REACTIVITY AND DURABILITY OF V$_2$O$_5$
CATALYSTS SUPPORTED ON SULFATED TiO$_2$
FOR SELECTIVE REDUCTION OF NO BY NH$_3$

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Abstract: The selective catalytic experiments using both sulfated/sulfur-free titania and V$_2$O$_5$/TiO$_2$ catalysts have been conducted for NO reduction by NH$_3$ in a packed-bed, down-flow reactor. The sulfated and vanadia loaded titania exhibited higher activity for NO removal than the sulfur-free catalysts, where > 90% NO removal was achieved over the sulfated V$_2$O$_5$/TiO$_2$ catalyst between 280–500°C. The surface structure of vanadia species on the catalyst surface played a critical role in the high performance of catalysts in which the existence of monomeric/polymeric vanadate is revealed by Raman spectra studies. Water vapor and SO$_2$ were added to the reacting system for the catalyst deactivation tests. At higher temperatures (T ≥ 350°C), little deactivation was observed over the sulfated V$_2$O$_5$/TiO$_2$ catalysts, showing good durability against SO$_2$ and water vapor, which is compared with deactivation at lower temperatures.

Key Words: Catalytic activity, Deactivation, V$_2$O$_5$/TiO$_2$, Sulfated catalyst, Nitric oxide, SCR

INTRODUCTION

The emissions of nitrogen oxides (NOx) from human activities, mostly combustion sources, are enormous and their impacts on environment are causing increasing concerns over particularly air quality. There are two conventional categories controlling NOx emissions; one is combustion modification suppressing the formation of NOx, and the other flue gas treatment such as well-known selective catalytic/noncatalytic reduction (SCR/SNCR) technologies.$^{1-3}$

Among them, the SCR technology has been widely employed to control NOx from stationary sources such as power plants, industrial boilers and even mobile diesel engines.$^{4-7}$ In the commercial SCR processes, typical V$_2$O$_5$/TiO$_2$ catalysts have shown high NOx removal activity and good selectivity to nitrogen, despite continuous and high flue gas streams containing low NOx concentrations. However, the durability of catalysts by mainly sulfur species, water vapor and other impurities contained in the actual flue gases remains still outstanding problems to be solved since this is directly related to the catalyst life time, and thus operating costs. The flue gases from the combustion sources (e.g. power plants) mostly contain 100–400 ppm SO$_2$, 6–8% H$_2$O and some amount of dusts, which certainly cause SCR catalysts to lose activity. Particularly, sulfur and water tolerances

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of catalyst are still needed for the better performance of commercial SCR catalysts. The deactivation phenomena by SO₂ might be mostly pore-filling of active sites and plugging of catalyst bed by the formation of salts such as ammonium sulfate/sulfite (e.g. (NH₄)₂SO₄, (NH₄)₂HSO₃). Alumina-based catalysts (V₂O₅/Al₂O₃) could lead to much easier deactivation by SO₂ forming Al₂(SO₄)₃, and thus are not proper for S-containing flue gases, despite various beneficial properties.⁹) On the other hand, titania-based catalysts are more resistant to SO₂ poisoning, showing higher activities with vanadia loading, even though they typically show the characteristics of low surface area.⁸) The influence of water vapor has also been known to be significant on catalyst deactivations, particularly promoting the formation of the above salts and competing with NH₃ for the adsorption sites.⁹) These effects must result in less catalytic activity for SCR reactions, while both are strongly temperature-dependent.

This work interestingly presents the catalytic activities of sulfated/sulfur-free titania and V₂O₅/ TiO₂ catalysts on NO removal reactions using simple gas mixtures. The influences of additional SO₂ and water vapor, typical ingredients in actual flue gases, are also observed on the activity and durability of the sulfated catalysts. Furthermore, the catalyst characterization using Raman spectroscopy is provided for the nature of the active species on the catalyst surface.

**EXPERIMENTAL**

Two kinds of TiO₂ (JRC1, JRC4) and V₂O₅/ TiO₂ (V1JRC1, V1JRC4) catalysts were employed in this work where JRC1 and V1JRC1 are the sulfated, and JRC4 and V1JRC4, sulfur-free catalysts, respectively. The physicochemical characteristics and preparation method of the catalysts are listed in Table 1. JRC1 and JRC4 were first dried at 120°C overnight in air atmosphere and then calcinated at 500°C for 5 hr to investigate the effect of the presence of sulfur species on TiO₂ support. 1wt% V₂O₅/TiO₂ catalysts were prepared by impregnating aqueous solution of NH₄VO₃ supplied from Sigma-Aldrich Co. diluted in oxalic acid on TiO₂. The catalysts were then dried again at 120°C for 2 hr, followed by calcination at 500°C for 5 hr, which resulted in slight decrease in their surface areas.

The catalytic measurements of NO removal by NH₃ in the presence of O₂, together with/without SO₂ and water vapor were conducted with a tubular downstream flow reactor operating under isothermal and atmospheric

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Table 1. Physicochemical properties of the catalyst materials

<table>
<thead>
<tr>
<th>Property</th>
<th>JRC1 (JRC-TI-1*)</th>
<th>JRC4 (JRC-TI-4*)</th>
<th>V1JRC1</th>
<th>V1JRC4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical composition</td>
<td>Ti(95%), S(3.6%)</td>
<td>Ti(&gt;99.5%), Al(&lt;0.3%), HCl(&lt;0.3%)</td>
<td>V (1%), S(2.1%)</td>
<td>V(1%)</td>
</tr>
<tr>
<td>Sᵦₑₐₜ (m²/g)</td>
<td>73</td>
<td>50</td>
<td>65</td>
<td>43</td>
</tr>
<tr>
<td>Phase</td>
<td>Anatase</td>
<td>Anatase + rutile (10%)</td>
<td>Anatase</td>
<td>Anatase + Rutile (10%)</td>
</tr>
<tr>
<td>Fire loss (%)**</td>
<td>15</td>
<td>5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Preparation method</td>
<td>Calcining metatitanic acid at 500°C</td>
<td>By oxidation of TiCl₄</td>
<td>Impregnating on JRC1</td>
<td>Impregnating on JRC4</td>
</tr>
</tbody>
</table>

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** Calcining up to 700°C
- Not available
The reaction of NO by NH₃ was carried out at a temperature range of 200–500°C in the vertical 3/8" aluminum tube containing 1 g of 20–30 mesh catalyst. The typical composition of the feed gas stream was 500 ppm NO, 500 ppm NH₃, 10% O₂ and balance N₂ in which gas hourly space velocity (GHSV) based on the ratio of the total gas flow rate to the volume of the catalyst bed was around 100,000 hr⁻¹. To observe the effects of SO₂ and water vapor on the NO removal reaction, 5% water vapor and 1,000–10,000 ppm SO₂ were also fed to the reaction system as necessary. Water was injected to the feed gas stream by bubbling N₂ into a water saturator with a small-pore frit immersed in de-ionized water. The concentration of NO was analyzed by a chemiluminescent NOx analyzer (Thermo Electron, Model 42C). Especially, the surface structure of vanadium supported on sulfated titania was characterized by the in-situ Raman spectroscopy. The Raman spectra were examined by an Ar⁺ laser (Renshaw Raman microscope, Model 3000). Self-supported wafer mounted on a glass cell was pre-treated at 400°C for 30 min and then cooled to ambient temperature before the measurement.

RESULTS AND DISCUSSION

Catalytic Activity for NO Removal

Figure 1 shows the NO removal activity by NH₃ over four catalysts adopted in the presence of 10% oxygen at the reaction temperatures between 200–500°C. JRC1 and JRC4 supports itself begin to show catalytic activity for NO removal around 300°C, which further increases with increasing temperature, and among which more than 95% NO removal is achieved above 400°C with JRC1. Especially, it turns out that the JRC1 support (sulfated titania) is more active than that of sulfur-free JRC4 over the entire temperature range. Furthermore, the addition of vanadium species to the TiO₂ support significantly enhances catalytic activity for NO removal particularly at lower reaction temperatures, compared with those of TiO₂ without vanadium species (JRC1 and JRC4). The effective temperature window with VIJRC1 for > 80% NO removal is formed between 250–500°C, while with VIJRC4 much narrower range, 300–450°C for > 70% NO removal. The dramatic increase in the catalytic activity with VIJRC1 and VIJRC4 at the lower reaction temperatures can be attributed to the vanadium species, compared with those of JRC1 and JRC4, offering new reaction sites on the catalyst surface.

One of the interesting features in this figure is that with the vanadium species supported on the TiO₂ catalysts, the maximum NO removals are obtained under these specific conditions. Particularly above 450°C, the catalytic activities of VIJRC1 and VIJRC4 begin to decline, respectively because of the onset of NH₃ oxidation reaction. Apparently, VIJRC1 catalyst seems to reveal more resistance to NH₃ oxidation reaction than VIJRC4. The sulfate species of VIJRC1 easily interact with adsorbed water to form Brönsted acid sites on the catalyst surface, promoting the NH₃ adsorption, as
discussed by Chen and Yang,\textsuperscript{10} which leads to high NO removal. Therefore, the sulfate species on catalyst surface must play a critical role in NO removal reaction at the whole temperature range, and particularly resisting to NH\textsubscript{3} oxidation at higher temperatures.

**Deactivation**

Catalyst deactivation in the SCR process has been relatively well known to be caused by mostly SO\textsubscript{2} and water vapor in actual flue gases.\textsuperscript{4} The effects of water vapor and reaction temperature on NO removal with the sulfated VIJRC1 catalyst were examined in the presence of 1,000 ppm SO\textsubscript{2} and with SV=50,000 hr\textsuperscript{-1}, as in Figure 2. Over the optimum temperature of 350°C, the initial activity for NO removal (−100%) remains unchanged during the time investigated, showing strong resistance to SO\textsubscript{2} and water vapor poisoning. At the lower temperature of for instance 240°C, the catalyst is unfortunately deactivated with increasing time on stream even by the SO\textsubscript{2} presence in which the addition of water vapor further decreases the catalytic activity until 30 hr. In case of the sulfur-free VIJRC4 catalyst, similar trends were mostly obtained under the same conditions, but slightly less activity was observed over the entire temperature range. Clearly, the catalyst deactivation in the SCR studies is related to the main factors, SO\textsubscript{2} and water vapor ingredients, and even reaction time. The addition of NH\textsubscript{3} into the SO\textsubscript{2}-containing flue gas could lead to the formation of various ammonium salts in the presence of water vapor, which particularly happens at lower temperatures by thermochemical reactions.\textsuperscript{4} These sticky salts certainly cause the plugging of catalyst micropores, and accumulate on the catalyst surface in the long run, which results in the catalyst deactivation, and even the presence of water vapor further accelerates these processes. Nonetheless, at higher temperatures above 270°C, such salts are known to be easily decomposed, and their formation is rather difficult,\textsuperscript{12} thus little deactivation is observed at T ≥ 350°C in this work. On the other hand, water vapor competes with NH\textsubscript{3} for adsorption on the active sites. Although the adsorption strength of NH\textsubscript{3} on V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} catalysts is superior, water vapor somehow contributes to the inhibition of NH\textsubscript{3} adsorption, which therefore leads to the decrease in NO removal over the V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} catalyst, as shown in Figure 2. Similar results over V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} catalysts were reported by Piehl et al.\textsuperscript{9} that little poisoning was observed by water vapor between 350−500 °C.

Continuously, Figure 3 shows the results of NO conversion over the VIJRC1 catalyst under the more severe conditions, which presents both deactivation tests at 400°C with/without flowing 10,000 ppm SO\textsubscript{2} and water vapor, and comparison of fresh catalyst with aged ones in the range of 200−350°C. For VIJRC1 catalyst, before the injection of SO\textsubscript{2} gas and water vapor, its initial activity for NO removal is maintained very high, almost 100% from 250 to 400°C, which decreases to about 75% at 200°C. This result is compared with that of Figure 1 obtained under GHSV=100,000 hr\textsuperscript{-1}. Again at the high temperature of 400°C, the above high
concentration of SO₂ together with water vapor started to flow for 30~70 hr, respectively, but still no deactivation is observed, indicating excellent resistance to SO₂ and water vapor and durability to reaction time. After each reaction time, the flows of SO₂ and water vapor were stopped, and then temperature was cooled down to investigate any activity change between fresh and aged catalysts in the range of 200~350°C. The catalysts exposed by SO₂ and water vapor for 30~50 hr show better activity even at the lower temperature of 200°C, indicating about 5~10% more NO removals than the fresh catalyst. This implies the small amount of sulfation on catalyst surface promotes the NO removal activity over the wide temperature range, as proved in Figure 1. However, it does not contradict the catalyst deactivation by gas flows of SO₂ in Figure 2.

Characterization

Figure 4 shows the Raman spectra of both V1JRC1 and V1JRC4 (1wt% V₂O₅) catalysts. The surface structure of vanadia supported on sulfur-free titania (V1JRC4) was observed dominantly as monomeric vanadyl species ((Ti-O)₂V =O) located at 1027 cm⁻¹. However, V1JRC1 catalyst containing sulfate species was already developed to polymeric vanadate at 920~960 cm⁻¹ as well as monomeric vanadyl species. Thus, the presence of sulfur species on the surface of V1JRC1 must have induced the polymeric vanadate species, which must be more beneficial structure for NO removal activity. These Raman spectra well support experimental phenomena in Figure 4. Firstly, there is no doubt that vanadia species mostly provide active reaction sites for NO removal as we found with both V1JRC1 and V1JRC4, compared with those of JRC1 and JRC4. Furthermore, the polymeric vanadate species of V1JRC1, caused by the presence of sulfur species and thus available surface reduction, are showing interesting characteristics such as strong resistance to SO₂ and water vapor, and excellent durability to reaction time, therefore leading to high NO removal activity over wide temperature windows, as discussed in Figures 1~3. Previously, this was known to be about 10 times higher than that of monomeric vanadyl species in NO removal activity.¹³¹ The additional information can come

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**Figure 3.** Accelerated deactivation tests using the V1JRC1 catalyst by severe flows of SO₂ and water vapor as a function of time ([NO] = [NH₃] = 500 ppm, [O₂] = 10%, ○: fresh; ■, ▲, ▼: aged catalysts by 10,000 ppm and 5% water vapor at 400 °C each time).

**Figure 4.** Raman spectra of 1wt% V₂O₅/TiO₂ catalysts (V1JRC1 and V1JRC4).
from the IR spectra of sulfated titania catalysts by NH$_3$ adsorption at ambient temperature, concerning the existence of both monomeric vanadyl and polymeric vanadate species with various V$_2$O$_5$ loadings and their acidic sites. Broad peaks representing Lewis (L) and Brønsted (B) acid sites were centered at 1610 and 1450 cm$^{-1}$, respectively where the ratio of B/L was bigger than unity. By the adsorption of sulfur species or SO$_2$ itself on the catalyst surface, the structure of VIJRCl has been presumably altered to enhanced acidic catalysts. According to Kijlstra et al., it was revealed that the SO$_2$ adsorption on the vanadia loaded catalysts enhanced the catalytic acidity and increased the amount of adsorbed NH$_3$, based upon the TPD and IR studies. Particularly, the formation of (TiO)$_3$SOOH species on the catalyst surface was reported by the cause of the sulfation in the presence of water vapor or excess OH groups, having a property of electron withdrawing sulfate groups, which induces the promotion of SCR activities. For these results, Topsoe et al. discussed that both V$^{5+}$=O sites and Brønsted acid sites were involved in the catalytic cycles of V$_2$O$_5$/TiO$_2$ catalysts. Thus, the activity of the sulfated VIJRCl catalyst for NO removal is believed to have been enhanced by the introduction of Brønsted acid sites until V$^{5+}$=O species become the limiting factor on the surface. This catalyst is considered promising, showing high NO removal activity over a wide temperature range and strong resistance to SO$_2$ and water vapor particularly at higher temperatures.

summary

The catalytic activities of both sulfated/sulfur-free TiO$_2$ and 1wt% V$_2$O$_5$/TiO$_2$ catalysts have been examined for NO removal and further their durability by additional SO$_2$ and water vapor in SCR reaction conditions. The sulfated JRC1 and VIJRCl catalysts exhibited higher activity for NO removal than those of the sulfur-free JRC4 and VIJRCl, respectively. The addition of vanadium species to titania further significantly enhanced catalytic activities where > 90% NO removal was achieved with the sulfated VIJRCl over the wide temperature range of 280~500 °C. The polymeric vanadate formed by the presence of surface sulfur species (VIJRCl) turned out to be the active reaction site for the present reaction system, while only monomeric vanadia appeared with sulfur-free VIJRCl. Catalyst deactivation by SO$_2$ and water vapor has not been developed with VIJRCl at higher temperatures, e.g. T ≥ 350°C, but at lower temperature (240°C) NO removal activity became deteriorated. Even, the severe flows of SO$_2$ together with water vapor hardly decreased catalytic activities at such high temperatures, and the small amount of sulfation must be more beneficial for NO removal activity. Consequently, the sulfated VIJRCl provides very encouraging results, showing high NO removal efficiency over a wide temperature range and strong resistance to SO$_2$ and water vapor poisoning.

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references