The Role of Fe$_2$O$_3$ Species in Depressing the Formation of N$_2$O in the Selective Reduction of NO by NH$_3$ over V$_2$O$_5$/TiO$_2$-Based Catalysts

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Abstract: Promotion of 2.73% Fe$_2$O$_3$ in an in-house-made V$_2$O$_5$-WO$_3$/TiO$_2$ (VWT) and a commercial V$_2$O$_5$-WO$_3$/TiO$_2$ (c-VWT) has been investigated as a cost effective approach to the suppression of N$_2$O formation in the selective catalytic reduction of NO by NH$_3$ (NH$_3$-SCR). The promoted VWT and c-VWT catalysts all gave a significantly decreased N$_2$O production at temperatures >400 °C compared to the unpromoted samples. However, such a promotion led to the loss in high temperature NO conversion, mainly due to the oxidation of NH$_3$ to N-containing gases, particularly NO. Characterization of the unpromoted and promoted catalysts using X-ray diffraction (XRD), NH$_3$ adsorption-desorption, and Raman spectroscopy techniques could explain the reason why the promotion showed much lower N$_2$O formation levels at high temperatures. The addition of Fe$_2$O$_3$ to c-VWT resulted in redispersion of the V$_2$O$_5$ species, although this was not visible for 2.73% Fe$_2$O$_3$/VWT. The iron oxides exist as a highly-dispersed noncrystalline α-Fe$_2$O$_3$ in the promoted catalysts. These Raman spectra had a new Raman signal that could be tentatively assigned to Fe$_2$O$_3$-induced tetrahedrally coordinated polymeric vanadates and/or surface V-O-Fe species with significant electronic interactions between the both metal oxides. Calculations of the monolayer coverage of each metal oxide and the surface total coverage are reasonably consistent with Raman measurements. The proposed vanadia-based surface polymeric entities may play a key role for the substantial reduction of N$_2$O formed at high temperatures by NH$_3$ species adsorbed strongly on the promoted catalysts. This reaction is a main pathway to greatly suppress the extent of N$_2$O formation in NH$_3$-SCR reaction over the promoted catalysts.

Keywords: NH$_3$-SCR reaction; V$_2$O$_5$-WO$_3$/TiO$_2$ catalyst; N$_2$O formation; Fe$_2$O$_3$ promotion; NH$_3$ oxidation; Raman spectra

1. Introduction

Commercially-available, anatase-type TiO$_2$-supported V$_2$O$_5$ catalysts with either WO$_3$ or MoO$_3$ as a structure stabilizer of the support and a surface acidity enhancer are typical for selective catalytic reduction (SCR) of NO$_x$ from relatively large scale stationary and mobile sources in the presence of N-containing reductants, such as gaseous NH$_3$ and aqueous urea [1,2]. They are usually formulated to 0.1–3% V$_2$O$_5$ and 7–10% WO$_3$ or 6–10% MoO$_3$ [3–8], depending on industrial application target, and V$_2$O$_5$-WO$_3$/TiO$_2$ systems are prevailed for such deNO$_x$ processes. The overall NH$_3$-SCR reaction with V$_2$O$_5$/TiO$_2$-based catalysts could be adequately described by [5–7]:

\[ 4\text{NO} + 4\text{NH}_3 + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}, \] (1)

\[ \text{NO} + \text{NO}_2 + 2\text{NH}_3 \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O}. \] (2)
The standard Reaction (1) takes place in the presence of excess oxygen, while Reaction (2) has been known as the fast SCR pathway in an equimolar mixture of NO and NO\textsubscript{2} and is known to be much faster than the Reaction (1) at low temperatures [6,9,10].

In addition to the main SCR reactions over V\textsubscript{2}O\textsubscript{5}-WO\textsubscript{3} (or MoO\textsubscript{3})/TiO\textsubscript{2} catalysts, many side reactions can occur, and among them, one is the production of N\textsubscript{2}O that is a greenhouse gas with a global warming potential of 310 at a 100-year time horizon, and the extent of its emissions can greatly depend on the loading and crystallinity of V\textsubscript{2}O\textsubscript{5}, the secondary component, reaction temperature, concentrations of H\textsubscript{2}O and O\textsubscript{2}, and so forth [3,6,11–15]. Such a formation of N\textsubscript{2}O in the NH\textsubscript{3}-SCR reaction is proposed by the following major routes [6,12–15]:

\begin{align}
4\text{NO} + 4\text{NH}_3 + 3\text{O}_2 & \rightarrow 4\text{N}_2\text{O} + 6\text{H}_2\text{O} \quad (3) \\
2\text{NH}_3 + 2\text{O}_2 & \rightarrow \text{N}_2\text{O} + 3\text{H}_2\text{O}. \quad (4)
\end{align}

These reactions predominantly occur at high temperatures when V\textsubscript{2}O\textsubscript{5}-WO\textsubscript{3}/TiO\textsubscript{2} catalysts are employed for deNO\textsubscript{x} SCR reaction and are associated with a decrease in high-temperature NO conversion and N\textsubscript{2} selectivity [12–15].

An attempt to minimize the formation of N\textsubscript{2}O in NH\textsubscript{3}-SCR processes has been reported: a direct coating of Fe-ZSM-5 onto a commercial V\textsubscript{2}O\textsubscript{5}-WO\textsubscript{3}/TiO\textsubscript{2} catalyst [16], a sequential configuration of V\textsubscript{2}O\textsubscript{5}-WO\textsubscript{3}/TiO\textsubscript{2} and Fe-ZSM-5 [17], and a modification of TiO\textsubscript{2} using Fe\textsubscript{2}O\textsubscript{3} before V\textsubscript{2}O\textsubscript{5} and WO\textsubscript{3} loadings [18,19]. These studies were started from the fact that Fe-exchanged zeolites, representatively Fe-ZSM-5, are a commercially proven catalyst not only for the NH\textsubscript{3}-SCR reaction but also for direct N\textsubscript{2}O decomposition; thereby, the decomposition of N\textsubscript{2}O produced in the SCR reaction into N\textsubscript{2} on Fe ions and/or its reduction by residual NH\textsubscript{3} species [20–23] is expected, and from that a nanosized iron oxide, γ-Fe\textsubscript{2}O\textsubscript{3} (maghemite), is active for the NH\textsubscript{3}-SCR reaction, although N\textsubscript{2}O production levels were not addressed for this system [24]. The Fe-ZSM-5-coated V\textsubscript{2}O\textsubscript{5}-WO\textsubscript{3}/TiO\textsubscript{2} catalysts could greatly depress the formation of N\textsubscript{2}O in NH\textsubscript{3}-SCR reaction, depending on the coating content [16], unlike the series configuration systems [17]. Samples of coprecipitated, Fe\textsubscript{2}O\textsubscript{3}-TiO\textsubscript{2}-supported 1% V\textsubscript{2}O\textsubscript{5}, and 1% V\textsubscript{2}O\textsubscript{5}-10% WO\textsubscript{3}/TiO\textsubscript{2} had similar NO conversions at 150–400 °C but at higher temperatures, lower ones, depending on the temperature, were indicated for the former sample [18]. This showed a better N\textsubscript{2} selectivity at high temperatures ≥400 °C [18]; however, this observation may be apparent because of the difference in NO conversion at the temperature region between the catalysts. All 1% V\textsubscript{2}O\textsubscript{5}-10% WO\textsubscript{3} catalysts dispersed on 1–5% Fe\textsubscript{2}O\textsubscript{3}/TiO\textsubscript{2} gave an improvement to N\textsubscript{2} selectivity at temperatures ≥450 °C, compared to the bare TiO\textsubscript{2}-based catalyst; in addition to that, they showed higher NO conversion below 350 °C but comparable NO conversion at higher temperatures [19].

Unsupported and supported Fe\textsubscript{2}O\textsubscript{3} are still suspicious of the tolerance to SO\textsubscript{2} existing in flue gases, depending strongly on their preparation techniques [19,24–26], but this point can be avoided for no sulfur applications, such as natural gas-fired plants. The earlier approaches to the reduction in N\textsubscript{2}O emissions from NH\textsubscript{3}-SCR reaction could advise us of an efficient way of promoting V\textsubscript{2}O\textsubscript{5}-WO\textsubscript{3}/TiO\textsubscript{2} catalysts using Fe\textsubscript{2}O\textsubscript{3}.Such a utilization of Fe\textsubscript{2}O\textsubscript{3} is cost effective, compared to Fe-zeolites whose preparation requires more complicated, expensive processes. Therefore, we have studied a promotional effect of Fe\textsubscript{2}O\textsubscript{3} in samples of laboratory-made V\textsubscript{2}O\textsubscript{5}-WO\textsubscript{3}/TiO\textsubscript{2} and commercial V\textsubscript{2}O\textsubscript{5}-WO\textsubscript{3}/TiO\textsubscript{2} on the suppression of N\textsubscript{2}O production in NH\textsubscript{3}-SCR reaction. The Fe\textsubscript{2}O\textsubscript{3} as a promoter was added to the V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2}-based catalysts using the well-known impregnation technique, and this is much simpler than the utilization of a coprecipitated Fe\textsubscript{2}O\textsubscript{3}-TiO\textsubscript{2} and a Fe\textsubscript{2}O\textsubscript{3}-coated TiO\textsubscript{2} to support V\textsubscript{2}O\textsubscript{5} and WO\textsubscript{3} reported in the literature.
2. Results and Discussion

2.1. Physicochemical Properties of Fe$_2$O$_3$-Promoted V$_2$O$_5$-WO$_3$/TiO$_2$ Catalysts

X-ray diffraction (XRD) patterns for VWT, 2.73% Fe$_2$O$_3$/VWT, c-VWT, and 2.73% Fe$_2$O$_3$/c-VWT at a 2θ value of 10–80° are shown in Figure 1. All the catalysts gave a predominant peak at 2θ = 25.31° with much smaller diffractions at higher 2θ values, as displayed in Figure 1a–d, and all these peaks were the same as those existing in the pattern for anatase TiO$_2$ shown in Figure 1e. No diffraction due to the crystalline WO$_3$ was shown for all the samples, indicating that WO$_3$ existing in them is amorphous WO$_x$ species [27]. There was also no presence of crystalline V$_2$O$_5$ phases, except for c-VWT, in which a weak reflection near 2θ = 21.64° appeared when the diffraction was magnified, as indicated in Figure 1c, which is assigned to the crystallographic (101) plane of a polycrystalline α-V$_2$O$_5$ (JCPDS card # 41-1426) by comparing it with the pure reference V$_2$O$_5$ with an orthorhombic structure as provided in Figure 1f [27,28]. However, the XRD peak disappeared in 2.73% Fe$_2$O$_3$/c-VWT, as shown in the magnified pattern in Figure 1d. It should be mentioned that all of the other catalysts gave no peak at the 2θ value, even in similar magnified spectra (not shown here).

![Figure 1. XRD patterns for: (a) VWT; (b) 2.73% Fe$_2$O$_3$/VWT; (c) c-VWT; (d) 2.73% Fe$_2$O$_3$/c-VWT; (e) pure anatase TiO$_2$; and (f) α-phase orthorhombic V$_2$O$_5$.](image)

Comparing hematite (α-Fe$_2$O$_3$), maghemite (γ-Fe$_2$O$_3$), magnetite (Fe$_3$O$_4$), goethite (α-FeOOH), akaganeite (β-FeOOH), lepidocrocite (γ-FeOOH), and feroxyhyte (δ-FeOOH) in the corresponding JCPDS card #s 33-0664, 39-1346, 02-1035, 29-0713, 34-1266, 08-98, and 29-712, neither of them were indicated in XRD patterns for 2.73% Fe$_2$O$_3$-promoted catalysts, as disclosed in Figure 1b,d. Even a sample of 8% Fe$_2$O$_3$/VWT after calcination at 500 °C gave no crystalline peaks due to the iron compounds (not shown here). Magnetite nanoparticles are easily transformed to γ-Fe$_2$O$_3$ and α-Fe$_2$O$_3$ when, respectively, calcined at 300 and 500 °C in air [29], and all the FeOOH phases can be altered to α-Fe$_2$O$_3$ even at relatively lower thermal energy [30]. Our XRD measurements, and the thermal stability of the iron oxides and oxyhydroxides, reasonably indicate that FeO$_x$ species existing in the promoted catalysts are in the form of α-Fe$_2$O$_3$ as a highly-dispersed noncrystalline particle, and that the Fe$_2$O$_3$ could significantly interact with V$_2$O$_5$ in c-VWT, thereby resulting in redispersion of the V$_2$O$_5$.

2.2. Textural Features of Fe$_2$O$_3$-Promoted V$_2$O$_5$-WO$_3$/TiO$_2$ Catalysts

N$_2$ sorption isotherm of 2.73% Fe$_2$O$_3$/VWT was similar to that measured for VWT and WT, as provided in Figure 2a–c. This case was the same for c-VWT and 2.73% Fe$_2$O$_3$/c-VWT (Figure 2d,e).
All the isotherms showed a typical character of mesoporous materials because of the desorption hysteresis at $P/P_0 = 0.53–0.67$ [31], depending on the sample.

**Figure 2.** $N_2$ sorption isotherms on: (a) WT; (b) VWT; (c) 2.73% Fe$_2$O$_3$/VWT; (d) c-VWT; and (e) 2.73% Fe$_2$O$_3$/c-VWT.

Values for the specific BET surface area ($S_{BET}$), the mesopore size ($d_m$), and the total pore volume ($V_t$) are listed in Table 1. The $S_{BET}$ value of WT decreased upon 1.6% V$_2$O$_5$ loading, which is due to some blockage of relatively small pores by the vanadia, but a further decrease after 2.73% Fe$_2$O$_3$ addition to the VWT was insignificant. These are consistent with changes in values for $d_m$ and $V_t$. On the other hand, the promotion of c-VWT using 2.73% Fe$_2$O$_3$ led to an increased $S_{BET}$ compared to the bare sample, and yielded somewhat smaller $d_m$ and larger $V_t$ values (Table 1). This might be caused by rearrangement of mechanical additives existing in c-VWT, such as glass fibers, during the sample preparation using an aqueous solution of the iron precursor [6,32,33].

**Table 1.** Chemical compositions and textural properties of V$_2$O$_5$/TiO$_2$-based catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Amount (%)</th>
<th>$S_{BET}$ (m$^2$/g)</th>
<th>$d_m$ (Å) $^a$</th>
<th>$V_t$ (cm$^3$/g) $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>V$_2$O$_5$</td>
<td>10</td>
<td>91</td>
<td>127</td>
<td>0.30</td>
</tr>
<tr>
<td>VWT</td>
<td>1.6</td>
<td>10</td>
<td>67</td>
<td>0.26</td>
</tr>
<tr>
<td>2.73% Fe$_2$O$_3$/VWT</td>
<td>1.6</td>
<td>10</td>
<td>60</td>
<td>0.23</td>
</tr>
<tr>
<td>c-VWT</td>
<td>1.44</td>
<td>9.42</td>
<td>70</td>
<td>0.27</td>
</tr>
<tr>
<td>2.73% Fe$_2$O$_3$/c-VWT</td>
<td>1.44</td>
<td>9.42</td>
<td>89</td>
<td>0.31</td>
</tr>
</tbody>
</table>

$^a$ Using the Barrett-Joyner-Halenda (BJH) mesopore model. $^b$ Calculated using $N_2$ sorption amounts at $P/P_0 \approx 0.994$.

2.3. Effect of Fe$_2$O$_3$ Species on NH$_3$-SCR Reaction and N$_2$O Formation

Conversions of NO and NH$_3$ in deNO$_x$ reaction with VWT, 2.73% Fe$_2$O$_3$/VWT, c-VWT, and 2.73% Fe$_2$O$_3$/c-VWT and N$_2$O production are shown in Figures 3 and 4, respectively. The VWT-only exhibited 100% NO conversion at 300–400 °C, while at higher temperatures, it decreased depending on the temperature, as provided in Figure 3a. This shape of activity loss is a common feature of NH$_3$-SCR reaction over V$_2$O$_5$/TiO$_2$-based catalysts due to some side reactions giving N$_2$O, N$_2$, and NO [1,13,34]. The commercial unpromoted catalyst, i.e., c-VWT, basically showed a similar
temperature vs. deNO\textsubscript{x} activity. These behaviors are consistent with those reported for 1.7–3.5\% V\textsubscript{2}O\textsubscript{5} dispersed on a commercial 10\% WO\textsubscript{3}/TiO\textsubscript{2} [1], 1.5\% V\textsubscript{2}O\textsubscript{5}-10\% WO\textsubscript{3}/TiO\textsubscript{2} [35], and 1–5\% V\textsubscript{2}O\textsubscript{5} on four different commercial WO\textsubscript{3}/TiO\textsubscript{2} supports with a WO\textsubscript{3} content of 4.7–6.8\% [36]. After addition of 2.73\% Fe\textsubscript{2}O\textsubscript{3} to VWT and c-VWT, these all gave a significant decrease in NO conversion above 400 °C. As an example, the 2.73\% Fe\textsubscript{2}O\textsubscript{3}/VWT had a NO conversion of 60\% at 480 °C, which is lower, by 20\%, than that indicated over the unpromoted catalyst. In case the 2.73\% Fe\textsubscript{2}O\textsubscript{3}/c-VWT was used, the extent of such a decrease was much smaller.

Figure 3b shows NH\textsubscript{3} conversions over the unpromoted and promoted catalysts. Each value for NH\textsubscript{3} conversion below 400 °C could be comparable to that indicated for NO (Figure 3a), which is consistent with the overall reaction described by Equations (1) and (2). However, at higher temperatures the value was 100\% regardless of the catalyst employed, and there is a difference in conversion between NH\textsubscript{3} and NO. This discrepancy depended not only on the catalyst employed but also on the presence of the iron oxide. The extent of the difference was smaller over the laboratory-made VWT than over the c-VWT, but this trend was reversed when 2.73\% Fe\textsubscript{2}O\textsubscript{3} was promoted to VWT and c-VWT (Figure 3a,b). Consequently, it is definitely represented that besides the general SCR mechanism, NH\textsubscript{3} would be consumed via undesired pathways at high temperatures >400 °C.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.png}
\caption{Conversions of (a) NO and (b) NH\textsubscript{3} in the reduction of NO by NH\textsubscript{3} over unpromoted and Fe\textsubscript{2}O\textsubscript{3}-promoted V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2}-based catalysts.}
\end{figure}

N\textsubscript{2}O could be produced over V\textsubscript{2}O\textsubscript{5}-WO\textsubscript{3} (or MoO\textsubscript{3})/TiO\textsubscript{2} catalysts widely used for stationary and mobile applications and it can approach about 750 ppm depending strongly on the catalyst formulation and reaction conditions [8,13,37]. Whether or not the formation of N\textsubscript{2}O in NH\textsubscript{3}-SCR reaction with Fe\textsubscript{2}O\textsubscript{3}-promoted V\textsubscript{2}O\textsubscript{5}-WO\textsubscript{3}/TiO\textsubscript{2} catalysts can be significantly depressed is of particular interest. Results are provided in Figure 4. A comparison between VWT and 2.73\% Fe\textsubscript{2}O\textsubscript{3}/VWT indicated that the Fe\textsubscript{2}O\textsubscript{3} promotion can greatly suppress N\textsubscript{2}O production. That is, the VWT catalyst had, respectively, ca. 60 and 110 ppm N\textsubscript{2}O at 450 and 480 °C, but the respective values decreased to about 25 and 45 ppm over the promoted VWT sample, corresponding to a reduction by 60\% regardless of the temperature. This catalyst lost a NO conversion by 12–20\% at 450–480 °C, compared to that observed for the VWT-only (Figure 3a). Although the indicated difference in NO conversion between c-VWT and 2.73\% Fe\textsubscript{2}O\textsubscript{3}/c-VWT at temperatures >400 °C was less than 10\% (Figure 3a), a depression effect on N\textsubscript{2}O formation was similar to that of the promoted VWT catalyst (Figure 4). It represents that the Fe\textsubscript{2}O\textsubscript{3} species in the VWT and c-VWT can be responsible for significant reduction in N\textsubscript{2}O emissions from NH\textsubscript{3}-SCR reaction at high temperatures.
The small changes in the textural properties of the Fe$_2$O$_3$-promoted catalysts (Table 1) might not contribute to the observed decrease in both NO removal and N$_2$O formation above 400 °C, because these reactions are predominantly determined by chemical compositions rather than textural features [8,38]. A commercial V$_2$O$_5$-WO$_3$/TiO$_2$ catalyst after prolonged usage at industrial deNO$_x$ plants could yield a large amount of N$_2$O via Equation (3) at high temperatures [6]. However, low N$_2$O production over the Fe$_2$O$_3$-promoted catalysts may not be due to significant inactivation of Equation (3), since in this circumstance, all NO and NH$_3$ conversions shall decrease by Equation (1). If the observed decrease in the NO conversion were because of Equation (4), the extent of the N$_2$O formed should increase. Based on the discussion, and the measured data for NO and NH$_3$ conversions, it is proposed that the oxidation of NH$_3$ into NO over the promoted catalysts at high temperatures, 

$$4\text{NH}_3 + 5\text{O}_2 \rightarrow 4\text{NO} + 6\text{H}_2\text{O},$$  

could occur. Thus, the NO gives rise to the decrease in deNO$_x$ activity while NH$_3$ conversion is still high. Such a NO generation even at 300 °C can take place over Fe$_2$O$_3$-containing mixed metal oxides, such as Fe$_2$O$_3$-TiO$_2$, which has been also highly active for NH$_3$-SCR reaction [39]. A 3% V$_2$O$_5$-9% WO$_3$/TiO$_2$ catalyst shows the formation of NO in NH$_3$ oxidation at temperatures >425 °C, depending on concentrations of O$_2$ in a feed gas stream [14]. Consequently, the addition of Fe$_2$O$_3$ to V$_2$O$_5$/TiO$_2$-based catalysts depresses the formation of N$_2$ in NH$_3$-SCR reaction at high temperatures, but unfortunately this approach can accompany the undesired pathway.

Another interest to us is whether or not different N$_2$O production levels of unpromoted and Fe$_2$O$_3$-promoted V$_2$O$_5$/TiO$_2$-based catalysts could result in a difference in absolute NO conversion between them. VWT had a NO conversion near 80% at 480 °C, and a similar value could be exhibited over 2.73% Fe$_2$O$_3$/VWT at 450 °C (Figure 3a). Therefore, both samples should give 50 ppm N$_2$O because of 100% conversion for NH$_3$ at each temperature (Figure 3b) and the fact that all the NH$_3$ was consumed according to Equation (4). However, the latter catalyst generated ca. 25 ppm N$_2$O at 450 °C (Figure 4), which is only a half of the concentration of N$_2$O expected using Equation (4), while the unpromoted one did ca. 110 ppm N$_2$O at 480 °C, which is over twice as high as the expected N$_2$O (Figure 4). These points represent that the VWT-only could produce N$_2$O via Equation (3) and that Fe$_2$O$_3$ species added to VWT can depress N$_2$O emissions in NH$_3$-SCR reaction. Such a role is probable, with an assumption not only that the promoted VWT could have more abundant NH$_3$ species strongly adsorbed on the
surface but also that the NH$_3$ could readily reduce N$_2$O produced [24]. This surface reaction can be successfully described as the overall stoichiometry [16,20,21],

$$4\text{N}_2\text{O} + 4\text{NH}_3 + \text{O}_2 \rightarrow 6\text{N}_2 + 6\text{H}_2\text{O},$$

(6)

and it is consistent with earlier studies that N$_2$O has been easily reduced by NH$_3$ over Fe-zeolites [20,21,40]. Furthermore, this pathway to decrease N$_2$O production was very similar to that reported in our previous work for a commercial V$_2$O$_5$-WO$_3$-TiO$_2$ catalyst coated by Fe-ZSM-5 [16], indicating that Fe$_2$O$_3$ is promised as a much cheaper, simpler promoter for significant reduction in N$_2$O emissions in NH$_3$-SCR reaction at high temperatures. On the other hand, 2.73% Fe$_2$O$_3$/c-VWT and c-VWT both showed much lower N$_2$O concentrations than maximum values that can be reached by only a single pathway of Equation (4) at similar a NO conversion to each other (Figures 3a and 4). Besides this, all the catalysts above 350 °C gave lesser N$_2$O production than those over the unpromoted and promoted VWT (Figure 4). It suggests that the c-VWT-based catalysts may possess much greater ability to catalyze Equation (6). Surface chemistry regarding this reaction occurring on the Fe$_2$O$_3$-promoted VWT and c-VWT catalysts will be evident in NH$_3$ TPD (temperature-programmed desorption) measurements below.

2.4. Role of Fe$_2$O$_3$ Species for the Suppression of N$_2$O Formation

In the TPD of NH$_3$ adsorbed on VWT, 2.73% Fe$_2$O$_3$/VWT, c-VWT, and 2.73% Fe$_2$O$_3$/c-VWT, mass spectra for the releasing NH$_3$ and gaseous products such as H$_2$O, N$_2$O, NO, and N$_2$ are provided in Figures 5 and 6. Predominant desorption of the adsorbed NH$_3$ occurred at temperatures ranging from 225 to 275 °C with bumps at 370–425 °C and high-temperature peaks at 650–690 °C, depending on the catalyst, as shown in spectra S1 to S4 in Figure 5a. Both a downward-shift of a maximum desorption temperature by 20–35 °C and an appreciable increase of the 650–690 °C NH$_3$ occurred on the Fe$_2$O$_3$-promoted samples (Figure 5a(S2,S4)). This implies that although the Fe$_2$O$_3$ species weakened the acid strength of sites for NH$_3$ desorbing at relatively low temperature region, they could significantly increase very stable NH$_3$ species. This agrees well with the discussion above. Figure 5b shown for H$_2$O generation is indicative of the oxidation of the adsorbed NH$_3$ to the N-containing products. The H$_2$O gave peaks with maxima around 250–260, 450–470, and 645–660 °C, depending on the sample (Figure 5b(S1–S4)). A relatively much higher H$_2$O production at the 645–660 °C region was detected for c-VWT and 2.73% Fe$_2$O$_3$/c-VWT (Figure 5b(S3,S4)), proposing that these catalysts can, to a much greater extent, oxidize the adsorbed NH$_3$ species into the N-containing gases, as shown below.

![Figure 5. Mass spectra for NH$_3$ desorbed and H$_2$O produced during NH$_3$ TPD runs with unpromoted and Fe$_2$O$_3$-promoted catalysts: (a) NH$_3$ and (b) H$_2$O. In (a) and (b), S1: VWT; S2: 2.73% Fe$_2$O$_3$/VWT; S3: c-VWT; S4: 2.73% Fe$_2$O$_3$/c-VWT.](image-url)
Mass spectra for \( \text{N}_2\text{O}, \text{NO}, \text{and N}_2 \) in the \( \text{NH}_3 \) TPD runs with the bare and \( \text{Fe}_2\text{O}_3 \)-promoted catalysts are provided in Figure 6. All these catalysts gave major NO peaks having a maximum at 240–280 °C with shoulders at 375–415 and 480–495 °C, and relatively small peaks at temperatures >570 °C (Figure 6a). The last peaks are indirect evidence of \( \text{NH}_3 \)-related species strongly adsorbed on the catalyst surface. It is clear that \( \text{NH}_3 \) adsorbed on the catalysts reacts with labile surface oxygen atoms existing in \( \text{VO}_x, \text{FeO}_x, \text{and WO}_x \) to create gaseous NO [41,42]. The most appropriate overall stoichiometry of this surface reaction can be described using Equation (5). Of course, the extent of the NO formation is small when the indicated size of the vertical solid bar in Figures 5 and 6 was compared each other.

Figure 6b shows \( \text{N}_2\text{O} \) production whose peaks at 270–285, 445–490, and 650–680 °C appear. Their intensity greatly depended on the catalyst, as seen in spectra S1–S4. c-VWT had an additional peak at 780 °C and showed a \( \text{N}_2\text{O} \) production profile similar to that reported for another commercial 1.68% \( \text{V}_2\text{O}_5\)-7.6% \( \text{WO}_3\)/\( \text{TiO}_2 \) catalyst [16]. The 780 °C \( \text{N}_2\text{O} \) peak disappeared after promotion with 2.73% \( \text{Fe}_2\text{O}_3 \) (Figure 6b(S4)). All these \( \text{N}_2\text{O} \) peaks might come from \( \text{NH}_4^+ \)-like species on Bronsted acid sites such as \( \text{W}^{5+}\text{-OH} \) and \( \text{WO}_3^\text{3-}-\text{induced V}^{4+}\text{-OH} \), and from \( \text{NH}_x \) moieties (\( x = 1–3 \)) adsorbed on Lewis acid sites, \( \text{VO}_x, \text{WO}_x, \text{and FeO}_x \) [43–45]. Both \( \alpha\)-\( \text{Fe}_2\text{O}_3 \) and \( \gamma\)-\( \text{Fe}_2\text{O}_3 \) have no Bronsted acidity [46,47]. An intensity of the 650–680 °C \( \text{N}_2\text{O} \) peak in VWT and 2.73% \( \text{Fe}_2\text{O}_3\)/VWT (S1 and S2) was very weak compared to that in the other samples (S3 and S4), which is in excellent agreement with the \( \text{H}_2\text{O} \) production levels (Figure 5b). All the unpromoted catalysts (spectra S1 and S3 in Figure 6b) gave \( \text{N}_2\text{O} \) peaks at 490 °C. This temperature was shifted to 445 °C over \( \text{Fe}_2\text{O}_3 \)-promoted samples (S2 and S4), implying that the \( \text{Fe}_2\text{O}_3 \) allows a decrease in the activation energy for the oxidation of adsorbed \( \text{NH}_3 \) to \( \text{N}_2\text{O} \). The promoted catalysts showed lesser \( \text{N}_2\text{O} \) emissions in \( \text{NH}_3\text{-SCR} \) reaction (Figure 4). It is well-known that direct oxidation of \( \text{NH}_3 \) to \( \text{N}_2 \) and \( \text{N}_2\text{O} \), not via adsorbed \( \text{NH}_x \) species (\( x = 1 \) or 2), is improbable and \( \text{NH}_x \) species on \( \text{V}^{5+}\text{=O} \) sites reacts with gas-phase NO to form \( \text{N}_2\text{O} \) and \( \text{V}^{4+}\text{-OH} \) [11,39,48]. This represents that gaseous NO is essential for such \( \text{N}_2\text{O} \) production, suggesting an involvement of NO molecules shown in Figure 6a because of no feed of NO upon \( \text{NH}_3 \) TPD experiments.

**Figure 6.** Mass spectra for the production of (a) NO, (b) \( \text{N}_2\text{O} \), and (c) \( \text{N}_2 \) in \( \text{NH}_3 \) TPD runs with unpromoted and promoted VWT-based catalysts. In (a–c), S1: VWT; S2: 2.73% \( \text{Fe}_2\text{O}_3\)/VWT; S3: c-VWT; S4: 2.73% \( \text{Fe}_2\text{O}_3\)/c-VWT.

Mass spectra for \( \text{N}_2 \) evolved in \( \text{NH}_3 \) TPD runs with the unpromoted and promoted catalysts are shown in Figure 6c. Each catalyst had a predominant peak at 450–465 °C with a shoulder at 280–350 °C and a broad peak at temperatures >600 °C, depending on the sample, as seen in profiles S1–S4. As for NO and \( \text{N}_2\text{O} \) in Figure 6a,b, all those \( \text{N}_2 \) peaks would be associated with ammonium ions and \( \text{NH}_x \) on Bronsted and Lewis acid centers [43–45]. The \( \text{NH}_4^+ \) species are oxidized to \( \text{N}_2 \) via NO-assistant route, as discussed [11,39,48]. The presence of \( \text{Fe}_2\text{O}_3 \) in VWT and c-VWT caused not only a shift of the major \( \text{N}_2 \) peak to lower temperatures, by 5–15 °C, but also a significant increase in their intensity,
and such changes were greater for the commercial-based catalysts (Figure 6c(S3,S4)). These are in good accordance with the observed trend in the water production of H₂O as an indicator of N-associated side reactions (Figure 5b). It is thought that the promotion by amorphous iron oxide particles can decrease the activation energy for the oxidation of the adsorbed NH₃ species into N₂ and significantly enhance this reaction.

Based on the results in NH₃ TPD experiments with the unpromoted and 2.73% Fe₂O₃-promoted catalysts, and the previous discussion, the iron oxide promotion could significantly increase surface NH₃ species, producing the 650–690 °C peak (Figure 5a), and this ammonia species can be oxidized to NO, N₂O, and N₂ at high temperatures >550 °C (Figure 6). The presence of the Fe₂O₃ is, to some extent, responsible for the loss in deNOₓ activity at temperatures >400 °C due to the NO formation (Figure 3a). The NO formed via Equation (5) and/or NO in the feed stream may act as an intermediate for the N₂ formation (Figure 4). This proposal is similar to that reported for great reduction in N₂O emissions over Fe-zeolites alone and Fe-ZSM-5-coated V₂O₅-WO₃/TiO₂ catalysts [16,20,21,23,40]. Consequently, Fe₂O₃ species existing in V₂O₅/TiO₂-based catalysts play a significant role for the suppression of N₂O formation in NH₃-SCR reaction at high temperature side, and this approach is a much simpler and more cost-effective compared to Fe-zeolite promotion techniques.

2.5. Surface Structure of Fe₂O₃, V₂O₅, and WO₃ Species

Figure 7 shows Raman spectra for reference materials and WT whose original signals have been reduced by 1/10–1/1000 for an easier comparison, but all bands have been kept unchanged even after such a data processing. α-phase V₂O₅ polycrystallites yielded a sharp peak at 990 cm⁻¹ with subsequent signals near 400, 470, 515, and 700 cm⁻¹, as seen in Figure 7a. Crystalline WO₃ had characteristic sharp bands around 800 and 715 cm⁻¹ (Figure 7b), and no Raman signals at frequencies >800 cm⁻¹ even in a magnified spectrum existed as indicated by the dashed line. The measured spectra for the V₂O₅ and monoclinic γ-WO₃ (P2₁/n) are in agreement with earlier studies [49,50]. Bands due to highly-dispersed amorphous WOₓ in a sample of WT that has been employed for preparing VWT and 2.73% Fe₂O₃/VWT catalysts can be differentiated by comparing with those existing in a bare anatase TiO₂ (Figure 7c,d). This support had Raman signals at 397, 515, and 638 cm⁻¹ (Figure 7c) with a predominant band at 145 cm⁻¹ and a weak one at 197 cm⁻¹ (not shown here). The 397, 515 and 145, and 197 and 638 cm⁻¹ bands correspond to the respective B₃g, A₁g + B₁g, and E₈ phonon vibrations of anatase-type TiO₂ [49,51–53]. A weak signal at 793 cm⁻¹ (see the magnified spectrum in Figure 7c) is due to the first overtone of the 395 cm⁻¹ [49,52,53]. Besides these peaks, bands at 882 and 980 cm⁻¹ existed in the WT sample, as provided in the magnified spectrum in Figure 7d. The 980 cm⁻¹ peak is assigned to two-dimensional polytungstate species with distorted octahedrally-coordinated environments that have been reported for calcined WO₃/TiO₂ samples not exceeding a monolayer coverage [53,54]. The 882 cm⁻¹ is associated with asymmetric W-O-W vibrations in polymeric surface WOₓ species [53]. It is represented that the WT sample has two different surface WOₓ species. The absence of the 800 and 715 cm⁻¹ bands reveals no crystalline WO₃ particles, indicating a very good dispersion of the tungsten oxide on the titania.

Raman spectra for VWT, 2.73% Fe₂O₃/VWT, c-VWT, and 2.73% Fe₂O₃/c-VWT are provided in Figure 8. All the catalysts had bands near 394, 515, 636, and 790 cm⁻¹, that are due to the TiO₂ support (Figure 7c), and they all also produced peaks at 880 and 981 cm⁻¹ (Figure 7a–d). Any of the catalysts indicated no band near 1020–1030 cm⁻¹ regarding isolated surface VOₓ species [35,55]. The 981 and 880 cm⁻¹ peaks had appeared even in the WT-only sample (Figure 7d). Regardless, these two bands may not be originated from the W=O and W-O-W structures in the surface tungsten oxide species. Symmetric V=O and W=O stretching vibrations occur at 950–990 cm⁻¹, making it
difficult to clearly distinguish between both species, but the V=O species have an interaction cross section that is almost four times greater than that of the W=O groups [53,55–57]; thus, a Raman signal by the V=O structures in surface vanadium oxide species would give much stronger intensity at the frequency region. Furthermore, it has been reported not only for no appreciable mutual effect on the surface structures of VO\textsubscript{x} and WO\textsubscript{x} species in V\textsubscript{2}O\textsubscript{5}-WO\textsubscript{5}/TiO\textsubscript{2} systems with low total VO\textsubscript{x} and WO\textsubscript{x} coverages but also for Raman bands at 940–987 cm\textsuperscript{-1}, due to two-dimensional VO\textsubscript{x} species in 1–4.5% V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} below a monolayer coverage, whose positions are usually higher, by 10–30 cm\textsuperscript{-1}, than that of surface WO\textsubscript{x} species in 1–7% WO\textsubscript{3}/TiO\textsubscript{2} [55,58]. Consequently, the 880 and 981 cm\textsuperscript{-1} bands correspond to the respective bridging V-O-V and terminal V=O structures in distorted octahedrally coordinated VO\textsubscript{6} species, even in the TiO\textsubscript{2}-supported binary and ternary component systems employed here, and indicate the presence of polymerized mono-oxo vanadate species [49,53,55,56,58].

![Figure 7](image.png)

**Figure 7.** Raman spectra for reference chemicals and a supported WO\textsubscript{3}-only sample: (a) V\textsubscript{2}O\textsubscript{5}; (b) WO\textsubscript{3}; (c) TiO\textsubscript{2}; (d) 10% WO\textsubscript{3}/TiO\textsubscript{2} (WT).

All the iron oxides discussed in the XRD measurements, except for magnetite, exhibit Raman bands at 1000–1600 cm\textsuperscript{-1} in which no Raman signals by TiO\textsubscript{2} appear [30,49,51,59]. However, all the 2.73% Fe\textsubscript{2}O\textsubscript{3}-promoted catalysts gave no bands in the frequency region as well as at 800–1100 cm\textsuperscript{-1} (Figure 8b,d). The latter is because of the absence of Fe=O bonds in the iron oxides. Of course, bands below 800 cm\textsuperscript{-1} by Fe-O in surface iron oxide species could not be visible due to very intense signals of the titania support itself. All the promoted samples also gave no peaks near 1320, and 1375 and 1580 cm\textsuperscript{-1} for crystalline α- and γ-Fe\textsubscript{2}O\textsubscript{3}, respectively [30]. The intensity of all the characteristic vibration modes of the support was maintained unchanged even after the addition of 2.73% Fe\textsubscript{2}O\textsubscript{3} to VWT and c-VWT, proposing that no great interaction of the iron oxide species with the titania surface occurred. There is no indication of the formation of V\textsubscript{2}O\textsubscript{5}, WO\textsubscript{3}, and Fe\textsubscript{2}O\textsubscript{3} crystals even in the titania-supported ternary systems, consistent with the previous discussion in the XRD measurements (Figure 1). This indicates that they all consist of submonolayer coverage of the metal oxides species. Table 2 lists the surface density of each metal oxide existing in the unpromoted and promoted catalysts that was estimated using its amount and their S\textsubscript{BET} value given in Table 1. Calculations of the surface coverage based on monolayer coverage of each metal oxide reported in the literature [60–66] are also provided in Table 2. Both VO\textsubscript{x} and FeO\textsubscript{x} were below monolayer coverage irrespective of the catalyst, but WO\textsubscript{x} in VWT, 2.73% Fe\textsubscript{2}O\textsubscript{3}/VWT and c-VWT could exceed the monolayer coverage, which is mainly due to a rather wide range of experimentally-determined WO\textsubscript{x} monolayer values, such as
4.6–7.0 µmol WO$_x$/m$^2$ [60,61,63,65,66]. The upper limit can give us a value near monolayer coverage. The calculated coverages are in reasonable agreement with the Raman measurements. The total surface coverage expressed as MeO$_x$ in Table 2 can be similarly explained, even though it was somewhat high for 2.73% Fe$_2$O$_3$/VWT. Finally, c-VWT after Fe$_2$O$_3$ promotion indicated a decrease in the surface coverages of each component, as well as of MeO$_x$, consistent with the redispersion of V$_2$O$_5$ in the promoted catalyst (Figure 1d).

The noticeable difference between the unpromoted samples and the promoted ones is a new shoulder around 945 cm$^{-1}$, broadening of the 981 cm$^{-1}$ band, and appreciable weakening of the phonon intensity of the 880 cm$^{-1}$ signal associated with polymeric surface VO$_x$ species (see the magnified spectra in Figure 8b,d). These strongly suggest an alteration of the molecular structure of surface vanadia and/or tungsta species when 2.73% Fe$_2$O$_3$ was introduced to VWT and c-VWT. However, it does not seem that there was a great structural interaction between the surface VO$_x$ species and the FeO$_x$ species, since the position of the 880 and 981 cm$^{-1}$ bands is the same even after the promotion [61]. The terminal V=O band broadening is because of small interactions between the surface metal oxides, perhaps VO$_x$ and FeO$_x$ [55,60,63]. This was indicated by the disappearance of the XRD peak due to V$_2$O$_5$ in 2.73% Fe$_2$O$_3$/c-VWT (see Figure 1c,d), although such a change was not visible for VWT and 2.73% Fe$_2$O$_3$/VWT. The interaction can increase the extent of the disorder of the catalyst surface, and this becomes more energetically heterogeneous, suggesting that an enhancement to the main NH$_3$-SCR routes and/or the side reactions over the promoted catalysts is probable. The new signal at 945 cm$^{-1}$ may be associated with rearrangement of the polymeric surface VO$_x$ species, because it appeared with the weakening of the 880 cm$^{-1}$ band. All samples of V$_2$O$_5$/TiO$_2$ and V$_2$O$_5$-WO$_3$/TiO$_2$ with low total surface coverage exhibited signals near 945 cm$^{-1}$ in their Raman spectra collected at ambient conditions, and these were assigned to surface metavanadate species [55]. On the other hand, not only a significant electronic interaction between Fe$^{3+}$ species and V$^{5+}$ ones in titania-supported iron vanadates that are highly active for NH$_3$-SCR reaction could be evident from the Fe and V K-edge X-ray absorption, but a reduced oxidation capability of the vanadium oxide in the V-O-Fe species was also proposed to give a better N$_2$ selectivity at high temperatures >300 °C [67]. Combining our Raman results with the earlier reports suggests that the tetrahedrally coordinated...
polymeric vanadates adjacent to Fe$_2$O$_3$ species play a role in the reduction of N$_2$O formed in NH$_3$-SCR reaction at high temperatures by strongly-adsorbed NH$_3$ residues.

Table 2. Surface density and surface coverages of the active ingredients in V$_2$O$_5$/TiO$_2$-based catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface Density (µmol/m$^2$)</th>
<th>Surface Coverage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>VO$_x$</td>
<td>WO$_x$</td>
</tr>
<tr>
<td>WT</td>
<td>2.63</td>
<td>6.44</td>
</tr>
<tr>
<td>VWT</td>
<td>2.93</td>
<td>7.19</td>
</tr>
<tr>
<td>2.73% Fe$_2$O$_3$/VWT</td>
<td>2.26</td>
<td>5.80</td>
</tr>
<tr>
<td>c-VWT</td>
<td>1.78</td>
<td>4.57</td>
</tr>
<tr>
<td>2.73% Fe$_2$O$_3$/c-VWT</td>
<td>2.26</td>
<td>5.80</td>
</tr>
</tbody>
</table>

Note: "-": not applicable or measured. a Sum of the surface density values for VO$_x$, WO$_x$, and FeO$_x$. b Based on monolayer coverage of 10.9-13.1 µmol VO$_x$/m$^2$ [60-64]. c Based on monolayer coverage of 4.6-7.0 µmol WO$_x$/m$^2$ [60,61,63,65,66]. d Based on monolayer coverage of ca. 6.5 µmol FeO$_x$/m$^2$ [61,63]. e Sum of the surface coverages of VO$_x$, WO$_x$, and FeO$_x$.

3. Experimental

3.1. Preparation of Catalyst Samples

A commercial powder-type 10% WO$_3$/TiO$_2$ (Tronox Ltd., formerly Kerr-McGee Corp., Stamford, CT, USA), hereafter designated to “WT”, was employed to prepare a V$_2$O$_5$-WO$_3$/TiO$_2$ catalyst. An appropriate amount of the WT (ca. 10 g) was calcined at 500 °C for 4 h in flowing 21% O$_2$/79% N$_2$ (Praxair, 99.999%, Changwon, Korea) at a total flow rate of 300 cm$^3$/min. A 1.6% V$_2$O$_5$/WT catalyst was prepared by impregnating the calcined WT with an aqueous NH$_3$·VO$_3$ (Aldrich, 99.99%, Saint Louis, MO, USA) solution with the corresponding vanadium content, which had been obtained by dissolving it in an aqueous solution of oxalic acid (Aldrich, ≥99%) with a pH near 2.5 dissolved in distilled, deionized water (DDI), referred to as “VWT”. A part of this sample was used for the preparation of approximately 5 g 2.73% Fe$_2$O$_3$/VWT that was made by impregnating the VWT with a aqueous solution of Fe(NO$_3$_)$_3$·9H$_2$O (Aldrich, ≥99.95%) dissolved in DDI water. A commercial extruded V$_2$O$_5$-WO$_3$/TiO$_2$ honeycomb was supplied from a domestic coal-fired power plant and crushed, finely ground, and calcined as for the WT, denoted to “c-VWT” to differentiate it from the VWT. A 2.73% Fe$_2$O$_3$/c-VWT catalyst was prepared using the calcined c-VWT in a fashion similar to that described for the VWT-supported iron oxide. All the catalysts used were dried at 110 °C overnight in an oven and then calcined as for the WT prior to using them for NH$_3$-SCR reaction and characterization. The N$_2$ and O$_2$ used were further purified by passing them through moisture trap and Oxytraps (Alltech Assoc., Deerfield, IL, USA). The amounts of V$_2$O$_5$ and WO$_3$ existing in the c-VWT were determined using ICP (inductively-coupled plasma) measurements.

3.2. NH$_3$-SCR deNO$_x$ Reaction and Determination of N$_2$O Formation

Details of the modified Model MARS 0.75 L/8.0 V White gas cell (Zemini Scientific Instr., Buena Park, CA, USA) combined with a Thermo Electron Nicolet 7600 FT-IR spectrophotometer (Thermo Fisher Scientific, Waltham, MA, USA) used in the present study to measure conversions of NO and NH$_3$ and the extent of N$_2$O production in NH$_3$-SCR reaction have been described earlier [6,68]. A continuous purge of this system was allowed by flowing a compressed air at a rate of 15 L/min that had passed through a train of large volume silica traps to remove H$_2$O in the air. The NH$_3$-SCR reaction with catalyst samples was conducted in a continuous flow type I-shaped 3/8” OD quartz reactor placed in a three-independent temperature adjustable electric furnace (Lindberg/Blue M Model HTF55347C, Thermo Electron Corp., Asheville, NC, USA) coupled with a Lindberg/Blue M Model CC584343PC PID controller [6,16,27,68]. All gas feed lines were maintained at a temperature near 180 °C to prevent the homogeneous reaction between NO and O$_2$, and the condensation of H$_2$O produced in the reaction.
A flowing mixture of 21% O\textsubscript{2}/79% N\textsubscript{2} at a total rate of 1000 cm\textsuperscript{3}/min was flowed through the reactor with typically 0.5 g catalyst sample to calcine it at 500 °C for 1 h, and then the temperature and oxygen concentration were changed to 200 °C and 5%, respectively. After this, the downstream was switched to the upstream, at which point the gas cell was fully purged prior to recording a background interferogram that was used for Fourier-transforming sample interferograms. Then NO and NH\textsubscript{3} were added to the gas flow so as to be 500 ppm, respectively. An interferogram before reaction was collected at their steady-state concentration. Following this, the gas mixture was flowed over the catalyst bed at chosen temperatures, corresponding to a gas hourly space velocity of 76,200 h\textsuperscript{−1}, and a sample interferogram was obtained after ca. 30 min. All interferograms were collected with a resolution of 0.5 cm\textsuperscript{−1} and a scan number of 100. The NO (Omega grade, 99.99%, Scott Specialty Gases, South Plainfield, NJ, USA) and NH\textsubscript{3} (Scott Specialty Gases, Electronic grade, 99.999%) were used without any purification, while the N\textsubscript{2} was flowed through an Alltech moisture trap. All gas flows were accurately controlled by using a Model 5850E mass flow controller (Brooks Instr., Hatfield, PA, USA) and a Model F-200CV one (Bronkhorst High-Tech, Ruurlo, The Netherlands). Details of the standard procedures to collect the gas-phase spectra have been provided elsewhere [6,68].

### 3.3. Characterization of Catalyst Samples

A Model D/MAX2500 PC diffractometer (Rigaku, Tokyo, Japan) with a Cu K\textalpha\textsubscript{α} (λ = 1.5405 Å) radiation source was employed for XRD measurements in which an X-ray tube voltage and current were 40 kV and 20 mA, respectively. Each calcined sample charged in a thin quartz holder was scanned from a 2θ value of 10 to 80° at a scanning rate of 0.1°/min to allow an accurate resolution.

A Model 3 Flex Version 3.01 system (Micromeritics Instr., Norcross, GA, USA) was used to determine textural properties of the catalysts, such as S\textsubscript{BET}, d\textsubscript{m}, and V\textsubscript{t}. A cell containing ca. 60 mg of each sample was directly connected to the system, evacuated at 300 °C overnight (under a high dynamic vacuum below 10\textsuperscript{−7} Torr (1 Torr = 133.3 Pa)) and allowed for a further evacuation at room temperature. Following this, N\textsubscript{2} was introduced into the sample cell at a liquid nitrogen temperature (−196 °C).

Temperature-programmed desorption (TPD) studies were conducted using a Model HPR-20 QIC quadrupole mass (Hiden Analytical, Warrington, UK) spectrometer system described in detail elsewhere [16,69,70]. For this, an adsorption cell with 160 mg of each sample was coupled with a gas handling system to calcine at 500 °C for 1 h in a flowing mixture of 21% O\textsubscript{2}/79% He (Praxair, 99,9999%) at a total flow rate of 100 cm\textsuperscript{3}/min. Then, 2% NH\textsubscript{3} in flowing He at the same flow rate was admitted to the cell at 100 °C for 1 h prior to fully purging it using the pure He flow. After the NH\textsubscript{3} approached a background level, it was heated to 800 °C at 10 °C/min in a He flow at a total rate of 20 cm\textsuperscript{3}/min. During this process, N-containing products, i.e., N\textsubscript{2}O, NO, and N\textsubscript{2}, were monitored at each corresponding m/z, but NH\textsubscript{3} desorbed was monitored at m/z = 16, because H\textsubscript{2}O formed upon the surface reaction, producing the nitrogenous products that could be fragmentized to OH [16,69]. All the gases were controlled using a Model 5850E mass flow controller (Brooks Instr., Hatfield, PA, USA). The He used has been further purified in a similar fashion as described above.

Ex situ Raman spectra for fresh catalysts calcined in a fashion similar to that described for the activity measurements were recorded in the range of 50–3400 cm\textsuperscript{−1} with a 2 cm\textsuperscript{−1} spectral resolution. V\textsubscript{2}O\textsubscript{5} (Aldrich, 99.99%), WO\textsubscript{3} (99.995%), TiO\textsubscript{2} (DT51D, Millennium Inorganic Chemicals, Henderson, Australia), and the WT were used as a reference material. The measurements were conducted using a Thermo Scientific DXR 2xi Raman spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) equipped with a liquid N\textsubscript{2}-cooled EM-CCD detector around −120 °C. A 532-nm diode laser was employed to excite the samples. A power of the laser at a surface of each sample was applied to be ca. 2 mW in order to minimize laser heating effects. Exposure of each sample to the laser beam was approximately 0.01–0.03 s with 500 to 800 averaged signal accumulations, depending on the sample. All spectra were collected with a powder under ambient conditions.
4. Conclusions

Fe₂O₃-promoted V₂O₅/TiO₂-based catalysts show no great changes in the textural features, and no XRD peaks due to crystalline Fe₂O₃ phases are indicated. Significant depression of N₂O emissions in NH₃-SCR reaction over V₂O₅-WO₅/TiO₂ catalysts at high temperatures could be successfully established by their promotion using Fe₂O₃ particles. This approach results in a decrease in NO conversion at high temperatures, which is mainly because of the oxidation of NH₃ to NO. NH₃ TPD measurements suggest that the Fe₂O₃ existing in VWT and c-VWT can significantly increase strongly-adsorbed NH₃ and NHₓ moieties, and these species participate in the reduction of N₂O formed at high temperatures. Raman spectra for the promoted catalysts propose the presence of Fe₂O₃-induced, tetrahedrally coordinated polyvanadates and/or surface V-O-Fe species that are probably responsible for the N₂O reduction. The reaction between NO and NH₃ may predominantly take place to form N₂O that can be readily reduced by the strongly adsorbed NH₃ over the Fe₂O₃-promoted catalysts.

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Author Contributions: The key approach to this study was designed by Moon Hyeon Kim who also determined a significance of all data and wrote this manuscript. Ki Hyuck Yang performed the experiments regarding activity and no XRD peaks due to crystalline Fe₂O₃ phases are indicated. Significant depression of N₂O emissions in NH₃-SCR reaction over V₂O₅-WO₅/TiO₂ catalysts at high temperatures could be successfully established by their promotion using Fe₂O₃ particles. This approach results in a decrease in NO conversion at high temperatures, which is mainly because of the oxidation of NH₃ to NO. NH₃ TPD measurements suggest that the Fe₂O₃ existing in VWT and c-VWT can significantly increase strongly-adsorbed NH₃ and NHₓ moieties, and these species participate in the reduction of N₂O formed at high temperatures. Raman spectra for the promoted catalysts propose the presence of Fe₂O₃-induced, tetrahedrally coordinated polyvanadates and/or surface V-O-Fe species that are probably responsible for the N₂O reduction. The reaction between NO and NH₃ may predominantly take place to form N₂O that can be readily reduced by the strongly adsorbed NH₃ over the Fe₂O₃-promoted catalysts.

Conflicts of Interest: The authors declare no conflict of interest.

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