In situ polarized total-reflection fluorescence X-ray absorption near-edge structure spectroscopy for the analysis of oriented structure of vanadium oxides on $ZrO_2(100)$

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The oriented structure of the exposed V=O bond of vanadium oxides on $ZrO_2(100)$ was studied by in situ polarized total-reflection fluorescence X-ray absorption near-edge structure (XANES) spectroscopy. The pre-edge peak intensity of s-polarized XANES was half the intensity of the p-polarized one. Moreover, both pre-edge peaks decreased in a similar way and eventually became zero by the reaction of V=O bonds with NH_3 at 423 K, suggesting that all of the observed V=O bonds behaved as active sites. The present technique suggests that the exposed V=O bonds are oriented to a 45°-direction from the normal to the $ZrO_2(100)$ surface.

Keywords: polarized total-reflection fluorescence XANES; vanadium oxides on $ZrO_2(100)$; oriented structure of V=O bonds; the reaction of V=O with NH_3

1. Introduction

Supported vanadium-oxide catalysts show high activities for various selective oxidation reactions [1]. The V=O double bonds have been demonstrated to be active sites, however, the activity and selectivity of vanadium-oxide catalysts depend on not only the number of the V=O double bonds but also the local structure derived from the interaction with the support surfaces. It has been reported that vanadium oxide has monolayer structures on TiO_2 and ZrO_2 [1,2]. Vejux and Courtine reported that the $V_2O_5(010)$ plane fits well the TiO_2(anatase) (001) plane geometrically [3]. The $V_2O_5(010)$ surface has V=O bonds protruding perpendicularly to the plane. It is possible to count the number of surface V=O bonds by a

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NH_3–NO titration and to compare the catalytic activity of vanadium oxides on different supports [4,5]. Extended X-ray absorption fine structure (EXAFS) provides information on the bond distance and coordination number for V=O [6–8], but the structural information given by traditional EXAFS in a transmission mode is averaged in every direction. Traditional X-ray absorption near-edge structure (XANES) also provides information on the local symmetry around V atoms like tetrahedral or octahedral symmetry on an average in every site and surface of the catalyst [9,10]. However, it is difficult to obtain direct evidence that the $V_2O_5(010)$ plane is exposed on supports, and that the double bond V=O is protruded perpendicularly to the plane by these previous experiments.

Polarized total-reflection fluorescence (PTRF) EXAFS is a powerful technique for structure analysis of solid species [11,12], which can determine the anisotropic structure of active metal or metal oxide sites supported on single crystal substrates and flat amorphous surfaces [13–16]. This technique can provide structural information separately in two different directions, parallel (s-polarization) and normal (p-polarization) to the support surface using polarized X-ray stemming from synchrotron radiation and TRF method as shown in fig. 1.

In this study, we report for the first time the in situ observation of tilted V=O bond in vanadium oxide supported on $ZrO_2(100)$, and the reaction of tilted bond with NH_3 by the PTRF XANES technique.

2. Experimental

Stabilized ZrO_2 substrate exposing the (100) plane (Earth Jewelry Ltd.; $30 \times 10 \times 1$ mm^3, containing Y_2O_3 20 atomic wt%) was calcined at 673 K for 2 h in air to remove volatile residual. The $ZrO_2(100)$ plane is a stable surface and its toplayer is composed of oxygen atoms [17]. $VO(OC_2H_5)_3$ was deposited on the $ZrO_2(100)$ by means of an impregnation method using an C_2H_5OH solution of

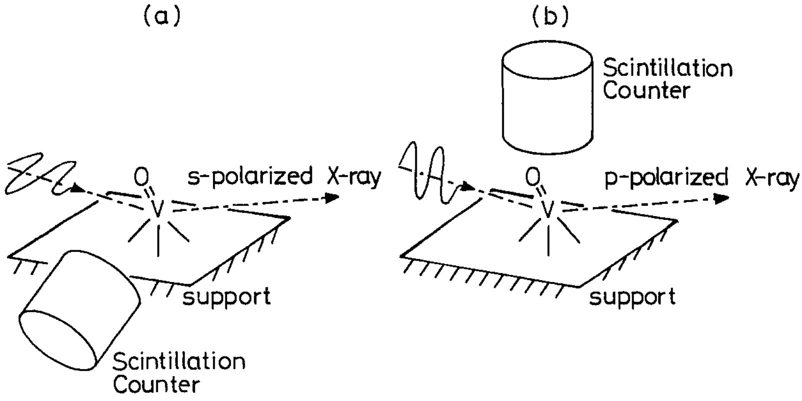

Fig. 1. Polarized total-reflection fluorescence XAFS; (a) s-polarization and (b) p-polarization.

$VO(OC_2H_5)_3$. The obtained samples were calcined at 823 K for 1 h in air. The 0.5 monolayer and 1.0 monolayer of vanadium oxide were supported on $ZrO_2(100)$ surface (1 monolayer is defined to be the amount of V atoms equal to the amount of surface oxygen atoms). The sample was put into the PTRF XAFS chamber [18,19] and fixed on the sample holder for in situ observation of the PTRF XANES. Before the PTRF XANES measurement, the sample was heated at 373 K for 1 h in situ in vacuum (base pressure: 1.33×10^{-4} Pa). To study the reaction of V=O bonds with NH_3 (dissociative adsorption), NH_3 gas of 133 Pa was admitted to the sample at 423 K in the chamber.

The PTRF XANES spectra of vanadium oxides on $ZrO_2(100)$ were measured at BL-7C of the Photon Factory in the National Laboratory for High Energy Physics (KEK-PF) (Proposals No. 92032 and 92G174). All the spectra at a total-reflection angle were measured at room temperature in the in situ PTRF EXAFS chamber [18,19]. The adjustment for the total-reflection condition was performed at 5900 eV. The beam spot did not change during the incident energy scan from 5440 to 5500 eV. The beam size was small enough at 1×0.1 mm^2 so that other parts of the sample were not irradiated. The incident X-ray was monitored by an ion chamber filled with N_2. The fluorescence X-ray from the sample was monitored by a NaI scintillation counter. Ti foil (thickness: 0.03 mm) was used as a filter to remove an elastic scattering from the sample. The X-ray Bragg-diffraction peak from the substrate was prevented by a Pb sheet (thickness: 1 mm), which was placed between the scintillation counter and the sample.

3. Results and discussion

The XANES spectra of vanadium oxides on $ZrO_2(100)$ surface are shown in fig. 2. The pre-edge peak ($1s \rightarrow 3d$ transition) was observed at 5467 eV for all spectra. The presence of the strong pre-edge peak in XANES suggests that vanadium atoms are located in a tetrahedral symmetry [20]. It has been reported that the pre-edge peak intensity of the oriented vanadium oxide on mica shows maximum when the electric-field vector of the incident X-ray was parallel to the V=O bond direction and zero when the vector was perpendicular to the V=O bond direction [21,22]. The intensity is proportional to $\cos^2 \theta$ (θ is the angle between the electric-field vector of the incident X-ray and the V=O bond direction). If the $V_2O_5(010)$ plane is exposed on $ZrO_2(100)$, the pre-edge peak intensity of the p-polarized XANES spectrum would show maximum and the intensity of the s-polarized one should show zero. The angle of the beam with respect to the sample surface was adjusted at 1.3 mrad to get the total-reflection condition. However, in the XANES spectra of both 0.5 and 1.0 ML vanadium oxides on $ZrO_2(100)$, the s-polarized pre-edge peak intensities were about half of the corresponding p-polarized ones. The angle between $ZrO_2(100)$ surface and V=O bond direction is not 90° for either sample. Furthermore, in the s-polarization spectra, the peak intensity is integrated

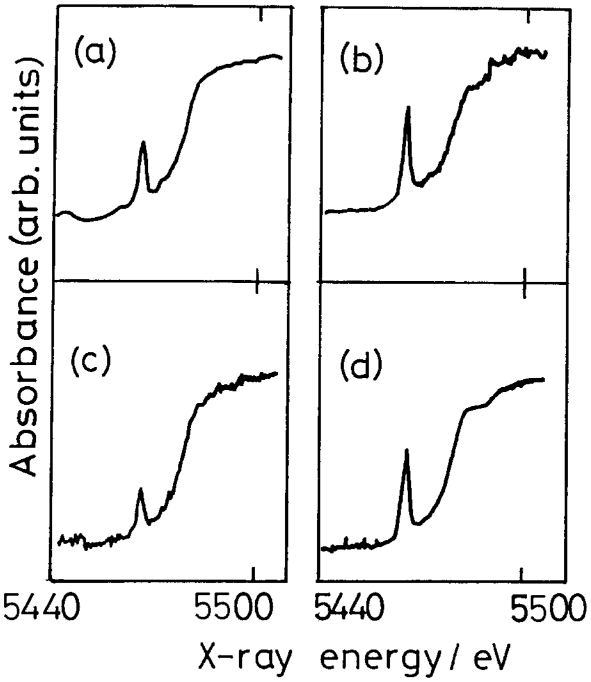

Fig. 2. The XANES spectra of vanadium oxide on $ZrO_2(100)$ for 0.5 ML; (a) s- and (b) p-polarization, and for 1.0 ML; (c) s- and (d) p-polarization.

in every direction at the surface; that is, the intensity integrated by the term $(2\pi)^{-1}\int_0^{2\pi}\cos^2\phi$ (ϕ denotes the angle between the V=O bonds and the polarized direction of the incident X-ray in surface plane). It means that the peak intensity of the s-polarization spectrum is half the peak intensity of the p-polarization spectrum if the angle between the V=O bond and the polarization vector is the same in s- and p-polarization as observed in fig. 2. This result is likely explained by the arrangement of the V=O bonds of vanadium oxides which are inclined to the $ZrO_2(100)$ surface by about 45°. The 45°-tilted V=O arrangement was observed with both the 0.5 and 1.0 ML vanadium oxides in fig. 2, the V=O orientation being independent of V loading.

The XANES spectra after NH_3 adsorption on the 1.0 ML vanadium oxide on $ZrO_2(100)$ are shown in fig. 3. The pre-edge peak intensities of both s- and p-polarization spectra decreased in a similar way and became zero by NH_3 adsorption at 423 K. It has been demonstrated that NH_3 adsorbs on V_2O_5/TiO_2 dissociatively [23]. The decrease of the pre-edge peak intensity is referred to the structure change from V=O to V–OH, where the vanadium oxide changes from tetrahedral structure to octahedral structure. The similar decrease in the peak intensity of both polarizations may reflect a uniform orientation of the V=O bonds on the $ZrO_2(100)$ surface. All of the tilted V=O bonds on $ZrO_2(100)$ were active for the reaction with NH_3 at 423 K as shown in fig. 3.

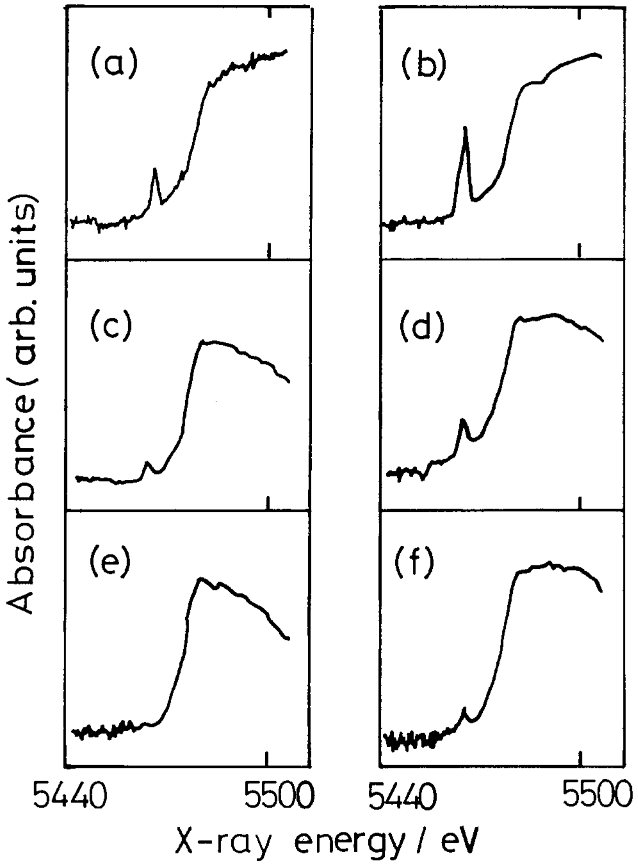

Fig. 3. The XANES spectra of 1.0 ML vanadium oxide on $ZrO_2(100)$ in vacuum (a, b) and after NH_3 adsorption for 30 min at 423 K (c, d) and for 2 h at 423 K (e, f). (a), (c) and (e) are the spectra for s-polarization. (b), (d) and (f) are the spectra for p-polarization.

4. Summary

(1) We have extended in situ polarized total-reflection fluorescence XANES spectroscopy to a new application.

(2) This technique provides information on the orientation of the V=O bonds in vanadium oxides by a selection rule for the intensity of the pre-edge peak (1s → 3d transition) in the polarization XANES spectra.

(3) The V=O bonds in the vanadium oxides (0.5 and 1 ML) on $ZrO_2(100)$ are suggested to be tilted about 45° from the surface normal.

(4) The NH_3 dissociation process on the V=O bonds was monitored in the two directions, s-polarization and p-polarization.

(5) All of the tilted V=O bonds behaved as active sites for adsorption of NH_3.

(6) Polarized total-reflection fluorescence EXAFS and XANES are useful for analyzing anisotropic structure and bond orientation of catalyst model surfaces.

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