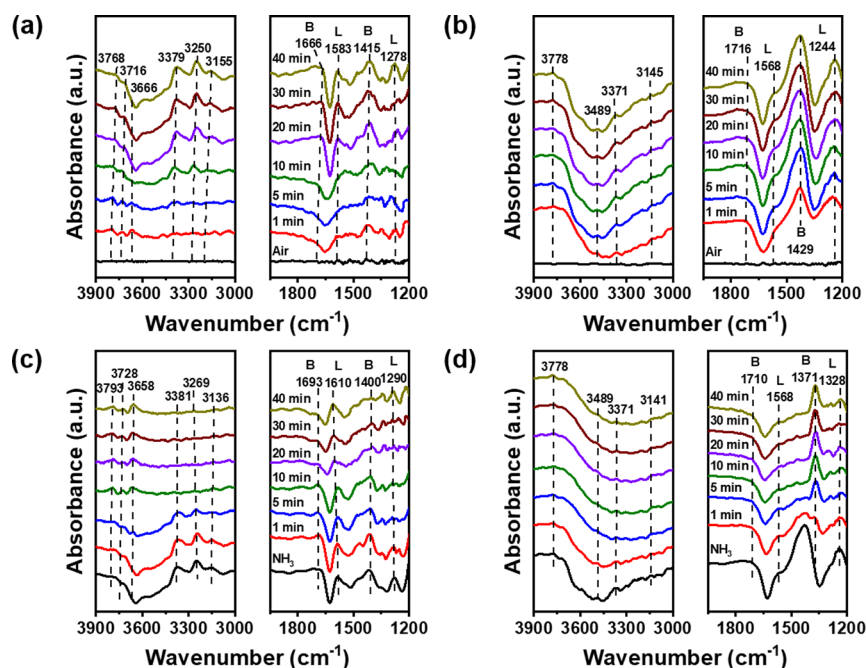


Figure 4. In situ Fourier transform infrared spectra of ammonia adsorption depending on the reaction time over (a) V_2O_5 - WO_3 / TiO_2 and (b) 0.05 M NH_4NO_3 . Nitrogen oxide and oxygen reacted with pre-adsorbed ammonia over (c) V_2O_5 - WO_3 / TiO_2 and (d) 0.05 M NH_4NO_3 at 200 °C. Conditions: $[NH_3] = 500$ ppm, $[NO] = 500$ ppm, $[O_2] = 5$ vol % (when used), and N_2 as the balance.

The NO_x removal efficiency, N_2 selectivity, and N_2O concentration were measured using a fixed-bed reactor to confirm the effect of the nitrate species that were formed on the V_2O_5 - WO_3 / TiO_2 catalyst surface on catalytic performance (Figure 3). Figure 3a shows that catalysts with nitrate species on the surface have higher NO_x removal efficiency than a fresh catalyst at temperatures below 300 °C. In the case of 0.05 M NH_4NO_3 , NO_x removal efficiency improved from 53–90% at 200 °C. These results were primarily due to the large number of NO_3^- species that formed on the catalyst surface, increasing catalytic performance at temperatures below 300 °C. However, 0.08 M NH_4NO_3 had a lower NO_x removal efficiency than 0.05 M NH_4NO_3 . This is because the excess ammonium nitrate blocked the V_2O_5 - WO_3 / TiO_2 catalyst pores. When adding 0.08 M NH_4NO_3 , the catalyst-specific surface area and pore properties decreased, resulting in a decrease in the active area of the catalyst (Table 1). Sulfur reacts directly with V_2O_5 - WO_3 / TiO_2 catalysts and decreases NO_x removal efficiency at temperatures below 300 °C, producing ammonium sulfates.³⁶ However, nitrated V_2O_5 - WO_3 / TiO_2 catalysts show a high NO_x removal efficiency in the presence of sulfur at temperatures below 300 °C; this high efficiency is largely because the nitrate species on the catalyst surface prevent its reaction with sulfur. Figure 3b shows N_2 selectivity; a trace amount of N_2O in the prepared catalyst was produced at 300 °C. The trend in N_2 selectivity was similar to that of the NO_x removal efficiency, and all prepared catalysts showed a similar N_2 selectivity at temperatures ranging from 150–350 °C.

We analyzed the NH_3 -TPD and H_2 -TPR profiles to obtain further information on the acidity and redox ability (Figure 3c,d). Figure 3c shows the NH_3 -TPD results for the V_2O_5 - WO_3 / TiO_2 , 0.03 M NH_4NO_3 , 0.05 M NH_4NO_3 , and 0.08 M NH_4NO_3 catalysts, respectively. The NH_3 -TPD profile of all prepared catalysts significantly varied in the temperature range of 100–900 °C. The thermal conductivity detector signals at the lower and higher temperatures were considered to be

Brønsted and Lewis acid sites, which are $NH_4^+_{ads}$ species and NH_3_{ads} species, respectively.³⁴ The desorbed NH_3 concentrations for 0.05 M NH_4NO_3 and 0.08 M NH_4NO_3 were higher, indicative of a greater capacity for NH_3 adsorption on the catalyst surface. According to these results, 0.05 M NH_4NO_3 and 0.08 M NH_4NO_3 contained more Brønsted and Lewis acid sites. Also, we produced H_2 -TPR profiles to investigate the V_2O_5 - WO_3 / TiO_2 , 0.03 M NH_4NO_3 , 0.05 M NH_4NO_3 , and 0.08 M NH_4NO_3 redox properties, respectively. (Figure 4b). V_2O_5 - WO_3 / TiO_2 has three apparent reduction peaks centered at 418.9, 469.7, and 783.3 °C, which could be assigned to the co-reduction of V^{5+} to V^{3+} , which corresponds to the surface vanadium species, on which we observed the reduction of W^{6+} to W^{4+} and the reduction of W^{4+} to W^0 in tungsten oxide.^{37,38} However, three main reduction peaks of 0.03, 0.05, and 0.08 M NH_4NO_3 catalysts shifted to lower temperatures at 401.4, 441.2, and 782.7 °C, respectively, and these results suggest that the nitrated surface has a relatively higher NO_x reducibility and reducing amount.

To investigate the formation and transformation of adsorbed species on the prepared catalyst surfaces, in situ FTIR spectra were obtained at 200 °C (Figure 4). After applying NH_3 gas to the V_2O_5 - WO_3 / TiO_2 catalyst for 20 min, bands (3379, 3250, 3155, 1583, and 1415 cm^{-1}) appeared, corresponding to coordinated NH_3 bound to the Lewis acid sites and ionic NH_4^+ bound to the Brønsted acid sites. Moreover, 0.05 M NH_4NO_3 -treated V_2O_5 - WO_3 / TiO_2 catalyst ammonia was chemically absorbed within 1 min. Furthermore, the Lewis and Brønsted acid site intensities were higher than those of pristine V_2O_5 - WO_3 / TiO_2 . This demonstrates that the nitrate ions (NO_3^-) on the 0.05 M NH_4NO_3 -treated V_2O_5 - WO_3 / TiO_2 catalyst surface quickly reacted with the applied ammonia gases and absorbed more ammonia on the surface. Figure 4c,d indicates in situ FTIR spectra of NO_x and oxygen that reacted with the pre-adsorbed ammonia on the catalyst surface. After inducing NO and O_2 gases on the catalyst, the number of adsorbed

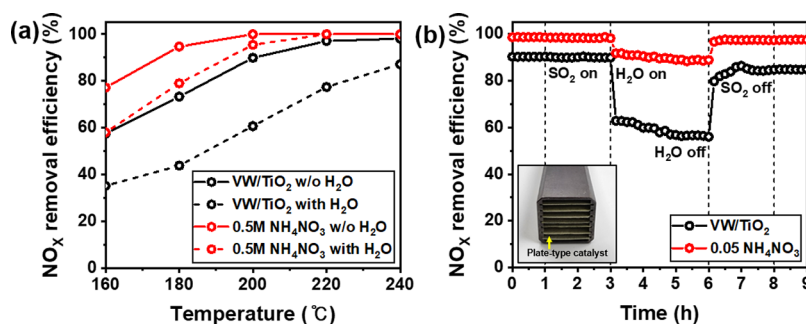


Figure 5. (a) NO_x removal efficiency under the influence of H₂O. (b) SO₂ and H₂O tolerance of the 4 wt % V₂O₅–10 wt % WO₃/TiO₂ and 0.05 M NH₄NO₃ catalyst at 200 °C (inset shows the microscope image of the plate-type catalyst). Reaction conditions: [NO] & [NH₃] & [SO₂] = 300 ppm, [O₂] = 5 vol %, [H₂O] = 10 vol %, [GHSV] = 60,000 h⁻¹.

Lewis and Brønsted acid sites gradually decreased with the reduction in NO gas. The V₂O₅-WO₃/TiO₂ catalyst required 10 min to remove the pre-absorbed ammonia, whereas the catalyst treated with ammonia nitrate quickly reduced NO gas on the surface in 5 min. This is because the nitrate ions (NO₃⁻) on the surface produced by the ammonia treatment induced “fast SCR”, causing fast chemisorption and reduction.

To apply the effect of ammonia nitrate treatment to a real SCR system, we fabricated plate-type catalysts and then evaluated them in a microreactor from 160–240 °C, as shown in Figure 5a. The V₂O₅-WO₃/TiO₂ catalyst showed a poor NO_x removal efficiency below 240 °C and the efficiency deteriorated with H₂O application into the reactor because the catalyst caused undesired SO₂ oxidation and NH₄HSO₄ and (NH₄)₂SO₄ formation. However, after ammonium nitrate treatment of the V₂O₅-WO₃/TiO₂ catalyst, the NO_x removal efficiency was dramatically enhanced at lower temperatures. Particularly over 180 °C, the efficiency was not significantly decreased by H₂O. The nitrate ions (NO₃⁻) on the surface treated by 0.05 M NH₄NO₃ suppress ammonium sulfate formation and lead to “fast SCR”, which improved NO_x removal efficiency. Figure 5b shows that SO₂ and H₂O affected the NO_x removal efficiency of the V₂O₅-WO₃/TiO₂ catalysts. When SO₂ gas was introduced into the reactor, the NO_x removal efficiencies of both V₂O₅-WO₃/TiO₂ catalysts and the 0.05 M NH₄NO₃-treated V₂O₅-WO₃/TiO₂ catalyst was maintained at 97 and 90%, respectively. However, H₂O was introduced into the reactor and the removal efficiencies of both of them decreased to 89 and 52%, respectively, and the catalyst without ammonium nitrate treatment deteriorated rapidly. After turning off H₂O and SO₂, the removal efficiency returned to 95 and 80%. While the 0.05 M NH₄NO₃-treated V₂O₅-WO₃/TiO₂ catalyst recovered its efficiency immediately, the V₂O₅-WO₃/TiO₂ catalysts did not recover quickly or fully. Because the nitrate ions (NO₃⁻) on the surface prevented ammonium sulfate creation and caused “fast SCR”, the catalyst after ammonium nitrate treatment exhibited high efficiency and good stability.

4. CONCLUSIONS

In this study, nitrate-treated V₂O₅-WO₃/TiO₂ catalysts were synthesized by adding ammonium nitrate using a general impregnation method, and the functional groups were controlled by varying the amount of added ammonium nitrate. By adding NH₄NO₃ to the V₂O₅-WO₃/TiO₂ catalyst, the NO₃⁻ and chemisorbed oxygen intensities increased simultaneously, inducing “fast SCR”. Nitrate-treated V₂O₅-WO₃/TiO₂

catalysts have more Brønsted and Lewis acid sites and a higher NO_x reducibility. These factors were linked to an improved catalytic performance at low temperatures (i.e., below 300 °C). However, superabundant nitrate blocked the V₂O₅-WO₃/TiO₂ catalyst pores, which caused a decrease in the catalyst active area and decreased the NO_x removal efficiency. Therefore, the proper nitrate, 0.05 M NH₄NO₃ catalyst exhibited the highest NO_x removal efficiency and N₂ selectivity. These results may contribute to the improvement of SCR catalysts and other classes of catalytic systems.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.3c05423>.

XRD patterns; schematic of the V₂O₅-WO₃/TiO₂ catalyst synthesis; SEM images; and TEM images and SAED patterns (PDF)

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Notes

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ABBREVIATIONS

AC:activated carbon
BET: Brunauer–Emmett–Teller
CNT: carbon nanotube
EELS: electron energy loss spectroscopy
FTIR: Fourier transform infrared spectroscopy
H₂-TPR: H₂ temperature-programmed reduction
NH₃-TPD: NH₃ temperature-programmed desorption
SCR: selective catalytic reduction
TEM: transmission electron microscopy
TPD: temperature-programmed desorption
XPS: X-ray photoelectron spectroscopy
XRD: X-ray diffraction
XRF: X-ray fluorescence spectrometry

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