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# XAFS Analysis on Vanadium Species Dispersed in Transparent Silica Glass

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## 1 Introduction

The vanadium(V) oxide highly dispersed on silica shows the photocatalytic activity for partial oxidation of alkane and alkene, because the local structure of the V(V) center is different from that in the bulk crystal [1]. It is important for improving the photocatalytic performance to understand the electronic state and the local structure of the photoexcited state. The pump and probe DXAFS method is a useful technique for analysis of photoexcited states. However, the excitation laser is scattered at the powder surface and it excites only the V(V) species located near the particle surface. Although it is not a problem for the photocatalysis reaction, the selective observation of such the active species is impossible for the DXAFS technique in the transmission mode. An efficient excitation method for the entire V(V) species is necessary to apply the DXAFS technique. One solution is to prepare a transparent glassy plate, in which the active V(V) species is dispersed. The purpose of this research is the chemical state analysis of V(V) species supported in a transparent silica glass during its preparation process.

## 2 Experiment

The V(V) oxide photocatalyst was prepared by the sol-gel method. The tetraethyl orthosilicate (TEOS), nitric acid, deionized water, and *N,N*-dimethylformamide were added into ethanol, and the solution was stirred for 1.5 h at 50 °C. Then, V(V) oxytriisopropoxide (VOTIP) and ammonium hydroxide were added into the solution to get the wet gel. It was dried for a week at 80 °C and for 3 h at 200 °C. The sample was then heated at 500 °C for 1.5 h in air.

The obtained sample was transparent and colorless just after the treatment at 500 °C, but the color was changed to reddish brown after cooling down. The *in-situ* XAFS measurement was performed at BL-9C of PF to analyze the chemical state change of the V species. The glassy sample plate with the thickness of 0.18 mm was set in the flow-type *in-situ* XAFS cell, and it was heated up to 500 °C under 10 vol% $O_2$/He gas flow as the heating treatment.

## 3 Results and Discussion

Only a broad diffraction line at 25° assigned to amorphous silica was appeared in the XRD pattern of the prepared sample. It indicates that supporting silica is formed by the hydrolysis and the condensation of TEOS and that the V species was highly dispersed in silica.

Figure 1 shows the XANES spectrum of the prepared V photocatalyst supported in the transparent silica glass. The absorption edge energy of the sample after the heating treatment at 500 °C agrees with that of $V_2O_5$, however the spectral shape was apparently different. Especially, the pre-edge peak intensity of the V(V) photocatalyst is stronger than that of $V_2O_5$. It is known that the pre-edge peak is assigned to the transition from 1s to 3d which is mixed with 2p of oxygen [2]. Therefore, the peak intensity is dependent on the geometry of binding O atoms around the V(V) center. A similar intense peak is observed for VOTIP and $NH_4VO_3$ with the similar $VO_4$ unit, which is contrast to the $V_2O_5$ with the tetragonal $VO_5$ unit. The present study revealed that the V(V) center with the $VO_4$ unit was dispersed in the transparent silica glass. After it was cooled down in air, the pre-edge peak intensity of XANES spectrum was drastically decreased. It is considered that the structure change from $VO_4$ to $VO_5$ was caused by the water molecule absorbed from air [3]. These results indicate that the protection against the water absorption is necessary to sustain the active $VO_4$ unit to carry out the pump and probe DXAFS experiment.

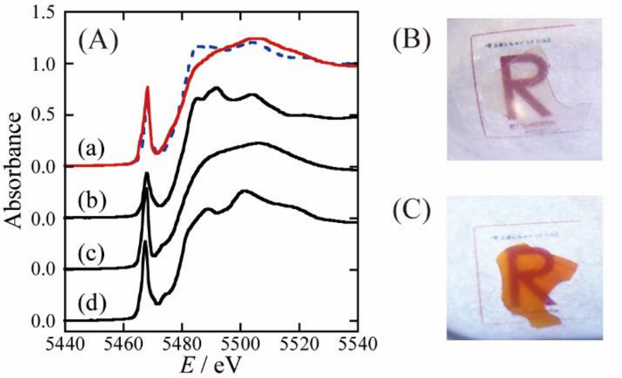

Fig. 1: XANES spectrum of the V photocatalyst supported in the transparent silica glass (A). For (a), the solid and dashed line shows the spectrum of the photocatalyst at 500 °C and at room temperature, respectively. The standard samples are $V_2O_5$ (b), VOTIP (c), and $NH_4VO_3$ (d). The pictures show the sample just after the heating treatment (B) and after the water absorption (C).

## References

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