

Structure of Low Concentration of Vanadium on/in Titanium Oxide Determined by X-ray Absorption Fine Structure Utilizing Fluorescence Spectrometry

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Introduction

Vanadium (V) on titanium (Ti) oxide is used for the reduction of nitric oxide with ammonia and selective oxidation of butane, naphthalene, and *o*-xylene. V site less than the concentration of monolayer on TiO₂ is generally active and selective for these reactions. In spite of the importance, it has been very difficult to measure XAFS data for low concentration of V in the TiO₂ matrix because V is next to Ti in the periodic table and the absorption/emission of Ti interferes to measure the signal of V. When a SSD (energy resolution ≈ 100 eV) is used, the V K α_1 (4952.2 eV) peak cannot be separated from the Ti K $\beta_{1,3}$ (4931.8 eV). The ratio of V K α_1 /Ti K $\beta_{1,3}$ is 0.058. In the *Activity Report 2001B*, p.31, the feasibility of XAFS utilizing fluorescence spectrometer to monitor low concentration of V on TiO₂ was demonstrated. In this report, the V site structure of V-TiO₂ samples prepared by several procedures was studied by the method.

Experimental Section

High surface area sample was prepared from V triisopropoxide oxide (**1**), Ti tetraisopropoxide (**2**), and dodecylamine (HSA V-TiO₂). HSA-TiO₂ was prepared similarly from **2** and was impregnated with **1** (V/HSA-TiO₂). V-TiO₂ was prepared in the absence of dodecylamine. The X-ray spectra were measured at 290 K using beamline 7C. A Si(111) monochromator was used and the beam was focused. The X-ray fluorescence from the sample was analyzed using a Rowland-type spectrometer ($R = 180$ mm) equipped with a Johansson-type Ge(331) crystal. The entire beam path was in helium, except for the I_0 ion chamber (N₂ 30% in He). The spectrometer was tuned to V K α_1 peak and the V K-edge XAFS was measured. The dwell time of each data point was 60s, and two/three scans were performed for each sample.

Results and Discussion

Figure 1 shows the normalized V K-edge XANES spectra. Similar structure to the case of Mn_{0.90}V_{1.80}Mo_{0.20}O₆ (**3**) (spectrum **g**) was proposed in the case of V/TiO₂ (a and b; P25 was used). The V site in **3**

was coordinated by two terminal oxo (1.661 – 1.693Å) and three oxygen atoms (1.913 – 2.151Å). V^{IV} site were substituted on the Ti sites of HSA (≈ 1200 m²g⁻¹) TiO₂ in the case of **c**. EXAFS combined with fluorescence spectrometry until k of 11Å⁻¹ gave an average V-O distance of 1.74Å in the case.

The pre-edge, rising edge, and two post-edge peaks appeared at 5468.5, 5481.1 – 5481.3, 5487 – 5488, and 5501 – 5504 eV and the FWHM of pre-edge peak was 2.4 – 2.5 eV for V/HSA-TiO₂ (**d**) and V-TiO₂ (**e**), very similar to the case of V/TiO₂ (**a** and **b**). Major V site structure may be common V^V species except for the sample of **c**.

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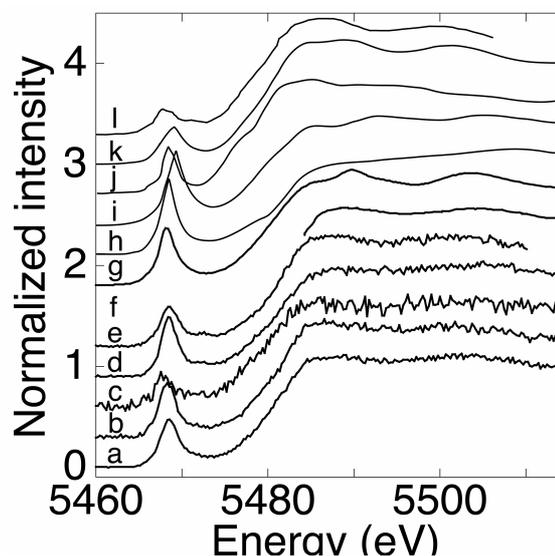


Figure 1. V K-edge XANES spectra for V+TiO₂ catalysts measured using a fluorescence spectrometer (a – e). Conventional V/TiO₂ of 3.0 (a) and 1.0 wt%-V (b), HSA V-TiO₂ (0.6 wt%-V, c), V/HSA-TiO₂ (1.0 wt%, d), and V-TiO₂ (2.0 wt%, e). Reference V (f – k) and Ti K-edge (l) XANES measured in transmission mode for V/TiO₂ (3.9 wt%-V, f), Mn_{0.90}V_{1.80}Mo_{0.20}O₆ (g), CrV^VO₄ (h), V^V₂O₅ (i), V^{IV}OSO₄·3H₂O (j), V^{IV}₂O₄ (k), and HSA-TiO₂ (l).