XAFS Study of Active Tungsten Species on WO₃/TiO₂ as a Catalyst for Photo-SCR

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Abstract. The activity of the photo-assisted selective catalytic reduction of NO with NH₃ (photo-SCR) was enhanced by the addition of WO₃ to TiO₂. From the result of XAFS analysis, the W species on TiO₂ had a WO₄ tetrahedral structure and agglutination took place as the addition of WO₃ was increased. We conclude that the isolated W species enhances the surface acidity and photo-SCR activity whereas the agglutinated W species is an inactive species.

Keywords: photo-SCR WO₃/TiO₂, photocatalyst, XAFS.

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INTRODUCTION

NOₓ is an air pollutant and causes town smog and acid rain [1,2]. Recently, it has become desirable to develop a low temperature SCR system (selective catalytic reduction of NO with NH₃) operated under 423 K in order to remove the exhausted NOₓ in a waste incinerator [3,5]. We have reported that the photo-assisted selective catalytic reduction of NO with NH₃ (photo-SCR) proceeds over TiO₂ under UV irradiation at room temperature [6,7]. However, the photo-SCR activity of TiO₂ is not enough in comparison with industrial SCR systems and it is necessary to improve the photo-SCR activity. In a previous study, we demonstrated that the photo-SCR proceeds according to Eley-Riedel mechanism, i.e., NO in the gas phase attacks NH₃ adsorbed on a Lewis acid site on TiO₂, and the photo-SCR activity is enhanced by improving the surface acidity of TiO₂ [7,8]. Therefore, it can be expected that the photo-SCR activity is enhanced by improving the surface acidity of TiO₂. It has been reported that the surface acidity of ZrO₂ and TiO₂ is enhanced by the addition of WO₃ [9-11]. However, the coordination environments of tungsten species over TiO₂ are not elucidated yet.

In the present work, we prepared WO₃/TiO₂ as catalysts showing improvement for the photo-SCR activity of TiO₂ and investigated the structure of tungsten species on WO₃/TiO₂ by means of W L₁ and L₃-edge XANES/EXAFS. The catalytic performances of WO₃/TiO₂ were tested in the photo-SCR and the effects of the coordination environments of tungsten species over TiO₂ on the catalytic performance and acidity are discussed.

EXPERIMENTAL

TiO₂ used in this study is Super Titania F-6 kindly supplied from SHOWA DENKO. The WO₃/TiO₂ catalysts were prepared by wet impregnation followed by evaporation to dryness. TiO₂ was impregnated with aqueous solutions of ammonium tungstate parapentahydrate at 353 K and concentrated at 353 K, followed by dryness at 383 K over night. All dried samples were calcined in dry air at 673 K for 3 h.

Photo-SCR was carried out in a conventional fixed bed flow system at room temperature. Catalysts were fixed with quartz wool and filled in a quartz reactor which had a flat facet (12 x 10 x 1 mm³). Before reactions, the catalysts were treated at 673 K by flowing 10 % O₂ diluted with Ar at 50 ml/min. The typical reaction gas composition was as follows: NH₃ 1000 ppm, NO 1000 ppm, O₂ 2%, Ar balance. A PERKIN-ELMER PE300BF 300 W Xe lamp was used as a light source and the samples were irradiated from the flat facet of the reactor. N₂ and N₂O products were analyzed by a SHIMADZU GC-8A TCD gas chromatograph with a MS-5A column for N₂ detection and Chromosorb 103 for N₂O.

The amount of acid sites on the catalyst was determined by the amount of NH₃ chemisorption, according to previous method [7]. X-ray absorption spectra around the W-L₁ and W-L₃ edges were recorded at the BL01B1 beam line at
SPring-8 of the Japan Synchrotron Radiation Research Institute (8 GeV, 100 mA). We used a Si(111) two crystal monochromator. Ion chambers filled with \( \text{N}_2(85\%)/\text{Ar}(15\%) \) and \( \text{N}_2(50\%)/\text{Ar}(50\%) \) were used for \( I_0 \) and \( I \) detection, respectively. A Lytle detector using Kr was used instead of \( I \) ion chamber in the fluorescence mode. The energy was calibrated by using a Cu foil. The samples pretreated by \( \text{O}_2 \) at 673 K were sealed into polyethylene bags under dry \( \text{N}_2 \). The data reduction was performed by the REX2000 Ver.2.3.3 program (Rigaku). The curve fitting parameters were created with the FEFF code [12].

**RESULTS AND DISCUSSION**

Activities of the \( \text{WO}_3/\text{TiO}_2 \) catalysts for the photo-SCR are shown in Fig. 1, together with the amount of acid sites estimated from the amount of \( \text{NH}_3 \) chemisorption. \( \text{N}_2 \) was the main product (>99%) and a trace of \( \text{N}_2\text{O} \) was detected in the photo-SCR over all \( \text{WO}_3/\text{TiO}_2 \) catalysts. The increase in \( \text{WO}_3 \) content up to 1.5wt.% monotonously increased the photo-SCR activity (NO conversion: 79%, \( \text{N}_2 \) selectivity: 100%). We have already reported that the active site of photo-SCR is the acid site over catalyst and the activity of photo-SCR depends on the amount of acid sites. Thus, the photo-SCR activity increased up to 1.5wt.% in content; if the content exceeded 1.5wt.%, the photo-SCR activity decreased, although the amount of acid site still increased up to 2.0wt.%. This result suggests that the photo-SCR activity is influenced by not only the amount of acid site but also by the local environment of tungsten species. Papp et al. reported a similar phenomena in the photo-degradation of 1,4-dichlorobenzene over \( \text{WO}_3/\text{TiO}_2 \) [11]. They observed the formation of inactive \( \text{WO}_3 \) species when the concentration of \( \text{WO}_3 \) increased.

The XRD pattern and Raman spectrum of pure \( \text{TiO}_2 \) indicated that the \( \text{TiO}_2 \) sample consists of 91.3% anatase and 8.7% rutile phases. However, when the content of \( \text{WO}_3 \) was low (<30wt.%), we could not obtain the structural information of tungsten species by means of XRD and Raman. The XANES spectra at the \( W-L_1 \) edge of \( \text{WO}_3/\text{TiO}_2 \), \( \text{WO}_3 \) and \( \text{Na}_2\text{WO}_4 \) are shown in Fig. 2. A characteristic feature of these XANES spectra can be seen in the pre-edge peak, appearing at ca. 12100 eV, attributed to the 2s-5d dipolar forbidden transition. This pre-edge peak of the \( W-L_1 \)-edge XANES spectrum is sensitive to the electronic and geometric structure of the tungsten site. Since the local symmetry around the tungsten is lowered from octahedral to tetrahedral coordination, the intensity of this peak tends to increase, i.e., 1tetrahedral > 1square pyramidal > 1octahedral \( \text{Na}_2\text{WO}_4 \), which possesses a tetrahedral coordination structure, showed the largest intensity, whereas \( \text{WO}_3 \) with octahedral coordination structure showed weak and broad absorption. The pre-peak intensities of the \( \text{WO}_3/\text{TiO}_2 \) samples were lower than that of \( \text{Na}_2\text{WO}_4 \), although higher than that of \( \text{WO}_3 \).

**FIGURE 2.** \( W-L_1 \) XANES spectra of references and \( \text{WO}_3/\text{TiO}_2 \) samples after \( \text{O}_2 \) pretreatment; (a) \( \text{WO}_3 \), (b) 1wt.%, (c) 1.5wt.%, (d) 2wt.%, (e) 5wt.%, (f) 10wt.% \( \text{WO}_3/\text{TiO}_2 \), (g) \( \text{Na}_2\text{WO}_4 \).
Fig. 3 shows the Fourier transforms of $k^2$-weighted EXAFS spectra. The peaks appearing at 1.5 Å are due to the scattering from the nearest-neighbor oxygen atoms. The W-M (M = Ti or W) peaks appear at 2.5-4 Å. The 1wt.% WO₃/TiO₂ sample exhibits a peak at 2.9 Å. This peak intensity decreased with increasing WO₃ content and a new peak at 3.5 Å appeared, suggesting that a change in second shell took place.

The curve fitting results of W-O shells are shown in Table 1, in which total coordination number is ca. four for each case, supporting the tetrahedral coordination of tungsten. In the case of 1-shell fit, large $R$ factors suggest the failure of fitting. In the case of 2-shell fit, each parameter is reasonable. Thereby, a WOₓ unit possesses two short and two long W-O bonds. Moreover, we found that the W species on 1wt.% WO₃/TiO₂ is isolated and the number of the agglutinated W species increases as the addition of WO₃ by the comparison of the envelope function of Fourier-filtered EXAFS function in the $R$ range of 2.6-4.0 Å with the theoretically calculated back scattering amplitudes of Ti and W reported by Teo and Lee [13].

From these results mentioned above, we conclude that the isolated and tetrahedrally coordinated tungsten sites over TiO₂ enhanced the acidity and the photo-SCR activity. When the W content exceeded 1.5wt.%, the agglutinated W species were formed over TiO₂ and this agglutinated W species were not effective.

**TABLE 1. Structural parameters for W-O shells of samples**

<table>
<thead>
<tr>
<th>Sample</th>
<th>C. N.</th>
<th>$R$ / Å</th>
<th>$\sigma^2$/Å²</th>
<th>$R$ (%)</th>
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<tr>
<td>1WT(1)</td>
<td>4.0</td>
<td>1.83</td>
<td>0.0051</td>
<td>17.2</td>
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<tr>
<td>1.5WT(1)</td>
<td>3.6</td>
<td>1.81</td>
<td>0.0048</td>
<td>16.8</td>
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<tr>
<td>2WT(1)</td>
<td>3.6</td>
<td>1.81</td>
<td>0.0050</td>
<td>21.2</td>
</tr>
<tr>
<td>5WT(1)</td>
<td>3.6</td>
<td>1.80</td>
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<td>34.6</td>
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<tr>
<td>10WT(1)</td>
<td>3.5</td>
<td>1.78</td>
<td>0.0067</td>
<td>40.0</td>
</tr>
<tr>
<td>1WT(2)</td>
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<td>1.77</td>
<td>0.0046</td>
<td>9.2</td>
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<td></td>
<td>2.1</td>
<td>1.90</td>
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</tr>
<tr>
<td>1.5WT(2)</td>
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<td>0.0048</td>
<td>8.1</td>
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<tr>
<td></td>
<td>1.8</td>
<td>1.89</td>
<td>0.0041</td>
<td></td>
</tr>
<tr>
<td>2WT(2)</td>
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<td>1.76</td>
<td>0.0046</td>
<td>9.9</td>
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<tr>
<td></td>
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<td>1.89</td>
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<td></td>
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<td>1.90</td>
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<tr>
<td>10WT(2)</td>
<td>1.9</td>
<td>1.76</td>
<td>0.0049</td>
<td>6.5</td>
</tr>
</tbody>
</table>

The filtering range 0.9-2.0 Å and $k$ fit range 3.0-11.6 Å⁻¹. ×WT(yy): xwt.% WO₃/TiO₂ fitted with y-shells. 'coordination number. 'bond distance. 'Debye-Waller. 'So-called $R$ factor.

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**REFERENCES**