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An X-ray absorption study on the local structures of highly dispersed supported titanium oxides prepared by a CVD method

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Titanium oxides supported on SiO_2 and Al_2O_3 prepared by a CVD method have been characterized by XANES/EXAFS technique. Titanium species on SiO_2 are highly dispersed in a tetrahedral coordination. Titanium species on Al_2O_3 are also highly dispersed in fivefold coordination. High dispersion was substantiated by their photoluminescence emitted by excitation at 300–350 nm.

Keywords: EXAFS/XANES; supported TiO_2; CVD; highly dispersed catalyst

1. Introduction

Many methods have been exploited for characterizing highly dispersed catalysts [1]. One is XAFS analysis which has the advantage that it provides both structural and electronic information [2]. A quantitative analysis of XANES spectra has been successfully applied to the identification of surface transition metal oxide species on supports [3]. There are a few papers on the structures and active species of titanium species in titanium silicalite (TS-1) which catalyzes epoxidation of olefins, ammoximation of cyclohexanone, hydroxylation of benzene [4]. This letter describes highly dispersed phases of supported titanium oxide species which were prepared by a CVD (chemical vapor deposition) technique on the basis of XAFS data.

2. Experimental

Titanium oxide species supported on silica and alumina were prepared by the CVD method. Silica or alumina (SIO-4 and ALO-4 of Reference Catalysts of Catalysis Society of Japan) was evacuated at 673 K for 2 h followed by reacting

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$Ti(OPr^i)_4$ vapor of saturated pressure at room temperature at 423 K without carrier gas. At this temperature all isopropoxy groups were not decomposed. Isopropoxytitanium species on a support was heated in air at 673 K for 4 h. XAFS samples were prepared as follows: supported titanium oxides were oxidized with 8 kPa of oxygen at 673 K for 2 h and were evacuated at the same temperature for 5 min. Sample powders were sealed into a Q-pack pouch in a dry box. The X-ray absorption experiments were carried out at the beam line 6B and 7C stations of the Photon Factory in the National Laboratory for High Energy Physics (Tsukuba) with a ring energy of 2.5 GeV and a ring current of 150–250 mA. A Si(111) double crystal was used to monochromatize X-rays. The absorption spectra were recorded by using a fluorescence detector at room temperature in the range of photon energies from 4.7 to 6.0 keV for Ti K edge (resolution energy of 0.5 eV at the edge). The data analyses were carried out in a similar manner to those reported previously [3,5].

The phosphorescence spectra were measured at 77 K with a Hitachi 850 fluorophotometer fitted with a phosphorescence attachment. Samples were heated in O_2 (2.7 kPa) at 673 K for 2 h followed by evacuation at the same temperature for 5 min.

3. Results and discussion

3.1. XANES SPECTRA OF Ti K EDGE

Fig. 1 depicts the normalized pre-edge peaks of titanium reference compounds and TiO_2/SiO_2 and TiO_2/Al_2O_3 in dried and hydrated states prepared by the CVD method. The pre-edge peak is assigned to 1s–3d transition. Anatase and rutile TiO_2 in which titanium atoms are in an octahedral symmetry have three small peaks in the pre-edge region. The pre-edge peak of $Ti(OPr^i)_4$ in a tetrahedral environment is very sharp and high. Two titanium alkoxides have different structures: $Ti(OPr^i)_4$ is monomeric and tetrahedral, but $Ti(OBu^n)_4$ is an oligomer composed of fivefold coordination [6]. Two shoulder peaks are seen at both sides of a main peak for $Ti(OBu^n)_4$. The high single pre-edge peak of TiO_2/SiO_2(dried) is very similar to that of $Ti(OPr^i)_4$ which is the precursor reagent. The XANES spectrum resembles that of TiO_2–SiO_2 glass [9]. On hydration the pre-edge peak is shifted to higher energy (1.5 eV) compared to that of the dried sample and is lowered with a shoulder at the higher energy side. The XANES spectrum of TiO_2/Al_2O_3(dried) is similar to that of $Ti(OBu^n)_4$ including the pre-edge peak. When water was adsorbed, the pre-edge peak is shifted to higher energy (0.7 eV), but a small change of XANES spectrum was observed.

XANES spectra were deconvoluted to obtain pre-edge areas (in units of eV) [3] (table 1). Among reference compounds the area of tetrahedral $Ti(OPr^i)_4$ is the largest. The area decreases with increasing coordination number. There is no explicit relation between the pre-edge position and the structure. The area of dried TiO_2/

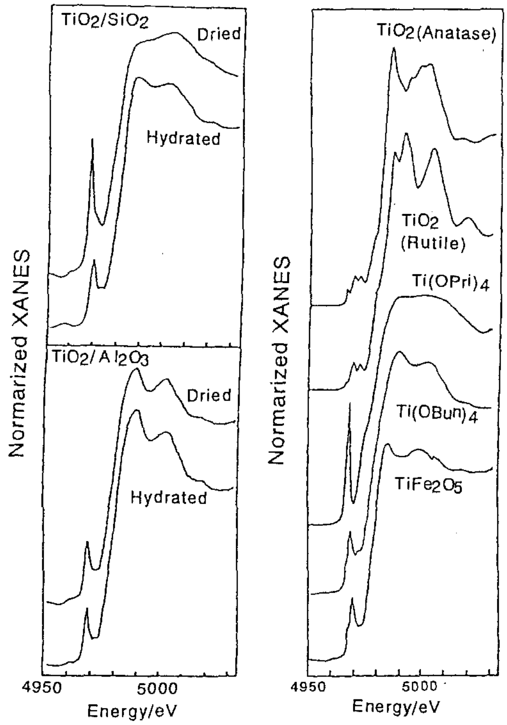

Fig. 1. XANES spectra of Ti-containing reference compounds and TiO/SiO$_2$ and TiO$_2$/Al$_2$O$_3$ in the dried and hydrated states.

Table 1
Positions and areas of pre-edge peaks

Compound	Pre-edge peak[a] (eV)	Area (eV)	
Ti(OPr^i)$_4$	−10.17(0)	1.04	TiO$_4$
Ti(OBu^n)$_4$	−9.40(0.8)	0.68	TiO$_5$
TiFe$_2$O$_5$	−10.47	0.52	TiO$_6$
TiO$_2$(anatase)	−11.92	0.14	TiO$_6$
TiO$_2$(rutile)	−11.27	0.14	TiO$_6$
TiO$_2$/SiO$_2$(dried)	−11.66	1.29	
TiO$_2$/SiO$_2$ (hydrated)	−10.1(1.5)	0.42	
TiO$_2$/Al$_2$O$_3$(dried)	−11.5	0.80	
TiO$_2$/Al$_2$O$_3$ (hydrated)	−10.84(0.7)	0.47	

[a] The peak position is relative to the absorption edge. The number in parentheses is the shift of the peak position on hydration.

SiO_2 is rather larger than that of tetrahedral $Ti(OPr^i)_4$. Titanium species in TiO_2/SiO_2 should be in tetrahedral coordination. The area decreases upon the adsorption of water parallel to higher coordination.

The pre-edge peak area of TiO_2/Al_2O_3(dried) is between those of tetrahedral and octahedral structures. It is rather close to the area of fivefold coordination compound. The area also decreases with the adsorption of water. The area of TiO_2/Al_2O_3(H_2O adsorbed) resembles that of $TiFe_2O_5$ in which titanium is in octahedral symmetry [7].

3.2. EXAFS OF Ti K EDGE

The magnitudes of Fourier transforms performed for EXAFS curves in the 3.5–12 $Å^{-1}$ region are displayed in fig. 2. No further shells are observed except the first shell of the 1–2 Å range which is assigned to Ti–O bonds in dried TiO_2/SiO_2. This should be ascribed to the fact that titanium atoms are well separated from each other and no TiO_2 particles are present. The peaks are centered at lower values than the real distances owing to the phase shift. When water was adsorbed, peaks in the first shell of TiO_2/SiO_2 and TiO_2/Al_2O_3 were broadened indicating that new Ti–O bonds linked to water molecules were formed.

The structural information for Ti–O bonds was derived from inverse Fourier transforms of the peaks in fig. 2 over the range of 0.55–2.15 Å and extracted by using single-scattering theory,

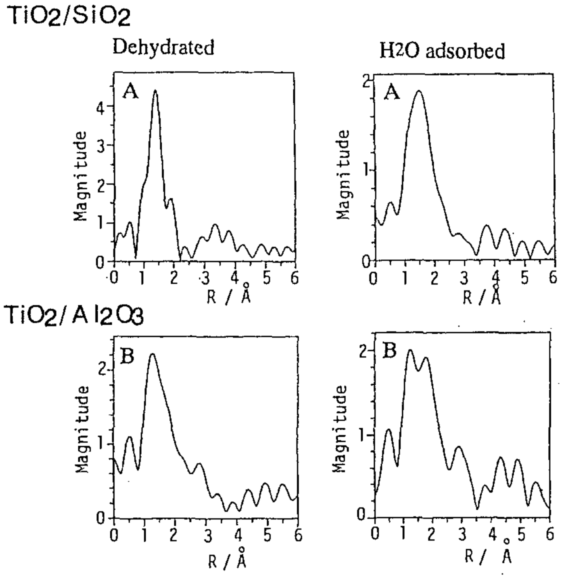

Fig. 2. Fourier transforms of EXAFS oscillations for TiO/SiO_2 and TiO_2/Al_2O_3 in the dried and H_2O-adsorbed states.

$$\chi(k) = \sum_j (N_j S_j / k r_j^2) F_j(k) \exp(-2\sigma_j^2 k^2) \exp(-2r_j/\lambda) \sin[2kr_j + \delta_j(k)] , \quad (1)$$

where N_j is the coordination number of the jth shell at the distance r_j from the X-ray absorbing atom, $F_j(k)$ the backscattering amplitude for the photoelectron wave number k, S_j the damping factor for compensation of the loss by inelastic scattering, δ_j the phase shift, σ_j the Debye–Waller factor, and λ the mean free path of the photoelectron (table 2). Tabulated values for $F_j(k)$ and $\delta_j(k)$ by Teo et al. [8] are used for curve-fitting procedures. The reliability of these structural parameters was ascertained with authentic samples of Ti foils and $Ti(OPr^i)_4$. The Ti–O bond distance of TiO_2/SiO_2 is 1.77 Å, very similar to that of $Ti(OPr^i)_4$. The bond distance is close to that of TiO_2–SiO_2 glass (1.79 Å) [9], but differs from those of titanium silicalite (TS-1, 1.87–1.89 Å) [4], titanium oxide (1.85 Å) in TiZSM-5 prepared by treatment of ZSM-5 with $TiCl_4$ [10] and TiO_2 (anatase, rutile, 1.94 and 1.99 Å). The corrected coordination number of Ti atom based on S_j (eq. (1)) is 3.5 indicating that titanium atoms are highly dispersed in tetrahedral coordination. The environment is very similar to that of TiO_2–SiO_2 glass in the Ti content of 2–10 wt% prepared by flame hydrolysis of $SiCl_4$ and $TiCl_4$ vapors [9]. Anatase or an anatase-like structure was obtained for highly dispersed or monolayer titanium oxide on SiO_2 prepared by impregnating of silica into organic solutions of $Ti(OPr^i)_4$ [11]. The structural difference between the two types of TiO_2/SiO_2 from the same precursor is attributed to the difference of the preparation method. The adsorption of water causes a disordered structure from a consideration of the increased Debye–Waller factor, and the additional Ti–O bond which has a longer bond distance (1.93 Å) was assigned to Ti–OH_2.

Although the Fourier transform of TiO_2/Al_2O_3 si not neatly depicted, inverse Fourier transforms were performed over the same region with that of TiO_2/SiO_2 to afford large Debye–Waller factor. The same Ti–O bond distance (1.77 Å) was obtained for TiO_2/Al_2O_3 along with a longer Ti–O bond (1.95 Å). The latter is not assigned to Ti–OH_2 bond, but should be assigned to Ti–O–Al. When water was

Table 2
Curve-fitting for Ti–O shells of supported TiO_2 catalysts

Support	Condition	Structure parameter [a]		
		R (Å)	CN	$\Delta\sigma^2$ (10^{-3} Å^2)
SiO_2	dried	1.77	3.5	7.27
SiO_2	hydrated	1.77	3.2	15.0
		1.93	0.63	4.19
Al_2O_3	dried	1.77	2.9	10.5
		1.95	0.39	0.20
Al_2O_3	hydrated	1.78	3.7	14.3
		1.98	0.66	0.37
$Ti(OPr^i)_4$	in xylene	1.77	4.0	9.82

[a] R: bond length; CN: coordination number; $\Delta\sigma^2$: Debye–Waller factor.

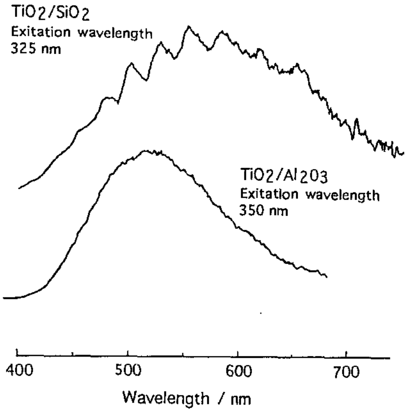

Fig. 3. Phosphorescence spectra of TiO/SiO_2 and TiO_2/Al_2O_3 at 77 K (excitation wavelength 325, 350 nm).

adsorbed, the total coordination number increases including additional Ti–OH_2 bond. The result of XANES/EXAFS data for TiO_2/Al_2O_3 gives the structure composed of fivefold coordination.

Highly dispersed states of TiO_2/SiO_2 and Al_2O_3 prepared by the CVD method were supported from the evidence that both catalysts gave photoluminescence by irradiation of around 300 nm light (fig. 3). The vibrational fine structure of photoluminescence of TiO_2/SiO_2 excited at 325 nm gives an energy separation of 966 cm^{-1} between (0, 1) and (0, 2) bands which corresponds to the vibration energy of Ti–O bond [12]. There is no vibrational fine structure for TiO_2/Al_2O_3, but the highest peak is shifted to lower wavelength than that of TiO_2/SiO_2.

The CVD technique in which $Ti(OPr^i)_4$ vapor was reacted with OH groups of supports at relatively low temperature is effective for preparing monolayer titanium oxide phases.

The different structure of these two catalysts is reflected in a preliminary test of catalysis for epoxidation of 1-octene with tert-butyl hydroperoxide [13]. High epoxidation activity was obtained for the TiO_2/SiO_2 catalyst, but no activity was observed for the TiO_2/Al_2O_3 catalyst. We may conclude that tetrahedral titanium species on silica is responsible for the active species in the epoxidation of olefins.

Further study on the relationship between structure and catalytic activity is in progress.

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