Polyol-Mediated Synthesis of V$_2$O$_5$–WO$_3$/TiO$_2$ Catalysts for Low-Temperature Selective Catalytic Reduction with Ammonia

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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 V$_2$O$_5$ and WO$_3$ 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 NH$_3$-temperature-programmed desorption and H$_2$-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 NH$_3$ and its reduction with NO and O$_2$ 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.

Keywords: polyol-mediated synthesis; NH$_3$-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, NO$_2$, and N$_2$O) 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, NH$_3$-SCR, which converts NO$_X$ in exhaust gas into N$_2$ and H$_2$O, 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]. V$_2$O$_5$–WO$_3$/TiO$_2$ 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, V$_2$O$_5$–WO$_3$/TiO$_2$ 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
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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$_2$O$_3$ catalysts to SO$_2$ (Han et al.) [33]. Yu et al. developed a Cu-SSZ-15 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 V$_2$O$_5$–Sb$_2$O$_3$ /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 NOX removal efficiency with the V$_2$O$_5$ /TiO$_2$ catalyst at 210 °C by co-doping S and N [40]. These catalysts form O$^-$ active sites, increasing chemisorbed oxygen and NH$_3$. Furthermore, Maqbol et al. reported CeO$_2$–Sb /V$_2$O$_5$ /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 NOX. The effect of the polyol process on the V$_2$O$_5$–WO$_3$ /TiO$_2$ catalyst was observed via transmission electron microscopy (TEM), Raman spectroscopy, and Brunauer–Emmett–Teller (BET) analysis. The NOx removal efficiency and N$_2$ selectivity of the catalyst were measured to compare the catalytic activities in the low-temperature range of 150–300 °C. NH$_3$-temperature-programmed desorption (NH$_3$-TPD), H$_2$-temperature-programmed reduction (H$_2$-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$_4$VO$_3$), ammonium metatungstate hydrate (AMT; (NH$_4$)$_6$H$_2$W$_12$O$_{40}$ × H$_2$O), and oxalic acid (C$_2$H$_2$O$_4$) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Ethylene glycol (C$_2$H$_4$O$_2$) was obtained from Daegung 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 V$_2$O$_5$–WO$_3$ /TiO$_2$ Catalysts

We prepared 2 wt.% V$_2$O$_5$–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. TiO$_2$ 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 V$_2$O$_5$ and WO$_3$, respectively. Moreover, V$_2$O$_5$(P)–WO$_3$(IM) and V$_2$O$_5$(IM)–WO$_3$(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 Ka (λ = 0.15406 nm) radiation in the 2θ 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.). NH$_3$-TPD was conducted using AutoChem II 2920 (Micromeritics Instrument Corp.). The samples were pretreated at 150 °C with a current of N$_2$ for 4 h to remove physically adsorbed NH$_3$ species and organic matter. NH$_3$ was then adsorbed with 10% NH$_3$/He gas at 150 °C for 1 h. H$_2$-TPR was conducted using the same instruments as NH$_3$-TPD, in addition to exposing the catalysts to a current of 10% H$_2$/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, NH$_3$ (NH$_3$/NO$_x$ = 1.0), and SO$_2$, and 5 vol.% of O$_2$ with a balance of N$_2$ 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 O$_2$ analyzer (Oxitec 5000; ENOTEC, Marienheide, Germany). The NO$_x$ removal efficiency and N$_2$ selectivity were calculated according to Equations (1) and (2), respectively:

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

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

2.5. In Situ FTIR Measurement

In situ FTIR spectra of all samples were measured using an FTIR spectrometer (VERTEX 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 NH$_3$ (500 ppm), NO (500 ppm), and O$_2$ (5 vol.%) with N$_2$ 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].

\[
\begin{align*}
\text{NH}_4\text{VO}_3 + \text{C}_2\text{H}_5\text{O}_2 & \Rightarrow \text{N}_2 + \text{VO(CH}_2\text{O})_2 + \text{H}_2\text{O} \Rightarrow V_2\text{O}_5 \quad (3) \\
\text{(NH}_4\text{)}_6\text{H}_2\text{W}_{12}\text{O}_{40} \times \text{H}_2\text{O} + \text{C}_2\text{H}_5\text{O}_2 & \Rightarrow \text{N}_2 + \text{WO(CH}_2\text{O})_2 + \text{H}_2\text{O} \Rightarrow \text{WO}_3 \quad (4)
\end{align*}
\]

**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                  | TiO₂ | V₂O₅ | WO₃ | SO₃ |
|-------------------------|------|------|-----|-----|
| $V_2O_5$(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 TiO₂ 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 $V_2O_5$–$WO_3$/TiO₂ catalysts were measured by XRD analysis and Raman spectroscopy. The XRD results showed the anatase phase of TiO₂ 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 TiO₂ support. Raman spectroscopy was used to understand the crystalline structure and particle size of $V_2O_5$–$WO_3$/TiO₂ catalysts. The Raman spectra of all catalysts contained TiO₂ 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 700–1100 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 $V_2O_5$–$WO_3$/TiO₂ than $V_2O_5$ nanoparticles.
cles (Table 2). V2O5(P)–WO3(P) and V2O5(IM)–WO3(P) with the polyol process applied to zation of the WO3 nanoparticles with a content of 5 wt.%, which is a relatively large portion of all catalysts contained TiO2 anatase peaks at 144.7, 197.3, 401.5, 518.5, and 639.1 cm\(^{-1}\) 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 because of the atomi-

3.2. Evaluation of Catalytic Activity

In the general NH3-SCR process, NO\(_X\) is converted to nitrogen and water through the reduction reaction of the NH3 and NO\(_X\) on catalysts (Equations (5)–(8)) [48].

\[
\begin{align*}
4\text{NO} + 4\text{NH}_3 + \text{O}_2 &\rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} & (5) \\
\text{NO} + \text{NO}_2 + 2\text{NH}_3 &\rightarrow 2\text{N}_2 + 3\text{H}_2\text{O} & (6) \\
2\text{NO}_2 + 4\text{NH}_3 + \text{O}_2 &\rightarrow 3\text{N}_2 + 6\text{H}_2\text{O} & (7) \\
6\text{NO}_2 + 8\text{NH}_3 &\rightarrow 7\text{N}_2 + 12\text{H}_2\text{O} & (8)
\end{align*}
\]

The SCR catalysts efficiently and selectively reduce NO\(_X\) to N\(_2\). The NO\(_X\) removal efficiency of the V2O5(P)–WO3(P), V2O5(P)–WO3(IM), and V2O5(IM)–WO3(P) catalysts was higher than that of V2O5(IM)–WO3(IM) at 150–300 °C (Figure 3a). At 250 °C, the NO\(_X\) removal efficiencies of V2O5(P)–WO3(P), V2O5(P)–WO3(IM), and V2O5(IM)–WO3(P) were 96%, 93%, and 86%, respectively, whereas that of V2O5(IM)–WO3(IM) was the lowest at 66%, and the high NO\(_X\) removal efficiencies of V2O5(P)–WO3(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 V2O5–WO3/TiO2 catalysts increases the specific surface area, leading to enhanced reactions sites for V2O5 and WO3. In particular, the polyol process for V2O5 nanoparticles was more critical to NO\(_X\) removal efficiency than WO3 nanoparticles, because the durability test (Figure S3). Based on these results, we found that adjusting the polyol process for the V2O5–WO3/TiO2 catalysts increases the specific surface area, leading to enhanced reactions sites for V2O5 and WO3. In particular, the polyol process for V2O5 nanoparticles was more critical to NO\(_X\) removal efficiency than WO3 nanoparticles, because
V2O5 as the main catalyst is more active than WO3. 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 ([NH4]HSO4) or ammonium bisulfate ([NH4]2SO4) 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 (NOx) removal efficiency. (b) N2O concentration and (c) N2 selectivity of V2O5(IM)–WO3(IM), V2O5(IM)–WO3(P), V2O5(P)–WO3(IM), and V2O5(P)–WO3(P). Reaction conditions: [NO] = [NH3] = [SO2] = 300 ppm, [O2] = 5 vol.%, N2 as a balance, and [GHSV] = 60,000 h−1.

Figure 3b,c illustrate the N2O concentration and N2 selectivity, respectively. Trace amounts of N2O in all catalysts were produced at temperatures over 250 °C. N2O produced from V2O5 as the main catalyst is more active than WO3. In contrast, all catalysts, including those from the polyol process, had lower N2O concentrations than those using the impregnation method, particularly V2O5(P)–WO3(P), which had the lowest N2O concentration of 1.375 ppm at 300 °C. According to the N2O concentrations, N2 selectivity of V2O5(P)–WO3(P), V2O5(P)–WO3(IM), V2O5(IM)–WO3(P), and V2O5(IM)–WO3(IM) reached 99.52%, 99.29%, 98.29%, and 97.11% at 300 °C, respectively.

3.3. NH3-TPD and H2-TPR Analyses

We further explained the effect of the polyol process on the catalytic performance of the V2O5–WO3/TiO2 catalysts using NH3-TPD and H2-TPR analyses (Figure 4). The NH3-TPD results for V2O5(IM)–WO3(IM), V2O5(IM)–WO3(P), V2O5(P)–WO3(IM), and V2O5(P)–WO3(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 NH3 desorption peaks at 100–200 °C, 300–500 °C, and above 500 °C, indicating weakly, intermediately, and strongly adsorbed NH3 related to Bronsted and Lewis acid sites with different intensities, respectively [49,50]. Generally, the adsorbed NH3 exists as NH4+ ions and coordinated NH3 when bonded to Bronsted acid sites and Lewis acid sites, respectively. In addition, the concentration of desorbed NH3 indicates the adsorption capability of the catalysts. The desorbed NH3 concentration for V2O5(IM)–WO3(IM), V2O5(IM)–WO3(P), V2O5(P)–WO3(IM), and V2O5(P)–WO3(P) was 32.86, 51.98, 57.10, and 54.50 cm3/g, respectively, in the NH3-TPD profile (Table 3). These results indicate that the catalysts from the polyol process have a larger amount of desorbed NH3 than those from the impregnation method, because the polyol process induces a large specific surface area and provides various sites for bonding with NH3. Particularly, V2O5(P)–WO3(P) showed higher thermal conductivity detector (TCD) signals belonging to Bronsted acid sites in the temperature range of 100–500 °C than V2O5(IM)–WO3(P) and V2O5(P)–WO3(IM), suggesting the explanation for the high catalytic performance of V2O5(P)–WO3(P).
WO3(P) were observed at 100–800 °C, which is important for the content and strength of reduction (H2-TPR) integral intensity 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.

NH3 desorption peaks at 100–200 °C, 300–500 °C, and above 500 °C, indicating weakly, intermediately, and strongly adsorbed NH3 related to Bronsted and Lewis acid sites, respectively. In addition, the concentration of desorbed NH3 indicates the adsorption capability of the catalysts. The desorbed NH3 concentration for V2O5(IM)–WO3(IM), V2O5(P)–WO3(IM), and V2O5(P)–WO3(P) in the temperature range of 100–500 °C is larger than for V2O5(IM)–WO3(P) and V2O5(P)–WO3(IM). The mechanism identified by the polyol process is a large specific surface area of V2O5 and WO3, promoting 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 NOx 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 activation capacity of the catalysts or the reaction mechanism between catalysts and reactive gases. Figure 5 illustrates the in situ FTIR spectra of 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$_2$O$_5$(IM)–WO$_3$(P) and V$_2$O$_5$(P)–WO$_3$(IM) were also observed under NH$_3$ gas at 200 °C (Figure S4). The catalysts showed intermediate catalytic activities between V$_2$O$_5$(P)–WO$_3$(P) and V$_2$O$_5$(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$_2$O$_5$(IM)–WO$_3$(IM) and (b) V$_2$O$_5$(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 NOx and oxygen reacted with pre-adsorbed ammonia over V$_2$O$_5$(IM)–WO$_3$(IM) and V$_2$O$_5$(P)–WO$_3$(P) at 200 °C. V$_2$O$_5$(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$_2$O$_5$(P)–WO$_3$(P) and 10 min for the V$_2$O$_5$(IM)–WO$_3$(IM) catalysts. The in situ FTIR spectra of V$_2$O$_5$(IM)–WO$_3$(P) and V$_2$O$_5$(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$_2$O$_5$(P)–WO$_3$(P) and V$_2$O$_5$(IM)–WO$_3$(IM). V$_2$O$_5$(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$_2$O$_5$(P)–WO$_3$(P) was confirmed when the adsorbed ammonia reacted with NO and O$_2$. 
This study provided an effective approach to synthesizing efficient low-temperature SCR catalysts by adopting a polyol process, and the prepared catalyst demonstrated high NOx 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 conventional 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 NOx removal efficiencies were enhanced by approximately 30% compared to the catalysts prepared using the conventional impregnation method. The NH3-TPD results demonstrated that the polyol process provided more surface acid sites generated at low temperatures. H2-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 NH3 and its reduction with NO and O2 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.

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 NOx 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). The small catalyst size enabled an increase in the surface area and catalytic acid sites. At temperatures between 200 and 250 °C, the NOx removal efficiencies were enhanced by approximately 30% compared to the catalysts prepared using the conventional impregnation method. The NH3-TPD results demonstrated that the polyol process provided more surface acid sites generated at low temperatures. H2-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 NH3 and its reduction with NO and O2 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/nano122103644/s1, Figure S1: Transmission electron microscope (TEM) images and selected area electron diffraction (SAED) patterns of (a) V2O5(IM)–WO3(IM), (b) V2O5(IM)–WO3(P), (c) V2O5(P)–WO3(IM), and (d) V2O5(P)–WO3(P). Figure S2: Raman spectra of V2O5(IM)–WO3(IM), V2O5(IM)–WO3(P), V2O5(P)–WO3(IM), and V2O5(P)–WO3(P). Figure S3: NOx removal efficiency of V2O5(P)–WO3(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) V2O5(IM)–WO3(P) and (b) V2O5(P)–WO3(IM) at 200 °C. Figure S5: In situ Fourier-transform infrared spectra of NO and O2 reacted with pre-adsorbed NH3 over (a) V2O5(IM)–WO3(P) and (b) V2O5(P)–WO3(IM) at 200 °C.
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