

Structure Analysis of Vanadium Species Supported on Alumina

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1. Introduction

Highly dispersed vanadium oxide species on silica is reported to form the V(V) species with the V-centered tetrahedral structure [1]. The V(V) species shows photo catalytic activity for the selective oxidation of olefins by an UV light illumination. Such a tetrahedral species is known to form during the calcination process after the impregnation of the V precursor on silica. The similar photo catalytic activity is also expected for the supported V species on alumina. This study sheds lights on the structure change of the V species during the calcination process of the supported V species on alumina prepared by the sol-gel method. The *in-situ* X-ray absorption fine structure (XAFS) measurements have been performed to analyze the local structure change around the V center. The structural characteristics will be discussed on the basis of the pre-edge peak intensity observed in the X-ray absorption near edge structure (XANES) spectra.

2. Experimental

Aluminum tri-sec-butoxide, $\text{Al}(\text{OC}_4\text{H}_9)_3$, was added in ion-exchanged water, and a small amount of hydrochloric acid was added into the solution after a stirring for 2 hours at room temperature. The solution was continuously stirred for 2 days at room temperature, and ammonium metavanadate, NH_4VO_3 , was added into the solution. The mixed solution was stirred for further 5 days at room temperature, and was dried for 60 h at 343 K. The obtained powder is labeled as VA_dry.

The *in-situ* XAFS measurements were carried out at BL-3 of the SR center (Ritsumeikan University) and BL-9A of the Photon Factory (KEK) at the V K edge in the transmission mode. The heating process of VA_dry was measured under O_2 gas flow diluted by He up to 773 K. The final state is labeled as VA_cal.

3. Results and Discussion

The observed XANES spectra during the calcination process are shown in Fig. 1. As clearly seen in Fig. 1, the edge energy of the K shell electron is maintained in the all temperature range, indicating that the valence state of the V atom is kept to be +5. The absorption energy of the sharp pre-edge peak is also kept constant during the calcination process. Furthermore, it is found that the peak intensity is gradually increased with the progress of the calcination. It is known that the pre-edge peak is assigned to the transition to the 3d orbital mixed with 2p of oxygen [2], and the peak intensity is thus strongly related to the geometry around the V center. The normalized peak height of the pre-edge peak is given in Fig. 2 together with the reference samples with the known structure. The peak height for the V species with a tetrahedral geometry is reported *ca.* 0.76, whereas the corresponding value for an octahedral V species is *ca.* 0.52. This study revealed that the peak height was enhanced from 0.57 to 0.78 by the calcination process. It is found that the geometry around the V center is changed from octahedral to tetrahedral during the calcination, and the dispersed V species with the VO₄ unit is thus generated and becomes the active center for the photo catalysis system.

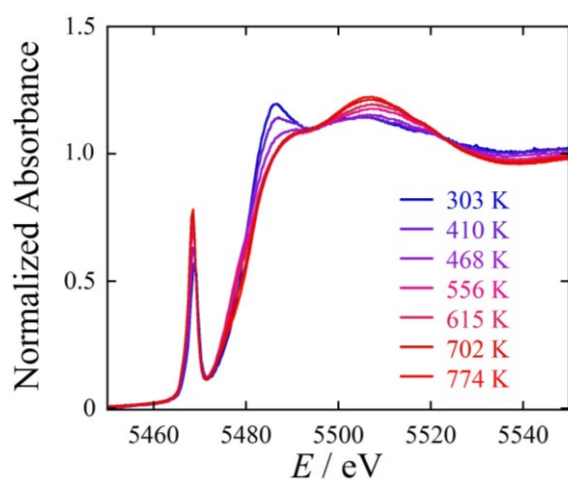


Fig.1 XANES spectral change of the V species supported on alumina during calcination process.

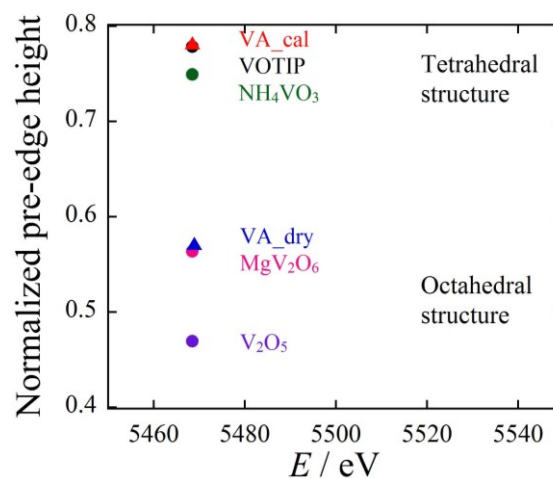


Fig.2 Comparing the normalized peak height of the pre-edge peak to V prepared samples and reference samples.

References

- [1] S. Yoshida, T. Tanaka, T. Hanada, T. Hiraiwa, H. Kanai and T. Funabiki, *Catal. Lett.*, **12**, 277 (1992).
- [2] T. Tanaka, H. Yamashita, R. Tsuchitani, T. Funabiki and S. Yoshida., *J. Chem. Soc., Faraday trans.* **84** 2987 (1988).