Research Article

Promotional Effect on Selective Catalytic Reduction of NO\textsubscript{x} with NH\textsubscript{3} over Overloaded W and Ce on V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} Catalysts

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W and Ce are known to be a good promoters to improve selective catalytic reduction (SCR) activity for V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} catalysts. This work aimed at finding the optimum ratio and loading of promoters (W and Ce) on V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} catalyst in order to improve SCR reactivity in low temperature region and to minimize N\textsubscript{2}O formation in high temperature region. In addition, we changed the order of impregnation between W and Ce precursors on V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} catalyst during the preparation and observed its effect on SCR activity and N\textsubscript{2}O selectivity. We utilized various analytical techniques, such as N\textsubscript{2} adsorption-desorption, X-ray diffraction (XRD), and temperature-programmed reduction with hydrogen (H\textsubscript{2} TPR) to investigate the physicochemical properties of catalysts. It was found that W- and Ce-overloaded V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} catalyst such as W/Ce/V/TiO\textsubscript{2} (15:15:1 wt%) showed the most remarkable DeNO\textsubscript{x} properties over the wide temperature region. Additionally, this catalyst significantly suppressed N\textsubscript{2}O formation during SCR reaction, especially in high temperature region (350–400°C). Based on the characterization results, we found that such superior activity originated from the improved reducibility and morphology of W and Ce species on V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} catalyst when they are incorporated together at high loading.

1. Introduction

Selective catalytic reduction of NO\textsubscript{x} with NH\textsubscript{3} (NH\textsubscript{3}-SCR) as reductant is well-known technology for removing NO\textsubscript{x} emissions from stationary source or diesel engine vehicles operated under highly oxidizing condition [1–5]. Generally, vanadia-titania-based NH\textsubscript{3}-SCR catalysts have been used in stationary sources due to high resistance to SO\textsubscript{2}, while Cu-based zeolite is being used for mobile source [6]. In spite of a high NO\textsubscript{x} conversion between 300 and 400°C, the side reactions such as the oxidation of NH\textsubscript{3} to N\textsubscript{2}O or NO and toxicity of the evaporated vanadium at high temperature are the major problems of V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} catalysts to overcome [7, 8].

Meanwhile, International Maritime Organization (IMO) announced the NO\textsubscript{x} regulations (Tier III) on vessels, which will take effect from 2016 [9]. It makes catalyst community pay attention to the DeNO\textsubscript{x} technology for marine application. In particular, the SCR catalyst for marine application requires higher DeNO\textsubscript{x} activity in the low temperature range (200–250°C) due to the low temperature exhaust from marine engine. In addition to needs to lower the SCR operation temperature, a concern for the emissions of N\textsubscript{2}O has been growing, since N\textsubscript{2}O has about 300 times greater greenhouse gas effect than CO\textsubscript{2}. During NH\textsubscript{3} SCR reaction, N\textsubscript{2}O is known to be produced in the following reaction:

\[4\text{NO} + 4\text{NH}_3 + 3\text{O}_2 \rightarrow 4\text{N}_2\text{O} + 6\text{H}_2\text{O}\]

In commercial catalysts, the loading of vanadia is generally as low as 1–1.5 wt% whereas the loading of promoters is about 6–10 wt%, respectively [3]. W-V/TiO\textsubscript{2} or Ce-V/TiO\textsubscript{2} is well-known SCR catalytic system for commercial application. However, there is no previous study regarding the overloading effect (higher than 10 wt%) of promoters on V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} SCR catalysts to our knowledge. Therefore, the aim of this study is to find the optimum condition to prepare V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} SCR catalyst with high DeNO\textsubscript{x} activity in low temperature and minimized N\textsubscript{2}O formation by loading the excessive amount of promoters (W and Ce) compared with vanadium loading. Additionally, we tried to change the order of impregnation between two promoters on V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} while focusing...
on the characteristics of catalysts. We also investigate whether the synergetic effect of promoters exists when they are loaded together on V₂O₅/TiO₂. To sum up, the effect of impregnation order and the ratio between promoters and vanadium in M/V₂O₅/TiO₂ catalyst on the NOₓ conversion and the N₂O selectivity during SCR reaction were addressed in this study.

2. Experimental

2.1. Catalysts Preparation. All catalysts were prepared by applying wet impregnation method of vanadium and promoter solution on anatase titania. Anatase TiO₂ powder (DT-51 Millennium Chemicals) was used as support. Ammonium metavanadate (99%, Sigma Aldrich) was dissolved in diluted oxalic acid solution (0.5 M) to produce the solution of vanadium precursor [10]. The samples with 1 wt%, 3 wt%, and 5 wt% V₂O₅ loading on TiO₂ were prepared. We used two promoters, W and Ce, to be impregnated on V₂O₅/TiO₂ catalyst. Ammonium tungstate (99.99%, Sigma Aldrich) and cerium(III) nitrate hexahydrate (99.9%, Sigma Aldrich) were used to produce promoter solution which was dissolved in diluted water. After drying at 105°C for 12 h, promoter precursor solution was added to V₂O₅/TiO₂ in a rotary evaporator again. After a series of impregnation processes, catalysts were dried and then calcined at 400°C for 4 h in air.

Sample was designated as the following notation MI/M2/VT (X : Y : Z), MI and M2 showed the promoters and sequence of impregnation, where M2 is firstly impregnated on V₂O₅/TiO₂, followed by the impregnation of MI on M2/V₂O₅/TiO₂. X and Y meant the weight loading of each promoter and Z is the weight loading of vanadium on TiO₂. For example, W/Ce/VT (15:15:1) indicated V₂O₅/TiO₂ catalyst with 1 wt% of vanadium loading which are promoted with W and Ce promoters with 15 wt% each.

2.2. Characterization. The specific surface area of catalysts was measured by ASAP 2010 (Micromeritics) apparatus and calculated by using BET method. The samples about 0.1 g were degassed at 250°C for 12 h before measurement. After the pretreatment step, N₂ adsorption-desorption isotherms were obtained at −196°C. The X-ray diffraction (XRD) patterns were obtained by using a Rigaku mode 1 Smartlab with Cu Ka radiation (λ = 0.1542 nm), 40 kV and 50 mA of voltage and current were applied and the XRD patterns were collected in a 2-theta range from 20 to 80° at a speed of 10°/min [11].

H₂ TPR was used to measure the reducibility of metal oxides by detecting the hydrogen consumption at elevated temperature with a thermal conductivity detector (TCD) in a BEL-CAT-BASIC (BEL Japan Inc.). Prior to the analysis, 0.03 g samples were pretreated at 350°C for 1 h in a flow of 30 mL/min Ar. After cooling down to room temperature, samples were then exposed to 5% H₂/Ar until the temperature reached 800°C at the rate of 10°C/min.

2.3. Reaction Test. SCR activity was measured in a fixed-bed quartz tubular reactor. Catalysts were sieved to 300–500 μm in diameter then loaded in the reactor. The composition of inlet gas was 500 ppm NO, 500 ppm NH₃, and 2% O₂ and was balanced with N₂. Space velocity of inlet gas was maintained to be 40,000 h⁻¹. We raised reaction temperature from 150°C to 400°C in increments of 50°C with the rate of 10°C/min. NOₓ conversion of outlet gas was analyzed by using NOₓ chemiluminescence analyzer (Model 42i High level, Thermo Scientific). Also, Fourier transform infrared (FT-IR) spectroscopy was applied to observe the N₂O concentration in the gas. We used the average data of 16 scans at a resolution of 1.0 cm⁻¹. A Nicolet 6700 (Thermo Scientific), with 2 m gas analysis cell heated to 120°C to exclude the effect of H₂O, was used for gas phase analysis. N₂ selectivity referred to in this study was calculated by using the following equation [2]:

\[
N_2 \text{ selectivity (\%)} = \frac{[[\text{NO}]_{\text{in}} + [\text{NH}_3]_{\text{in}}] - ([\text{NO}]_{\text{out}} - 2[\text{N}_2\text{O}]_{\text{out}})}{[[\text{NO}]_{\text{in}} + [\text{NH}_3]_{\text{in}}]} \times 100\%.
\]

3. Result and Discussion

Two representative elements, W and Ce, were chosen as promoters to V₂O₅/TiO₂. The order of impregnation and loading was changed to find the optimum catalyst. All results of prepared catalysts were displayed in Table 1. Since high SCR activity at low temperature and low N₂O formation at high temperature are regarded as two main requirements for novel SCR catalysts, we chose NOₓ conversion at 200°C and N₂O concentration at 400°C to compare the samples we tested in this study. Firstly, Figure 1 showed NOₓ conversion and N₂O concentration of various samples containing 3 wt% Ce/VT(9:1) indicated V₂O₅/TiO₂ catalyst with 1 wt% of vanadium loading which are promoted with W and Ce promoters with 15 wt% each.

<table>
<thead>
<tr>
<th>Sample</th>
<th>NOₓ conversion (%) at 200°C</th>
<th>N₂O concentration (ppm) at 400°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 wt% V₂O₅/TiO₂</td>
<td>10</td>
<td>15.4</td>
</tr>
<tr>
<td>3 wt% V₂O₅/TiO₂</td>
<td>55</td>
<td>41.3</td>
</tr>
<tr>
<td>5 wt% V₂O₅/TiO₂</td>
<td>67</td>
<td>42.1</td>
</tr>
<tr>
<td>W/VT (9:3)</td>
<td>67</td>
<td>36.2</td>
</tr>
<tr>
<td>Ce/VT (9:3)</td>
<td>63</td>
<td>10.8</td>
</tr>
<tr>
<td>W/Ce/VT (9:9:3)</td>
<td>58</td>
<td>14.4</td>
</tr>
<tr>
<td>Ce/W/VT (9:9:3)</td>
<td>51</td>
<td>13.2</td>
</tr>
<tr>
<td>W/VT (9:1)</td>
<td>34</td>
<td>6.9</td>
</tr>
<tr>
<td>Ce/VT (9:1)</td>
<td>41</td>
<td>5.6</td>
</tr>
<tr>
<td>W/Ce/VT (9:9:1)</td>
<td>36</td>
<td>5.0</td>
</tr>
<tr>
<td>Ce/W/VT (9:9:1)</td>
<td>33</td>
<td>5.2</td>
</tr>
<tr>
<td>W/VT (15:1)</td>
<td>28</td>
<td>6.7</td>
</tr>
<tr>
<td>Ce/VT (15:1)</td>
<td>44</td>
<td>3.7</td>
</tr>
<tr>
<td>W/Ce/VT (15:15:1) (b)</td>
<td>68</td>
<td>4.2</td>
</tr>
<tr>
<td>Ce/W/VT (15:15:1) (c)</td>
<td>55</td>
<td>3.7</td>
</tr>
</tbody>
</table>

(a), (b), and (c) were chosen as the promising catalysts.
$V_2O_5$ with different amounts of W and Ce. Each SCR reaction result was compared with standard SCR catalysts with same vanadium loading.

As shown in Figure 1, the addition of 9 wt% promoters on 3 wt% $V_2O_5/TiO_2$ (W/VT (9:3) or Ce/VT (9:3)) demonstrated the slightly higher NO$_x$ conversion than 3 wt% $V_2O_5/TiO_2$ catalysts not only in the low temperature region (250°C) but also in the high temperature region (400°C). However, W/Ce/VT (9:9:3) or Ce/W/VT (9:9:3) catalyst, which were expected to show synergistic effect of two promoters, showed similar SCR activity in low temperature region below 250°C to standard sample, implying that no synergism between two promoters exists at this condition. It must be pointed out that all W- and Ce-containing catalysts displayed lower N$_2$O formation at 400°C than 3 wt% $V_2O_5/TiO_2$, 3 wt% $V_2O_5/TiO_2$ catalyst showed 81% N$_2$ selectivity whereas Ce-containing catalysts showed about 91%.

The ratio of promoter to vanadium was increased by lowering the vanadium loading to 1 wt% to see whether the promotional effect is enhanced. As shown in Figure 2, all the promoter-containing catalysts demonstrated considerably improved NO$_x$ conversion, especially in low temperature range, compared with 1 wt% $V_2O_5/TiO_2$, implying that the promotional effect is remarkably enhanced over the catalyst with the low vanadium loading (1 wt%). As observed in the Figure 1, however, the addition of two promoters, for example, W/Ce/VT (9:9:3), did not give rise to the enhanced NO$_x$ conversion over all temperature ranges.

Since we observed the promotional effect of adding promoters (9 wt% Ce or W) on SCR activity, we further increased the amount of promoters to 15 wt%. As shown in Figure 3, the increase in W loading from 9 wt% to 15 wt% resulted in the rather decrease in the activity at 200°C, while that of Ce loading showed almost the same activity. More drastic enhancement of activity in the low temperature region was observed for the samples such as W/Ce/VT (15:15:1) or Ce/W/VT (15:15:1). For example, W/Ce/VT (15:15:1) catalyst displayed 68% of NO$_x$ conversion at 200°C which was the best activity among all catalysts. This value was as high as that of W/VT (9:3:3) catalyst; however, more important thing to note would be even lower N$_2$O production (30 ppm versus 5 ppm) at 400°C.

Noteworthy is that the synergism between Ce and W elements is observed only at higher ratio of promoters to vanadium. For the case of W/Ce/VT (9:9:1) catalyst, there is no promotional effect upon simultaneous loading of two promoters. On the other hand, we observed confident synergistic effect over W/Ce/VT (15:15:1) sample, especially the NO$_x$ conversion in the low temperature region, although there is not much difference in N$_2$O production. It must be pointed out that, for most cases, the change of the impregnation order of W and Ce did not reveal remarkable effect on NO$_x$ conversion and N$_2$O formation during SCR reaction. According to the references, WO$_3/TiO_2$ [12] and CeO$_x/TiO_2$ [13] catalysts showed low emission of N$_2$O at high temperature, although the reason of low N$_2$O formation was not fully identified. Generally, vanadium-containing catalysts usually emit more N$_2$O than vanadium-free catalysts while the former has higher deNO$_x$ activity than the latter. Therefore, the result of reduced N$_2$O formation on vanadium-containing catalysts the same level as nonvanadium metal oxide catalysts on TiO$_2$ was a remarkable accomplishment of our study.

Figure 4 displayed how overloaded W- and Ce-containing catalysts improve SCR activity compared with pure $V_2O_5/TiO_2$ catalysts. W/Ce/VT (15:15:1) and Ce/W/VT (15:15:1) showed slightly higher NO$_x$ conversion than 5 wt% $V_2O_5/TiO_2$ catalyst over all temperature ranges; more importantly, they produced about 88% less N$_2$O at 400°C. It is worth
to mention that the higher activity and excellent N$_2$ selectivity can be obtained at low vanadium loading, which is regarded as the toxic element.

We applied various analytic techniques to investigate which characteristics made the difference in SCR reaction among variety of samples with different amount of promoters. Firstly, BET surface area of catalysts was measured by using N$_2$ adsorption-desorption method. Even samples containing overloaded Ce and W, in other words, Ce/W/VT (15:15:1) and W/Ce/VT (15:15:1) catalysts, showed the BET surface area of 60 m$^2$/g and 66 m$^2$/g, respectively. Since pure TiO$_2$ has the surface area of 87 m$^2$/g, it is confirmed that the overloading of W and Ce does not change the textural property of the catalyst too much, for example, by the blockage of pore.

As presented in Figure 5(a), XRD patterns were obtained to investigate the crystallinity of various catalysts containing 3 wt% of vanadium. Only anatase TiO$_2$ phase was observed in these catalysts with the peaks at 2 theta equal to 26°, 36°, 37°, 48°, 54°, 55°, 63°, 69°, 70°, and 75° [14, 15], except for the Ce/VT (9:3) sample in which very small peak at 28.5° arising from CeO$_2$ phase was brought out. This means that most of W or Ce promoters exist in the amorphous form or in a highly dispersed state on TiO$_2$ support.

When the vanadium loading decreased to 1 wt%, all catalysts also showed only TiO$_2$ main peaks, except for Ce/W/VT (9:9:1) catalyst displaying small CeO$_2$ peaks at 2 theta equal to 28°, 34°, 47°, and 56°, as demonstrated in Figure 5(b). However, the sample with the reversed impregnation order,
in other words, W/Ce/VT (9:9:1) catalyst, does not show any peaks other than TiO$_2$, implying that the impregnation order affects the crystallinity of the sample. As presented in Figure 5(c), all samples displayed small peaks in XRD patterns arising from either CeO$_2$ or WO$_3$. Specifically, broad CeO$_2$ peaks were observed in all 15 wt% Ce-containing catalysts. The samples containing both 15 wt% W and 15 wt% Ce, in other words, Ce/W/VT (15:15:1) and W/Ce/VT (15:15:1) catalysts, had lower crystalline CeO$_2$ phase compared with Ce/VT (15:1), implying that W aided in dispersing CeO$_2$ in the catalyst. In addition, crystalline WO$_3$ phase [16] was observed in the XRD pattern of W/VT (15:1) catalyst, which might have a negative effect on the activity as shown in Figure 3. However, the WO$_3$ phase was not detected for the samples such as W/Ce/VT (15:1:1) and Ce/W/VT (15:1:1) catalysts, where both Ce and W promoters were incorporated. Summarizing XRD patterns and activity measurement, it can be clearly confirmed that the synergistic effect observed in the samples such as W/Ce/VT (15:1:1) and Ce/W/VT (15:1:1) catalysts originated from the formation of highly dispersed Ce or W elements in the catalysts.

H$_2$ TPR is a widely used technique to investigate the redox properties of the catalysts. The H$_2$ TPR profiles of the prepared catalysts are shown in Figure 6. For the case of W/VT (15:1) sample, two H$_2$ consumption peaks at 500°C and 750°C were shown, which were assigned to the reduction of vanadium oxide and tungsten oxide, respectively [17]. On the other hand, Ce/VT (15:1) sample had the peak at 475°C, arising from the reduction of Ce$^{4+}$ to Ce$^{3+}$ reaction. The reduction behavior of the elements has changed when two promoters were incorporated together (W/Ce/VT or Ce/W/VT). It was reported that the introduction of Ce not only improved the oxygen storage capacity but also enhanced the redox activity by interaction between W and Ce species. The improvement of redox activity is confirmed by comparing the peak area of each sample. The peak area increased in the following order: W/VT (15:1) < Ce/VT (15:1) < W/Ce/VT (15:1:1) < Ce/W/VT (15:1:1). It is noticeable that two-promoter-containing catalysts showed larger peak area than only one promoter impregnated on V$_2$O$_5$/TiO$_2$. Samples which have larger peak area had more reducible form of metal oxide on their surfaces assisting higher NO$_x$ reduction capability. Furthermore, the shift of the reduction peak of W/Ce/VT (15:1:1) and Ce/W/VT (15:1:1) compared with W/VT and Ce/VT indicated the close interaction between Ce and W species, resulting in the different Ce or W species on the surface. In addition, the fact that W/Ce/VT (15:1:1) showed higher NO$_x$ conversion than Ce/W/VT (15:1:1) in low temperature region can be explained by the difference in reduction behavior of catalyst. Therefore, the simultaneous introduction of W and Ce could create a new center for oxygen storage and release, which can act as an active site for SCR reaction.

4. Conclusion

The promotional effect of loading W and Ce on V$_2$O$_5$/TiO$_2$ catalyst was investigated while changing different loading ratio between promoters and vanadium and the order of loading promoters in order to find the optimum catalyst for SCR reaction. Among the catalysts, W/Ce/VT (15:1:1) catalyst demonstrated the most desirable reaction behavior with high NO$_x$ conversion and less N$_2$O formation during SCR reaction. It was found that highly dispersed CeO$_2$ and WO$_3$ phases were present even at high loading of W and Ce. Combined XRD and H$_2$ TPR results confirmed that the simultaneous impregnation of W and Ce on V$_2$O$_5$/TiO$_2$ at high loading leads to the change in the reducibility and

Figure 4: NO$_x$ conversion and N$_2$O concentration of promising catalysts compared with 1 wt%, 3 wt%, and 5 wt% V$_2$O$_5$/TiO$_2$. 

![Figure 4: NO$_x$ conversion and N$_2$O concentration of promising catalysts compared with 1 wt%, 3 wt%, and 5 wt% V$_2$O$_5$/TiO$_2$.](image-url)
morphology of elements in catalysts that eventually facilitated SCR reaction in low temperature region and minimized the amount of N₂O formed in high temperature region.

**Conflict of Interests**

The authors declare that there is no conflict of interests regarding the publication of this paper.

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