



Article

Polyol-Mediated Synthesis of V_2O_5 – WO_3 /TiO₂ Catalysts for Low-Temperature Selective Catalytic Reduction with Ammonia

Min Seong Lee [†], Yeong Jun Choi [†] , Su-Jeong Bak, Mingyu Son, Jeehoon Shin and Duck Hyun Lee ^{*}

Green Materials and Processes R&D Group, Korea Institute of Industrial Technology, Ulsan 44413, Korea

^{*} Correspondence: dulee@kitech.re.kr[†] These authors contributed equally to this work.

Abstract: We demonstrated highly efficient selective catalytic reduction catalysts by adopting the polyol process, and the prepared catalysts exhibited a high nitrogen oxide (NO_x) removal efficiency of 96% at 250 °C. The V₂O₅ and WO₃ catalyst nanoparticles prepared using the polyol process were smaller (~10 nm) than those prepared using the impregnation method (~20 nm), and the small catalyst size enabled an increase in surface area and catalytic acid sites. The NO_x removal efficiencies at temperatures between 200 and 250 °C were enhanced by approximately 30% compared to those of the catalysts prepared using the conventional impregnation method. The NH₃-temperature-programmed desorption and H₂-temperature-programmed reduction results confirmed that the polyol process produced more surface acid sites at low temperatures and enhanced the redox ability. The in situ Fourier-transform infrared spectra further elucidated the fast absorption of NH₃ and its reduction with NO and O₂ on the prepared catalyst surfaces. This study provides an effective approach to synthesizing efficient low-temperature SCR catalysts and may contribute to further studies related to other catalytic systems.



Citation: Lee, M.S.; Choi, Y.J.; Bak, S.-J.; Son, M.; Shin, J.; Lee, D.H. Polyol-Mediated Synthesis of V₂O₅–WO₃/TiO₂ Catalysts for Low-Temperature Selective Catalytic Reduction with Ammonia. *Nanomaterials* **2022**, *12*, 3644. <https://doi.org/10.3390/nano12203644>

Academic Editor: Lyudmila M. Bronstein

Received: 1 October 2022

Accepted: 15 October 2022

Published: 18 October 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

Keywords: polyol-mediated synthesis; NH₃-selective catalytic reduction; small catalysts

1. Introduction

Over recent decades, chemical impurities such as nitrogen oxides (NO_x), sulfur oxides, carbon oxide (CO), volatile organic compounds, and particulate matter generated from the usage of biomass as a fuel at power plants, boilers, and mobile sources have polluted the atmospheric environment [1,2]. Among these, NO_x (NO, NO₂, and N₂O) are extremely dangerous, as they cause various environmental issues, such as acid rain, smog, ozone depletion, and even harm to human health [3–6]. Several processes, such as selective catalytic reduction (SCR), selective noncatalytic reduction (SNCR), nonselective catalytic reduction (NSCR), and photocatalytic degradation of NO_x [7–12], have been proposed to eliminate NO_x [13]. Among them, NH₃-SCR, which converts NO_x in exhaust gas into N₂ and H₂O, is the most commercialized technology owing to its 80–100% advanced efficiencies and economic feasibility [14,15]. Several types of composites, including transition metals (Fe, Cu, V, and Mn), are used as SCR catalysts [16,17]. V₂O₅–WO₃/TiO₂ are representative SCR catalysts, owing to their high catalytic acidity in high temperature ranges of 300–400 °C and lower chemical contamination possibility than other elements [18]. However, V₂O₅–WO₃/TiO₂ catalysts exhibit low catalytic performance at low temperatures below 300 °C [19,20].

Currently, most coal-fired power plants have adopted a high-dust system with an exhaust gas pretreatment such as installing an economizer at the rear end of the SCR system [21]. Consequently, the SCR catalyst becomes abraded and contaminated by dust and sulfur, reducing the utilization efficiency over time. Therefore, numerous studies have been conducted to develop new catalysts efficient at temperatures below 300 °C [9,22–25]. The low-temperature catalyst installed at the rear end of the electrostatic precipitator and

desulfurization facility enables the realization of the tail-end SCR system and reduces reheating costs [26].

Comprehensive research has been conducted to develop low-temperature SCR catalysts, and Mn- and Cu-based catalysts reportedly exhibit high SCR catalytic performances at low temperatures [16,27–31]. However, they are severely deactivated by sulfur contamination [32]. A mesoporous TiO_2 shell can improve the resistance of Fe_2O_3 catalysts to SO_2 (Han et al.) [33]. Yu et al. developed a Cu-SSZ-13 zeolite–metal oxide hybrid catalyst with high SO_2 resistance by forming Zn sulfate [34]. Additional studies on low-temperature catalysts entailed applying functional chemicals to improve the catalytic activity [35–39]. Chae et al. developed a $\text{V}_2\text{O}_5\text{--Sb}_2\text{O}_3/\text{TiO}_2$ catalyst with a high catalytic performance at temperatures below 300°C by adding ammonium nitrate, which promoted NO oxidation and rapid SCR mechanism reaction at temperatures below 300°C [39]. Zhao et al. reported 90% of NO_x removal efficiency with the $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst at 210°C by co-doping S and N [40]. These catalysts form O^{2-} active sites, increasing chemisorbed oxygen and NH_3 . Furthermore, Maqbol et al. reported $\text{CeO}_2\text{--Sb}/\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts pretreated with SO_2 under oxidizing conditions [41] forming sulfate species on the surface and a high NH_3 -desorption and catalytic performance due to cerium (III) sulfate formation. However, previous studies have limitations concerning the complexity of the synthesis process, restricting catalyst composition and limiting their commercial application.

The crystalline quality and morphology of nanomaterials are important in regulating the physicochemical properties of catalysts. In the polyol process, the liquid organic compound, a polyol, including 1,2-diols and ether glycols, acts both as a solvent of the solid precursor and as a reducing agent determining important process characteristics [42,43]: (1) the high boiling point allows synthesis at relatively high temperatures and ensures well-crystallized nanomaterials; (2) the reducing medium protects the as-prepared particles from contamination, as long as they remain in the medium; and (3) the high viscosity of the medium minimizes coalescence and favors a diffusion-controlled regime for particle growth, resulting in controlled structures and morphologies. Thus, the polyol process offers several advantages, including the easy control of nanomaterials, low cost, and verified scalability for industrial applications [42,44].

Herein, we adopted a polyol process to synthesize highly efficient SCR catalysts and compared their catalytic properties with those of a catalyst prepared using the conventional impregnation method. The catalysts synthesized through the polyol process formed small-sized nanoparticles within a short time and, thus, had numerous active sites that could react with NO_x . The effect of the polyol process on the $\text{V}_2\text{O}_5\text{--WO}_3/\text{TiO}_2$ catalyst was observed via transmission electron microscopy (TEM), Raman spectroscopy, and Brunauer–Emmett–Teller (BET) analysis. The NO_x removal efficiency and N_2 selectivity of the catalyst were measured to compare the catalytic activities in the low-temperature range of $150\text{--}300^\circ\text{C}$. NH_3 -temperature-programmed desorption ($\text{NH}_3\text{-TPD}$), H_2 -temperature-programmed reduction ($\text{H}_2\text{-TPR}$), and in situ Fourier-transform infrared (FTIR) spectroscopy were performed to elucidate the enhancement of the catalytic activities.

2. Materials and Methods

2.1. Materials

Ammonium metavanadate (AMV; NH_4VO_3), ammonium metatungstate hydrate (AMT; $(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40} \times \text{H}_2\text{O}$), and oxalic acid ($\text{C}_2\text{H}_2\text{O}_4$) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$) was obtained from Daejung Chemicals (Siheung-si, Korea), and titanium dioxide (TiO_2) was obtained from NANO Co., Ltd. (Seoul, Korea). All chemicals were of reagent grade and used without further purification.

2.2. Preparation of $\text{V}_2\text{O}_5\text{--WO}_3/\text{TiO}_2$ Catalysts

We prepared 2 wt.% $\text{V}_2\text{O}_5\text{--}5$ wt.% WO_3/TiO_2 catalysts using the impregnation and polyol processes. In the impregnation method, AMV (0.128 g, 99.99%) or AMT (0.266 g, 99.99%) was dissolved in 50 mL of deionized water with 0.196 g oxalic acid. TiO_2 powder

(4.650 g, NT-01) was mixed with the prepared solution and 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. The obtained powder was then sintered at 500 °C in a furnace for 5 h under atmospheric pressure. In the polyol process, AMV (0.128 g, 99.99%) or AMT (0.266 g, 99.99%) was dissolved in 100 mL ethylene glycol with 0.196 g oxalic acid. TiO₂ powder (4.650 g, NT-01) was mixed with the prepared solution and stirred for 2 h. The solution was heated in a microwave (Multiwave 5000; Anton Paar, Graz, Austria) for 10 min at 180 °C. The reacted solution was filtered, washed, and placed in an oven at 110 °C for 12 h. The obtained powder was calcinated at 500 °C in a furnace for 5 h under standard atmospheric pressure. The synthesized catalysts were denoted as IM and P according to the method applied to V₂O₅ and WO₃, respectively. Moreover, V₂O₅(P)–WO₃(IM) and V₂O₅(IM)–WO₃(P) catalysts were impregnated before the polyol process.

2.3. Catalyst Characterization

We investigated the morphology of the catalysts using a field emission scanning electron microscope (FESEM; SU8020; Hitachi, Tokyo, Japan) and transmission electron microscope (TEM; JEM-2100F; JEOL Ltd., Tokyo, Japan) at an accelerating voltage of 15.0 kV to understand the effect of the synthesis method on catalysts. The chemical compositions of the catalysts were measured using an X-ray fluorescence spectrometer (XRF; Zetium; Malvern Panalytical, Malvern, UK). The crystallinity and impurities of the catalysts were analyzed by X-ray diffraction (XRD; Ultima IV; Rigaku, Tokyo, Japan), with Cu K α (λ = 0.15406 nm) radiation in the 2 θ range of 10–90° at a scan rate of 1°/min and Raman spectra (alpha300s; WITec, Ulm, Germany) with a 532 nm laser. The textural properties of the catalysts were analyzed using the BET method (ASAP2020; Micromeritics Instrument Corp., Norcross, GA, USA). NH₃-TPD was conducted using AutoChem II 2920 (Micromeritics Instrument Corp.). The samples were pretreated at 150 °C with a current of N₂ for 4 h to remove physisorbed NH₃ species and organic matter. NH₃ was then adsorbed with 10% NH₃/He gas at 150 °C for 1 h. H₂-TPR was conducted using the same instruments as NH₃-TPD, in addition to exposing the catalysts to a current of 10% H₂/Ar and measuring in the 100–900 °C temperature range.

2.4. Catalytic Activity Evaluation

The catalytic performance was evaluated in a fixed-bed reactor under atmospheric pressure. The operating temperature varied from 150 °C to 300 °C, and the reactive gas comprised 300 ppm NO, NH₃ (NH₃/NO_x = 1.0), and SO₂, and 5 vol.% of O₂ with a balance of N₂ at a total flow rate of 500 sccm. During the evaluation, 0.35 mg of the powdered catalyst (sieved to 40–60 mesh) was tested, yielding a gas hourly space velocity (GHSV) of 60,000 h^{−1}. The reactive gas concentration was continuously monitored through FTIR spectroscopy (CX-4000; Gasmet Technologies, Vantaa, Finland) and an O₂ analyzer (Oxitec 5000; ENOTEC, Marienheide, Germany). The NO_x removal efficiency and N₂ selectivity were calculated according to Equations (1) and (2), respectively.

$$\text{NO}_x \text{ removal efficiency (\%)} = \frac{\text{NO}_x \text{ inlet} - \text{NO}_x \text{ outlet}}{\text{NO}_x \text{ inlet}} \times 100 \quad (1)$$

$$\text{N}_2 \text{ selectivity (\%)} = \frac{\text{NO inlet} - \text{NO outlet} - \text{NO}_2 \text{ outlet} - \text{N}_2\text{O outlet}}{\text{NO inlet} - \text{NO outlet}} \times 100 \quad (2)$$

2.5. In Situ FTIR Measurement

In situ FTIR spectra of all samples were measured using an FTIR spectrometer (VERT-EX 70v FTIR; Bruker, Billerica, MA, USA) [45] under operating conditions and accumulated 16 scans with a resolution of 4 cm^{−1} in the range of 4000–400 cm^{−1}. The gas 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

Figure 1a illustrates the formation of vanadium and tungsten oxide nanoparticles on titania with short nucleation and controlled particle growth during the polyol process ($V_2O_5(P)-WO_3(P)$). We controlled the reaction between the V, W precursor, and ethylene glycol under microwave irradiation at 180 °C for 10 min in an enclosed chamber. The optimized $V_2O_5-WO_3/TiO_2$ nanoparticles were obtained using multifunctional microwave equipment. The samples were filtered from the unreacted precursor and ethylene glycol and dried in an oven at 110 °C. Ethylene glycol acts as a stabilizer to limit particle growth and prevent agglomeration. Finally, we obtained green-colored samples with vanadium glycolate and tungsten glycolate. After calcination at 500 °C, the catalysts were transformed into $V_2O_5-WO_3$ nanoparticles with a yellow color. This polyol process is a facile synthesis process ideal for processing very fine powders with high purity, high crystallinity, good reproducibility, narrow particle size distribution, uniformity, and high reactivity. The overall reactions of vanadium and tungsten are given as Equations (3) and (4), respectively [46].

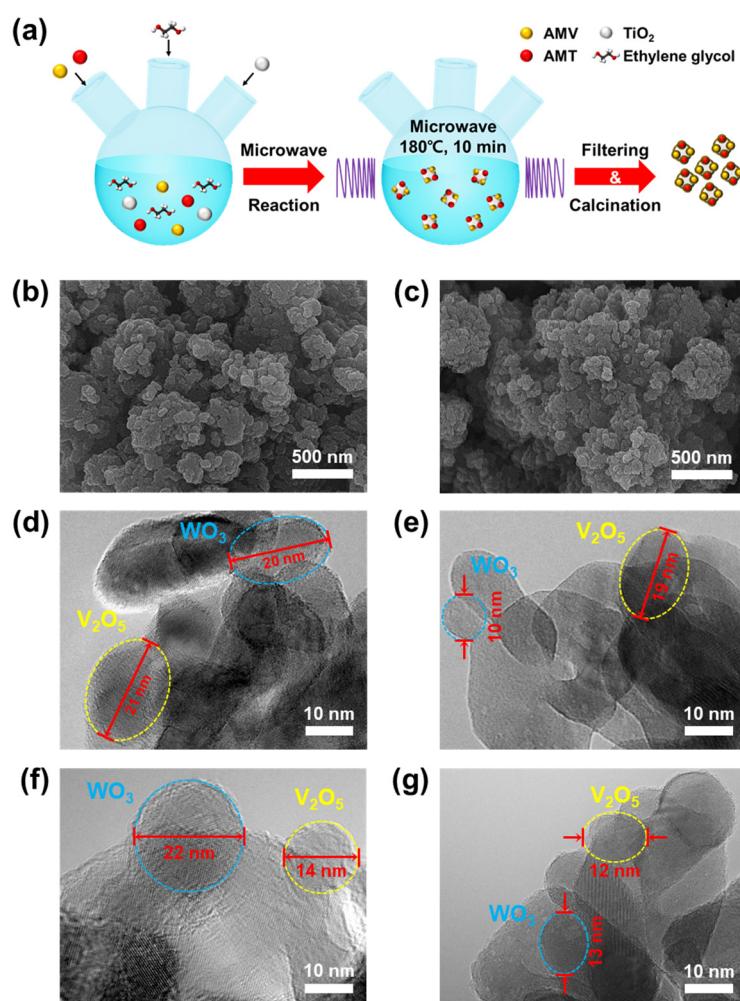
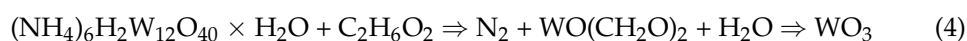
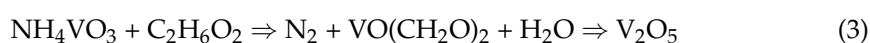


Figure 1. (a) Schematic of the polyol process on $V_2O_5-WO_3/TiO_2$ catalysts using a microwave at 180 °C for 10 min. Field emission scanning electron microscope images of (b) $V_2O_5(IM)-WO_3(IM)$ and (c) $V_2O_5(P)-WO_3(P)$. Transmission electron microscope images of (d) $V_2O_5(IM)-WO_3(IM)$, (e) $V_2O_5(IM)-WO_3(P)$, (f) $V_2O_5(P)-WO_3(IM)$, and (g) $V_2O_5(P)-WO_3(P)$.

Table 1 shows the V_2O_5 , WO_3 , TiO_2 , and SO_3 weight fractions of the catalysts. The weight fractions synthesized using the polyol process and impregnation method were similar, except that SO_3^- was present in TiO_2 .

Table 1. X-ray fluorescence analysis of $V_2O_5(IM)-WO_3(IM)$, $V_2O_5(IM)-WO_3(P)$, $V_2O_5(P)-WO_3(IM)$, and $V_2O_5(P)-WO_3(P)$.

Sample	TiO_2	V_2O_5	WO_3	SO_3
$V_2O_5(IM)-WO_3(IM)$	92.33	1.93	5.02	0.72
$V_2O_5(IM)-WO_3(P)$	92.43	2.02	4.89	0.66
$V_2O_5(P)-WO_3(IM)$	92.29	1.91	5.08	0.72
$V_2O_5(P)-WO_3(P)$	92.44	1.88	4.97	0.71

3.1. Catalyst Characterization

FE-SEM and TEM were used to compare morphologies of the V_2O_5 and WO_3 nanoparticles synthesized using the impregnation and polyol process, respectively (Figure 1b–g). Figure 1b,c show FE-SEM images of $V_2O_5(IM)-WO_3(IM)$ and $V_2O_5(P)-WO_3(P)$, respectively. The clusters of both catalysts had similar particle sizes and shapes with diameters of approximately 20–30 nm, such as those of titania. Therefore, V_2O_5 and WO_3 nanoparticles are difficult to distinguish from the TiO_2 particles. In contrast, Figure 1d–g show the distinct V_2O_5 and WO_3 nanoparticles through TEM and diffraction patterns analysis of the samples. $V_2O_5(IM)-WO_3(IM)$, $V_2O_5(IM)-WO_3(P)$, $V_2O_5(P)-WO_3(IM)$, and $V_2O_5(P)-WO_3(P)$ have V_2O_5/WO_3 particle sizes of 21 nm/20 nm, 14 nm/22 nm, 10 nm/19 nm, and 13 nm/12 nm, respectively (Figure S1). The catalyst particle size is very important, because the active area that determines the performance of the catalyst is very important, and these results demonstrate that the polyol process formed smaller V_2O_5 and WO_3 particles than the impregnation method, with up to 55% reduction in particle size.

The crystalline structure and phase purity of the $V_2O_5-WO_3/TiO_2$ catalysts were measured by XRD analysis and Raman spectroscopy. The XRD results showed the anatase phase of TiO_2 at 25.36° , 37.05° , 37.91° , 38.67° , 48.16° , 54.05° , 55.20° , 62.87° , 68.98° , 70.48° , 75.30° , and 82.93° in all catalysts (Figure 2a). However, the V_2O_5 and WO_3 phases were not observed in any of the catalysts, because the peak positions of V_2O_5 and WO_3 were very similar to those of the anatase phase, and low contents of 2 wt.% V_2O_5 and 5 wt.% WO_3 were uniformly dispersed on TiO_2 support. Raman spectroscopy was used to understand the crystalline structure and particle size of $V_2O_5-WO_3/TiO_2$ catalysts. The Raman spectra of all catalysts contained TiO_2 anatase peaks at 144.7, 197.3, 401.5, 518.5, and 639.1 cm^{-1} (Figure S2). Figure 2b shows the structure of vanadium and tungsten oxides in the range of $700\text{--}1100\text{ cm}^{-1}$. The states of the vanadium and tungsten species on the surface of the catalysts play a crucial role in the SCR catalytic action [47]. The Raman signal at 988.7 cm^{-1} could be attributed to the V–O vibration of crystalline vanadium oxide and at 800.5 cm^{-1} to the W–O–W stretching of octahedrally coordinated W units. $V_2O_5(IM)-WO_3(IM)$ exhibited higher Raman signals than $V_2O_5(P)-WO_3(P)$ at 988.7 cm^{-1} and 800.5 cm^{-1} (Figure 2b), indicating that the impregnation method formed large-sized particles of vanadium and tungsten oxides with high crystallinity, whereas the polyol method formed small-sized particles with low crystallinity. Furthermore, the textural details are listed in Figure 2c,d and Table 2 with the nitrogen adsorption–desorption measurements. All catalysts had similar isotherm plots, corresponding to the H3-type hysteresis loop with a mesoporous structure (Figure 2c). In contrast, the specific surface area, pore volume, and pore size were the highest in the order of $V_2O_5(P)-WO_3(P)$, $V_2O_5(IM)-WO_3(P)$, $V_2O_5(P)-WO_3(IM)$, and $V_2O_5(IM)-WO_3(IM)$, due to the effect of size on vanadium oxide and tungsten oxide particles (Table 2). $V_2O_5(P)-WO_3(P)$ and $V_2O_5(IM)-WO_3(P)$ with the polyol process applied to tungsten oxides had a higher pore size of 14.90 and 14.77 nm, respectively, than $V_2O_5(P)-WO_3(IM)$ (11.68 nm) and $V_2O_5(IM)-WO_3(IM)$ (11.01 nm) (Figure 2d) because of the atomization of the WO_3 nanoparticles with a content of 5 wt.%, which is a relatively large portion of $V_2O_5-WO_3/TiO_2$ than V_2O_5 nanoparticles.

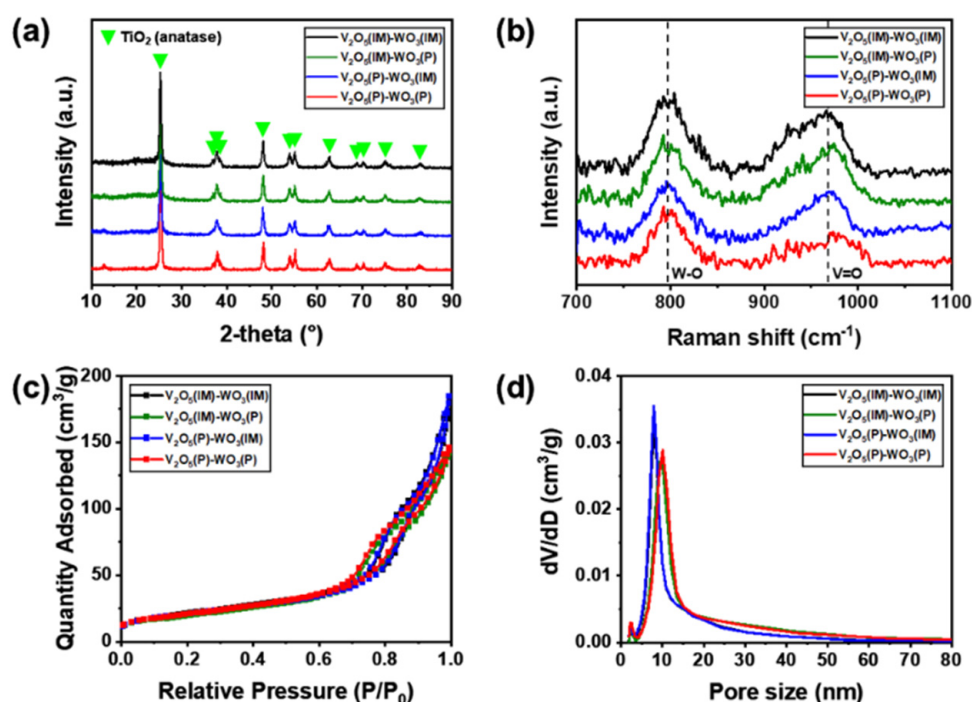


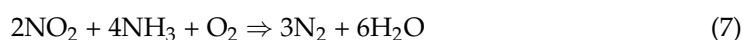
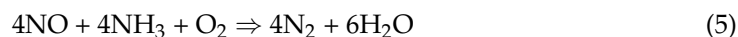
Figure 2. (a) X-ray diffraction patterns. (b) Raman spectra in the range of 1100 cm^{-1} to 700 cm^{-1} . (c) N_2 adsorption–desorption isotherms, and (d) Barrett–Joyner–Halenda (BJH) pore size distribution curves of $\text{V}_2\text{O}_5(\text{IM})\text{--WO}_3(\text{IM})$, $\text{V}_2\text{O}_5(\text{IM})\text{--WO}_3(\text{P})$, $\text{V}_2\text{O}_5(\text{P})\text{--WO}_3(\text{IM})$, and $\text{V}_2\text{O}_5(\text{P})\text{--WO}_3(\text{P})$.

Table 2. Brunauer–Emmet–Teller (BET) results of $\text{V}_2\text{O}_5(\text{IM})\text{--WO}_3(\text{IM})$, $\text{V}_2\text{O}_5(\text{IM})\text{--WO}_3(\text{P})$, $\text{V}_2\text{O}_5(\text{P})\text{--WO}_3(\text{IM})$, and $\text{V}_2\text{O}_5(\text{P})\text{--WO}_3(\text{P})$.

Sample	S_{BET} (m^2/g)	Pore Volume (cm^3/g)	Pore Size (nm)
$\text{V}_2\text{O}_5(\text{IM})\text{--WO}_3(\text{IM})$	71.33	0.22	11.01
$\text{V}_2\text{O}_5(\text{IM})\text{--WO}_3(\text{P})$	74.23	0.28	14.77
$\text{V}_2\text{O}_5(\text{P})\text{--WO}_3(\text{IM})$	75.67	0.22	11.68
$\text{V}_2\text{O}_5(\text{P})\text{--WO}_3(\text{P})$	75.83	0.28	14.90

3.2. Evaluation of Catalytic Activity

In the general NH_3 -SCR process, NO_x is converted to nitrogen and water through the reduction reaction of the NH_3 and NO_x on catalysts (Equations (5)–(8)) [48].



The SCR catalysts efficiently and selectively reduce NO_x to N_2 . The NO_x removal efficiency of the $\text{V}_2\text{O}_5(\text{P})\text{--WO}_3(\text{P})$, $\text{V}_2\text{O}_5(\text{P})\text{--WO}_3(\text{IM})$, and $\text{V}_2\text{O}_5(\text{IM})\text{--WO}_3(\text{P})$ catalysts was higher than that of $\text{V}_2\text{O}_5(\text{IM})\text{--WO}_3(\text{IM})$ at $150\text{--}300^\circ\text{C}$ (Figure 3a). At 250°C , the NO_x removal efficiencies of $\text{V}_2\text{O}_5(\text{P})\text{--WO}_3(\text{P})$, $\text{V}_2\text{O}_5(\text{P})\text{--WO}_3(\text{IM})$, and $\text{V}_2\text{O}_5(\text{IM})\text{--WO}_3(\text{P})$ were 96%, 93%, and 86%, respectively, whereas that of $\text{V}_2\text{O}_5(\text{IM})\text{--WO}_3(\text{IM})$ was the lowest at 66%, and the high NO_x removal efficiencies of $\text{V}_2\text{O}_5(\text{P})\text{--WO}_3(\text{P})$ were stable for 4 h of the durability test (Figure S3). Based on these results, we found that adjusting the polyol process for the $\text{V}_2\text{O}_5\text{--WO}_3/\text{TiO}_2$ catalysts increases the specific surface area, leading to enhanced reactions sites for V_2O_5 and WO_3 . In particular, the polyol process for V_2O_5 nanoparticles was more critical to NO_x removal efficiency than WO_3 nanoparticles, because

V_2O_5 as the main catalyst is more active than WO_3 . In contrast, all catalysts, including those from the polyol process, exhibited low catalytic activity at 150 °C, demonstrating that vanadium oxide was ineffective, and ammonium sulfate (NH_4HSO_4) or ammonium bisulfate ($(NH_4)_2SO_4$) were easily formed on the catalysts by reacting with sulfur dioxide, unreacted ammonia, and water, blocking the most active sites at temperatures below 150 °C.

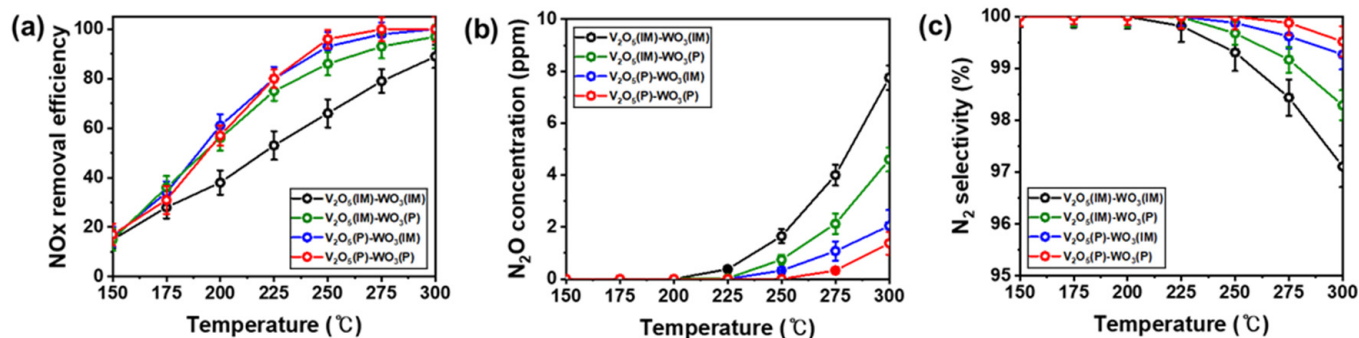


Figure 3. (a) Nitrogen oxide (NO_x) removal efficiency. (b) N_2O concentration and (c) N_2 selectivity of $V_2O_5(IM)-WO_3(IM)$, $V_2O_5(IM)-WO_3(P)$, $V_2O_5(P)-WO_3(IM)$, and $V_2O_5(P)-WO_3(P)$. Reaction conditions: $[NO] = [NH_3] = [SO_2] = 300$ ppm, $[O_2] = 5$ vol.%, N_2 as a balance, and $[GHSV] = 60,000$ h $^{-1}$.

Figure 3b,c illustrate the N_2O concentration and N_2 selectivity, respectively. Trace amounts of N_2O in all catalysts were produced at temperatures over 250 °C. N_2O produced from SCR side reactions is a secondary pollutant, which is important for determining the reaction accuracy. $V_2O_5(IM)-WO_3(IM)$ produced N_2O at 225 °C, and the amount was relatively large. In contrast, $V_2O_5-WO_3/TiO_2$ catalysts formed using the polyol process showed lower N_2O concentrations than those using the impregnation method, particularly $V_2O_5(P)-WO_3(P)$, which had the lowest N_2O concentration of 1.375 ppm at 300 °C. According to the N_2O concentrations, N_2 selectivity of $V_2O_5(P)-WO_3(P)$, $V_2O_5(P)-WO_3(IM)$, $V_2O_5(IM)-WO_3(P)$, and $V_2O_5(IM)-WO_3(IM)$ reached 99.52%, 99.29%, 98.29%, and 97.11% at 300 °C, respectively.

3.3. NH_3 -TPD and H_2 -TPR Analyses

We further explained the effect of the polyol process on the catalytic performance of the $V_2O_5-WO_3/TiO_2$ catalysts using NH_3 -TPD and H_2 -TPR analyses (Figure 4). The NH_3 -TPD results for $V_2O_5(IM)-WO_3(IM)$, $V_2O_5(IM)-WO_3(P)$, $V_2O_5(P)-WO_3(IM)$, and $V_2O_5(P)-WO_3(P)$ were observed at 100–800 °C, which is important for the content and strength of the surface acidic sites on the prepared catalysts (Figure 4a). All curves showed three distinct NH_3 desorption peaks at 100–200 °C, 300–500 °C, and above 500 °C, indicating weakly, intermediately, and strongly adsorbed NH_3 related to Bronsted and Lewis acid sites with different intensities, respectively [49,50]. Generally, the adsorbed NH_3 exists as NH_4^+ ions and coordinated NH_3 when bonded to Bronsted acid sites and Lewis acid sites, respectively. In addition, the concentration of desorbed NH_3 indicates the adsorption capability of the catalysts. The desorbed NH_3 concentration for $V_2O_5(IM)-WO_3(IM)$, $V_2O_5(IM)-WO_3(P)$, $V_2O_5(P)-WO_3(IM)$, and $V_2O_5(P)-WO_3(P)$ was 32.86, 51.98, 57.10, and 54.50 cm 3 /g, respectively, in the NH_3 -TPD profile (Table 3). These results indicate that the catalysts from the polyol process have a larger amount of desorbed NH_3 than those from the impregnation method, because the polyol process induces a large specific surface area and provides various sites for bonding with NH_3 . Particularly, $V_2O_5(P)-WO_3(P)$ showed higher thermal conductivity detector (TCD) signals belonging to Bronsted acid sites in the temperature range of 100–500 °C than $V_2O_5(IM)-WO_3(P)$ and $V_2O_5(P)-WO_3(IM)$, suggesting the explanation for the high catalytic performance of $V_2O_5(P)-WO_3(P)$.

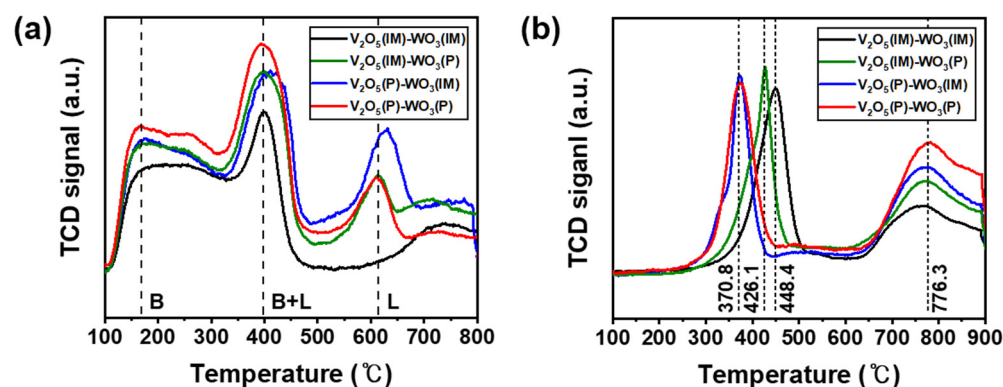


Figure 4. (a) NH₃-temperature-programmed desorption (NH₃-TPD) profiles and (b) H₂-temperature-programmed reduction (H₂-TPR) profiles of V₂O₅(IM)-WO₃(IM), V₂O₅(IM)-WO₃(P), V₂O₅(P)-WO₃(IM), and V₂O₅(P)-WO₃(P). B and L indicate Bronsted and Lewis acid sites, respectively.

Table 3. NH₃-temperature-programmed desorption (NH₃-TPD) and H₂-temperature-programmed reduction (H₂-TPR) integral intensity of V₂O₅(IM)-WO₃(IM), V₂O₅(IM)-WO₃(P), V₂O₅(P)-WO₃(IM), and V₂O₅(P)-WO₃(P).

Sample	S _{BET} (m ² /g)	Pore Volume (cm ³ /g)
V ₂ O ₅ (IM)-WO ₃ (IM)	71.33	0.22
V ₂ O ₅ (IM)-WO ₃ (P)	74.23	0.28
V ₂ O ₅ (P)-WO ₃ (IM)	75.67	0.22
V ₂ O ₅ (P)-WO ₃ (P)	75.83	0.28

Moreover, we identified the mechanism by which the polyol process affected the redox performance of the catalysts in NH₃-SCR. The redox performances of V₂O₅(IM)-WO₃(IM), V₂O₅(IM)-WO₃(P), V₂O₅(P)-WO₃(IM), and V₂O₅(P)-WO₃(P) in the temperature range of 100–900 °C by H₂-TPR analysis are illustrated in Figure 4b and Table 3. The V₂O₅(IM)-WO₃(IM) has three apparent peaks centered at 413.5, 449.5, and 771.0 °C, indicating the co-reduction of V⁵⁺ to V³⁺ corresponding to the surface vanadium species, reduction of W⁶⁺ to W⁴⁺, and reduction of W⁴⁺ to W⁰ in tungsten oxide, respectively. In contrast, the reduction peaks of V₂O₅(IM)-WO₃(P), V₂O₅(P)-WO₃(IM), and V₂O₅(P)-WO₃(P), indicating V⁵⁺ to V³⁺ co-reduction and W⁶⁺ to W⁴⁺ reduction, shifted to lower temperatures at 400.9 °C/426.3 °C, 340.5 °C/373.7 °C, and 336.3 °C/373.7 °C, respectively, because the increased specific surface area of V₂O₅ and WO₃ promoted the release of lattice oxygen to reduce vanadium and tungsten species, thereby reducing a large amount of hydrogen. Particularly, catalysts that apply polyol to vanadium oxides as active catalysts exhibited remarkable shift changes and reduced a large amount of hydrogen at low temperatures. Therefore, V₂O₅(P)-WO₃(IM) and V₂O₅(P)-WO₃(P) have superior reducing ability, which is one of the reasons for their high NO_x removal efficiencies at temperatures below 300 °C.

3.4. In Situ FTIR Measurement

In situ FTIR analysis elucidates the formation and transformation of adsorbed species on the surface of a catalyst, providing information such as the activation capacity of the catalysts or the reaction mechanism between catalysts and reactive gases. Figure 5 illustrates the in situ FTIR spectra of the adsorbed species on the surfaces of V₂O₅(IM)-WO₃(IM) and V₂O₅(P)-WO₃(P) derived from NH₃ gas at 200 °C. After introducing NH₃ gas at 200 °C, V₂O₅(P)-WO₃(P) catalysts reacted with NH₃, and they were mainly covered by coordinated NH₃ bound to the Lewis acid sites (1244, 1294, 1583, 3153, 3250, 3359, and 3394 cm^{−1}) and ionic NH₄⁺ bound to the Bronsted acid sites (1427, 1466, and 1695 cm^{−1}) in 5 min, whereas V₂O₅(IM)-WO₃(IM) reacted with NH₃ for 20 min [46]. The intensities of the Lewis and Bronsted acid sites were greater in V₂O₅(P)-WO₃(P) than in V₂O₅(IM)-WO₃(IM),

demonstrating that the catalysts produced by the polyol process were smaller in size, providing more adsorption sites for ammonia. The FTIR spectra of the adsorbed species on the surfaces of $V_2O_5(IM)-WO_3(P)$ and $V_2O_5(P)-WO_3(IM)$ were also observed under NH_3 gas at 200 °C (Figure S4). The catalysts showed intermediate catalytic activities between $V_2O_5(P)-WO_3(P)$ and $V_2O_5(IM)-WO_3(IM)$. The higher specific surface area of the active catalysts (Table 2) provided more Lewis and Bronsted acid sites, resulting in an increase in NH_3 binding to the catalyst surfaces.

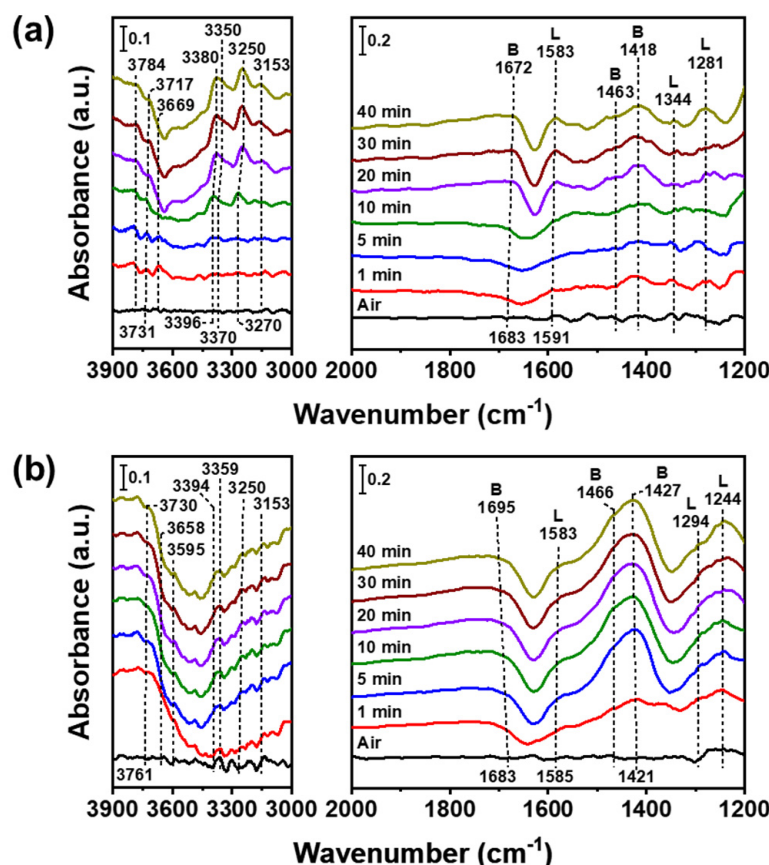


Figure 5. In situ Fourier–transform infrared spectra of ammonia adsorption depending on the reaction time over (a) $V_2O_5(IM)-WO_3(IM)$ and (b) $V_2O_5(P)-WO_3(P)$ at 200 °C. Conditions: $[NH_3] = 500$ ppm (when used) and N_2 as the balance.

Figure 6 shows in situ FTIR spectra of NO_x and oxygen reacted with pre-adsorbed ammonia over $V_2O_5(IM)-WO_3(IM)$ and $V_2O_5(P)-WO_3(P)$ at 200 °C. $V_2O_5(P)-WO_3(P)$ was primarily covered by coordinated NH_3 bound to the Lewis acid sites (1232, 1287, 1589, 3142, 3250, 3359, and 3394 cm^{-1}) and ionic NH_4^+ bound to the Bronsted acid sites (1412, 1452, and 1705 cm^{-1}). The adsorbed Lewis and Bronsted acid sites gradually decreased by selectively reducing NO gas, and their reduction was evident in 5 min for $V_2O_5(P)-WO_3(P)$ and 10 min for the $V_2O_5(IM)-WO_3(IM)$ catalysts. The in situ FTIR spectra of $V_2O_5(IM)-WO_3(P)$ and $V_2O_5(P)-WO_3(IM)$ were also observed under NO and O_2 gas with pre-adsorbed NH_3 at 200 °C (Figure S5). The catalysts showed an intermediate reduction time between $V_2O_5(P)-WO_3(P)$ and $V_2O_5(IM)-WO_3(IM)$. $V_2O_5(P)-WO_3(P)$ catalysts showed that the Bronsted acid site disappeared before the Lewis acid site, indicating that the adsorption site corresponds to the Bronsted acid sites, and NO and O_2 were first bonded. Therefore, the excellent catalytic activity of $V_2O_5(P)-WO_3(P)$ was confirmed when the adsorbed ammonia reacted with NO and O_2 .

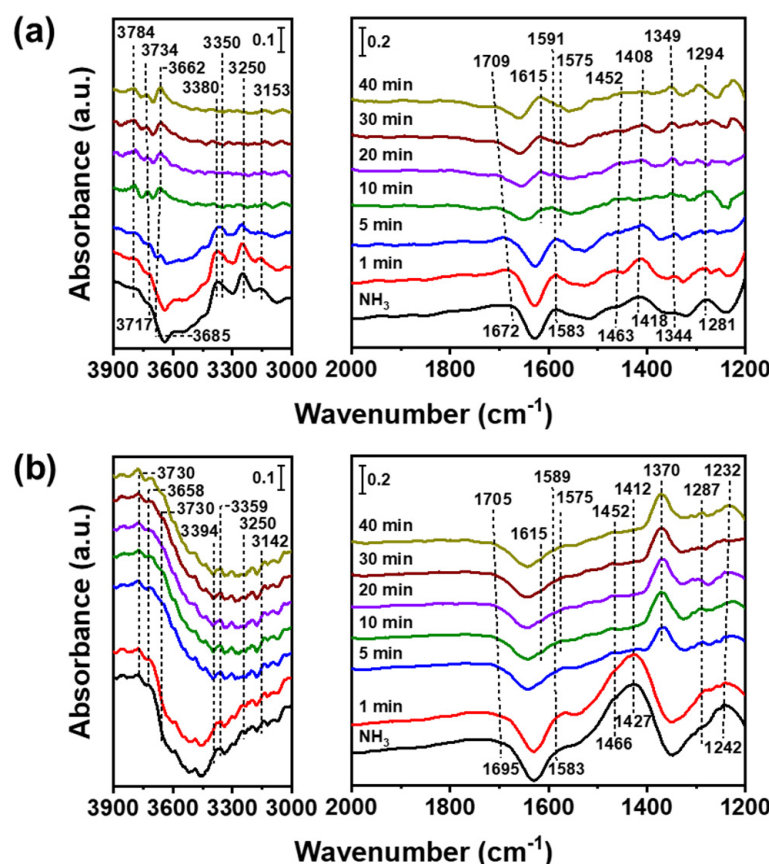


Figure 6. In situ Fourier-transform infrared spectra of nitrogen oxide and oxygen reacted with pre-adsorbed ammonia over (a) $V_2O_5(IM)-WO_3(IM)$ and (b) $V_2O_5(P)-WO_3(P)$ at 200 °C. Conditions: $[NO] = 500$ ppm (when used), $[O_2] = 5$ vol.% (when used), and N_2 as the balance.

4. Conclusions

In this study, we explored a facile synthetic process to obtain highly efficient SCR catalysts by adopting a polyol process, and the prepared catalyst demonstrated high NO_x removal efficiency of 96% at 250 °C. The V_2O_5 and WO_3 catalyst nanoparticles prepared using the polyol process were smaller (~10 nm) than those prepared using the impregnation method (~20 nm). The small catalyst size enabled an increase in the surface area and catalytic acid sites. At temperatures between 200 and 250 °C, the NO_x removal efficiencies were enhanced by approximately 30% compared to the catalysts prepared using the conventional impregnation method. The NH_3 -TPD results demonstrated that the polyol process provided more surface acid sites generated at low temperatures. H_2 -TPR revealed the enhanced redox ability and reducing characteristics of the catalysts, which promoted a rapid SCR reaction. The in situ FTIR spectra elucidated the fast absorption of NH_3 and its reduction with NO and O_2 on the prepared catalyst surfaces at low temperatures. This study provided an effective approach to synthesizing efficient low-temperature SCR catalysts and may contribute to further studies related to other catalytic systems.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/nano12203644/s1>, Figure S1: Transmission electron microscope (TEM) images and selected area electron diffraction (SAED) patterns of (a) $V_2O_5(IM)-WO_3(IM)$, (b) $V_2O_5(IM)-WO_3(P)$, (c) $V_2O_5(P)-WO_3(IM)$, and (d) $V_2O_5(P)-WO_3(P)$. Figure S2: Raman spectra of $V_2O_5(IM)-WO_3(IM)$, $V_2O_5(IM)-WO_3(P)$, $V_2O_5(P)-WO_3(IM)$, and $V_2O_5(P)-WO_3(P)$. Figure S3: NO_x removal efficiency of $V_2O_5(P)-WO_3(P)$ measured for 4 h at 250 °C. Figure S4: In situ Fourier-transform infrared spectra of ammonia adsorption, depending on the reaction time over (a) $V_2O_5(IM)-WO_3(P)$ and (b) $V_2O_5(P)-WO_3(IM)$ at 200 °C. Figure S5: In situ Fourier-transform infrared spectra of NO and O_2 reacted with pre-adsorbed NH_3 over (a) $V_2O_5(IM)-WO_3(P)$ and (b) $V_2O_5(P)-WO_3(IM)$ at 200 °C.

Author Contributions: Conceptualization, D.H.L.; investigation, M.S.L. and Y.J.C.; methodology, M.S.L. and Y.J.C.; formal analysis, M.S.L. and J.S.; validation, S.-J.B. and M.S.; writing—original draft preparation, M.S.L., Y.J.C. and M.S.; writing—review and editing, D.H.L.; and project administration, D.H.L. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the Ministry of Economy and Finance (MOEF) (grant number EM220004) and the Ministry of Trade, Industry, and Energy (MOTIE), South Korea (grant number 20005721).

Data Availability Statement: Data are contained within the article.

Conflicts of Interest: There are no conflict to declare.

References

1. Fernando, S.; Hall, C.; Jha, S. NO_x Reduction from biodiesel fuels. *Energy Fuels* **2006**, *20*, 376–382. [\[CrossRef\]](#)
2. Lee, M.J.; Kim, D.H.; Lee, M.; Ye, B.; Jeong, B.; Lee, D.; Kim, H.D.; Lee, H. Enhanced NO_x removal efficiency for SCR catalyst of well-dispersed Mn-Ce nanoparticles on hexagonal boron nitride. *Environ. Sci. Pollut. Res. Int.* **2019**, *26*, 36107–36116. [\[CrossRef\]](#) [\[PubMed\]](#)
3. Fu, M.; Li, C.; Lu, P.; Qu, L.; Zhang, M.; Zhou, Y.; Yu, M.; Fang, Y. A review on selective catalytic reduction of NO_x by supported catalysts at 100–300 °C—Catalysts, mechanism, kinetics. *Catal. Sci. Technol.* **2014**, *4*, 14–25. [\[CrossRef\]](#)
4. Ye, B.; Lee, M.; Jeong, B.; Kim, J.; Lee, D.H.; Baik, J.M.; Kim, H.-D. Partially reduced graphene oxide as a support of Mn-Ce/TiO₂ catalyst for selective catalytic reduction of NO_x with NH₃. *Catal. Today* **2019**, *328*, 300–306. [\[CrossRef\]](#)
5. Boningari, T.; Smirniotis, P.G. Impact of nitrogen oxides on the environment and human health: Mn-based materials for the NO_x abatement. *Curr. Opin. Chem. Eng.* **2016**, *13*, 133–141. [\[CrossRef\]](#)
6. Hoek, G.; Krishnan, R.M.; Beelen, R.; Peters, A.; Ostro, B.; Brunekreef, B.; Kaufman, J.D. Long-term air pollution exposure and cardio-respiratory mortality: A review. *Environ. Health* **2013**, *12*, 43. [\[CrossRef\]](#) [\[PubMed\]](#)
7. Zeshan, M.; Bhatti, I.A.; Mohsin, M.; Iqbal, M.; Amjed, N.; Nisar, J.; AlMasoud, N.; Alomar, T.S. Remediation of pesticides using TiO₂ based photocatalytic strategies: A review. *Chemosphere* **2022**, *300*, 134525. [\[CrossRef\]](#)
8. Wafi, M.A.E.; Ahmed, M.A.; Abdel-Samad, H.S.; Medien, H.A.A. Exceptional removal of methylene blue and p-aminophenol dye over novel TiO₂/RGO nanocomposites by tandem adsorption-photocatalytic processes. *Mater. Sci. Energy Technol.* **2022**, *5*, 217–231. [\[CrossRef\]](#)
9. Balayeva, N.O.; Mamiyev, Z. Chapter 5—Integrated processes involving adsorption, photolysis, and photocatalysis. In *Hybrid and Combined Processes for Air Pollution Control*; Assadi, A., Amrane, A., Nguyen, T.A., Eds.; Elsevier: Amsterdam, The Netherlands, 2022; pp. 117–153.
10. Khanal, V.; Balayeva, N.O.; Günnemann, C.; Mamiyev, Z.; Dillert, R.; Bahnemann, D.W.; Subramanian, V. Photocatalytic NO_x removal using tantalum oxide nanoparticles: A benign pathway. *Appl. Catal. B Environ.* **2021**, *291*, 119974. [\[CrossRef\]](#)
11. Balayeva, N.O.; Fleisch, M.; Bahnemann, D.W. Surface-grafted WO₃/TiO₂ photocatalysts: Enhanced visible-light activity towards indoor air purification. *Catal. Today* **2018**, *313*, 63–71. [\[CrossRef\]](#)
12. Lee, B.-T.; Han, J.-K.; Gain, A.K.; Lee, K.-H.; Saito, F. TEM microstructure characterization of nano TiO₂ coated on nano ZrO₂ powders and their photocatalytic activity. *Mater. Lett.* **2006**, *60*, 2101–2104. [\[CrossRef\]](#)
13. Lee, M.S.; Kim, S.I.; Jeong, B.; Park, J.W.; Kim, T.; Lee, J.W.; Kwon, G.; Lee, D.H. Ammonium ion enhanced V₂O₅-WO₃/TiO₂ catalysts for selective catalytic reduction with ammonia. *Nanomaterials* **2021**, *11*, 2677. [\[CrossRef\]](#)
14. Radojevic, M. Reduction of nitrogen oxides in flue gases. *Environ. Pollut.* **1998**, *102*, 685–689. [\[CrossRef\]](#)
15. Jeong, B.; Ye, B.; Kim, E.-S.; Kim, H.-D. Characteristics of selective catalytic reduction (SCR) catalyst adding graphene-tungsten nanocomposite. *Catal. Commun.* **2017**, *93*, 15–19. [\[CrossRef\]](#)
16. Meng, D.; Zhan, W.; Guo, Y.; Guo, Y.; Wang, L.; Lu, G. A highly effective catalyst of Sm-MnO_x for the NH₃-SCR of NO_x at low temperature: Promotional role of Sm and its catalytic performance. *ACS Catal.* **2015**, *5*, 5973–5983. [\[CrossRef\]](#)
17. Kwak, J.H.; Tran, D.; Burton, S.D.; Szanyi, J.; Lee, J.H.; Peden, C.H.F. Effects of hydrothermal aging on NH₃-SCR reaction over Cu/zeolites. *J. Catal.* **2012**, *287*, 203–209. [\[CrossRef\]](#)
18. Lee, M.S.; Kim, S.I.; Lee, M.J.; Ye, B.; Kim, T.; Kim, H.D.; Lee, J.W.; Lee, D.H. Effect of catalyst crystallinity on V-based selective catalytic reduction with ammonia. *Nanomaterials* **2021**, *11*, 1452. [\[CrossRef\]](#)
19. Roy, S.; Hegde, M.S.; Madras, G. Catalysis for NO_x abatement. *Appl. Energy* **2009**, *86*, 2283–2297. [\[CrossRef\]](#)
20. Busca, G.; Liotti, L.; Ramis, G.; Berti, F. Chemical and mechanistic aspects of the selective catalytic reduction of NO by ammonia over oxide catalysts: A Review. *Appl. Catal. B* **1998**, *18*, 1–36. [\[CrossRef\]](#)
21. Kling, A.; Andersson, C.; Myringer, A.; Eskilsson, D.; Järås, S.G. Alkali deactivation of high-dust SCR catalysts used for NO_x reduction exposed to flue gas from 100MW-scale biofuel and peat fired boilers: Influence of flue gas composition. *Appl. Catal. B* **2007**, *69*, 240–251. [\[CrossRef\]](#)
22. Li, J.; Chang, H.; Ma, L.; Hao, J.; Yang, R.T. Low-temperature selective catalytic reduction of NO_x with NH₃ over metal oxide and zeolite catalysts—A review. *Catal. Today* **2011**, *175*, 147–156. [\[CrossRef\]](#)
23. Liu, C.; Shi, J.-W.; Gao, C.; Niu, C. Manganese oxide-based catalysts for low-temperature selective catalytic reduction of NO_x with NH₃: A review. *Appl. Catal. A* **2016**, *522*, 54–69. [\[CrossRef\]](#)

24. Tang, C.; Zhang, H.; Dong, L. Ceria-based catalysts for low-temperature selective catalytic reduction of NO with NH₃. *Catal. Sci. Technol.* **2016**, *6*, 1248–1264. [\[CrossRef\]](#)
25. Shan, W.; Liu, F.; He, H.; Shi, X.; Zhang, C. A superior Ce-W-Ti mixed oxide catalyst for the selective catalytic reduction of NOx with NH₃. *Appl. Catal. B* **2012**, *115–116*, 100–106. [\[CrossRef\]](#)
26. Mladenović, M.; Paprika, M.; Marinković, A. Denitrification techniques for biomass combustion. *Renew. Sustain. Energy Rev.* **2018**, *82*, 3350–3364. [\[CrossRef\]](#)
27. Shen, M.; Li, C.; Wang, J.; Xu, L.; Wang, W.; Wang, J. New insight into the promotion effect of Cu doped V₂O₅/WO₃-TiO₂ for low temperature NH₃-SCR performance. *RSC Adv.* **2015**, *5*, 35155–35165. [\[CrossRef\]](#)
28. Li, W.; Zhang, C.; Li, X.; Tan, P.; Zhou, A.; Fang, Q.; Chen, G. Ho-modified Mn-Ce/TiO₂ for low-temperature SCR of NO with NH₃: Evaluation and characterization. *Chin. J. Catal.* **2018**, *39*, 1653–1663. [\[CrossRef\]](#)
29. Huang, J.; Huang, H.; Jiang, H.; Liu, L. The promotional role of Nd on Mn/TiO₂ catalyst for the low-temperature NH₃-SCR of NOx. *Catal. Today* **2019**, *332*, 49–58. [\[CrossRef\]](#)
30. Sun, P.; Guo, R.-T.; Liu, S.-M.; Wang, S.-X.; Pan, W.-G.; Li, M.-Y. The enhanced performance of MnOx catalyst for NH₃-SCR reaction by the modification with Eu. *Appl. Catal. A* **2017**, *531*, 129–138. [\[CrossRef\]](#)
31. Hu, H.; Xie, J.L.; Fang, D.; He, F. Study of Co-Mn/TiO₂ SCR catalyst at low temperature. *Adv. Mater. Res.* **2015**, *1102*, 11–16. [\[CrossRef\]](#)
32. Xu, W.; He, H.; Yu, Y. Deactivation of a Ce/TiO₂ Catalyst by SO₂ in the selective catalytic reduction of NO by NH₃. *J. Phys. Chem. C* **2009**, *113*, 4426–4432. [\[CrossRef\]](#)
33. Han, L.; Gao, M.; Hasegawa, J.-Y.; Li, S.; Shen, Y.; Li, H.; Shi, L.; Zhang, D. SO₂-tolerant selective catalytic reduction of NOx over meso-TiO₂@Fe₂O₃@Al₂O₃ metal-based monolith catalysts. *Environ. Sci. Technol.* **2019**, *53*, 6462–6473. [\[CrossRef\]](#) [\[PubMed\]](#)
34. Yu, R.; Zhao, Z.; Huang, S.; Zhang, W. Cu-SSZ-13 Zeolite-metal oxide hybrid catalysts with enhanced SO₂-tolerance in the NH₃-SCR of NOx. *Appl. Catal. B* **2020**, *269*, 118825. [\[CrossRef\]](#)
35. Chen, L.; Li, J.; Ge, M. DRIFT study on cerium-tungsten/titania catalyst for selective catalytic reduction of NOx with NH₃. *Environ. Sci. Technol.* **2010**, *44*, 9590–9596. [\[CrossRef\]](#)
36. Gao, X.; Jiang, Y.; Zhong, Y.; Luo, Z.; Cen, K. The activity and characterization of CeO₂-TiO₂ Catalysts prepared by the sol-gel method for selective catalytic reduction of NO with NH₃. *J. Hazard. Mater.* **2010**, *174*, 734–739. [\[CrossRef\]](#)
37. Purbia, R.; Choi, S.Y.; Kim, H.J.; Ye, B.; Jeong, B.; Lee, D.H.; Park, H.; Kim, H.-D.; Baik, J.M. Cu- and Ce-promoted nano-heterostructures on vanadate catalysts for low-temperature NH₃-SCR activity with improved SO₂ and water resistance. *Chem. Eng. J.* **2022**, *437*, 135427. [\[CrossRef\]](#)
38. Ye, B.; Kim, J.; Lee, M.-J.; Chun, S.-Y.; Jeong, B.; Kim, T.; Lee, D.H.; Kim, H.-D. Mn-Ce oxide nanoparticles supported on nitrogen-doped reduced graphene oxide as low-temperature catalysts for selective catalytic reduction of nitrogen oxides. *Microporous Mesoporous Mater.* **2021**, *310*, 110588. [\[CrossRef\]](#)
39. Bae, Y.K.; Kim, T.-W.; Kim, J.-R.; Kim, Y.; Ha, K.-S.; Chae, H.-J. Enhanced SO₂ tolerance of V₂O₅-Sb₂O₃/TiO₂ Catalyst for NO reduction with Co-use of ammonia and liquid ammonium nitrate. *J. Ind. Eng. Chem.* **2021**, *96*, 277–283. [\[CrossRef\]](#)
40. Zhou, W.; Rajic, L.; Meng, X.; Nazari, R.; Zhao, Y.; Wang, Y.; Gao, J.; Qin, Y.; Alshawabkeh, A.N. Efficient H₂O₂ Electrogeneration at Graphite Felt Modified via Electrode Polarity Reversal: Utilization for Organic Pollutants Degradation. *Chem. Eng. J.* **2019**, *364*, 428–439. [\[CrossRef\]](#)
41. Maqbool, M.S.; Pullur, A.K.; Ha, H.P. Novel sulfation effect on low-temperature activity enhancement of CeO₂-added Sb-V₂O₅/TiO₂ catalyst for NH₃-SCR. *Appl. Catal. B* **2014**, *152–153*, 28–37. [\[CrossRef\]](#)
42. Fiévet, F.; Ammar-Merah, S.; Brayner, R.; Chau, F.; Giraud, M.; Mammeri, F.; Peron, J.; Piquemal, J.Y.; Sicard, L.; Viau, G. The polyol process: A unique method for easy access to metal nanoparticles with tailored sizes, shapes and compositions. *Chem. Soc. Rev.* **2018**, *47*, 5187–5233. [\[CrossRef\]](#)
43. Nohra, B.; Candy, L.; Blanco, J.-F.; Guerin, C.; Raoul, Y.; Mouloungui, Z. From petrochemical polyurethanes to biobased polyhydroxyurethanes. *Macromolecules* **2013**, *46*, 3771–3792. [\[CrossRef\]](#)
44. Bak, S.J.; Kim, S.I.; Lim, S.Y.; Kim, T.; Kwon, S.H.; Lee, D.H. Small reduced graphene oxides for highly efficient oxygen reduction catalysts. *Int. J. Mol. Sci.* **2021**, *22*, 12300. [\[CrossRef\]](#)
45. Srinivasan, P.D.; Patil, B.S.; Zhu, H.; Bravo-Suárez, J.J. Application of modulation excitation-phase sensitive detection-DRIFTS for in situ/operando characterization of heterogeneous catalysts. *React. Chem. Eng.* **2019**, *4*, 862–883. [\[CrossRef\]](#)
46. Chen, L.; Li, J.; Ge, M. Promotional effect of Ce-doped V₂O₅-WO₃/TiO₂ with low vanadium loadings for selective catalytic reduction of NOx by NH₃. *J. Phys. Chem. C* **2009**, *113*, 21177–21184. [\[CrossRef\]](#)
47. Lai, J.-K.; Wachs, I.E. A perspective on the selective catalytic reduction (SCR) of NO with NH₃ by supported V₂O₅-WO₃/TiO₂ catalysts. *ACS Catal.* **2018**, *8*, 6537–6551. [\[CrossRef\]](#)
48. Han, L.; Cai, S.; Gao, M.; Hasegawa, J.-Y.; Wang, P.; Zhang, J.; Shi, L.; Zhang, D. Selective catalytic reduction of NOx with NH₃ by using novel catalysts: State of the art and future prospects. *Chem. Rev.* **2019**, *119*, 10916–10976. [\[CrossRef\]](#)
49. Ma, L.; Cheng, Y.; Cavataio, G.; McCabe, R.W.; Fu, L.; Li, J. In situ DRIFTS and temperature-programmed technology study on NH₃-SCR of NOx over Cu-SSZ-13 and Cu-SAPO-34 catalysts. *J. Appl. Catal. B* **2014**, *156*, 428–437. [\[CrossRef\]](#)
50. Lezcano-Gonzalez, I.; Deka, U.; Arstad, B.; Van Yperen-De Deyne, A.; Hemelsoet, K.; Waroquier, M.; Van Speybroeck, V.; Weckhuysen, B.M.; Beale, A.M. Determining the storage, availability and reactivity of NH₃ within Cu-chabazite-based ammonia selective catalytic reduction systems. *Phys. Chem. Chem. Phys.* **2014**, *16*, 1639–1650. [\[CrossRef\]](#)