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► **To cite this version:**

S. Yoshida, S. Takenaka, T. Tanaka, T. Funabiki. Ultrahighly Dispersed Titanium Oxide on Silica : Effect of Precursors on the Structure and Photocatalysis. *Journal de Physique IV Proceedings*, 1997, 7 (C2), pp.C2-859-C2-861. 10.1051/jp4:1997259 . jpa-00255342

HAL Id: jpa-00255342

<https://hal.science/jpa-00255342>

Submitted on 4 Feb 2008

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Ultrahighly Dispersed Titanium Oxide on Silica: Effect of Precursors on the Structure and Photocatalysis

S. Yoshida, S. Takenaka, T. Tanaka and T. Funabiki

Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-01, Japan

Abstract. The effect of precursor on the dispersion and catalytic performance of titanium oxide supported on silica has been investigated. The catalysts were prepared by a simple impregnation method with three kinds of titanium complexes of different ligands (bis(isopropylato)-bis(pivaroylmethanato) titanium (IV) (DPM)₂(O-iPr)₂, acetylacetonato: ACAC, tetrakis(isopropylato) titanium (IV) (IPRO) with the aim of preparing ultrahighly dispersed titanium oxide on silica. The XAFS study revealed that titanium species in the catalyst prepared from the complex with DPM ligand was a mononuclear species of an almost regular tetrahedral TiO₄. The species prepared from the complex with ACAC ligand was also mononuclear but the titanium ion was coordinated by five oxygen atoms. The complex with IPRO ligand resulted in preparation of a catalyst containing some aggregated titanium species. These catalysts exhibited a remarkable difference in photooxidation of propane.

1. INTRODUCTION

TiO₂ catalyses the photooxidation of alkanes. The selectivity to partial oxidation is reported as 67 % at a very low conversion of 0.74 % [1]. However, the selectivity is reduced very much at a substantial conversion level such as 10 % as demonstrated in this report. In a previous work, we found that titanium oxide highly dispersed on silica exhibits a high selectivity to the partial oxidation of propane [2]. The catalysts were prepared by an impregnation method using tetrakis(isopropylato)titanium(IV) and bis(isopropylato)-bis(pivaroylmethanato)titanium (Ti(DPM)₂(O-iPr)₂) as precursors. The loading amount was adjusted as α 4.5 wt% as TiO₂. XAFS studies revealed some aggregation of TiO₆ or TiO₅ clusters and the degree of aggregation affected the photoactivity and the selectivity. In case of vanadium oxide supported on silica, mononuclear VO₄ species is the active species in the photooxidation of olefins [3]. Thus, it is intriguing to investigate the catalytic activity of mononuclear TiO_x species. In the present work, we have prepared titanium oxide catalysts ultrahighly dispersed on silica by using three kinds of titanium complexes as precursors and investigated the local structure by X-ray absorption spectroscopy.

2. EXPERIMENTAL

2.1 Catalyst Preparation

Silica support (BET surface = 630 m² g⁻¹) was prepared by the hydrolysis of twice-distilled silicon tetraethoxide. The silica was impregnated with a toluene solution of bis(isopropylato)-bis(pivaroylmethanato)titanium(IV) (Ti(DPM)₂(O-iPr)₂), bis(acetylacetonato)oxotitanium(IV) (TiO(acac)₂) and tetrakis(isopropylato)titanium(IV) (Ti(O-iPr)₄) for 2 h under reflux condition. The filtrate was dried and calcined for 5 h at 773 K. The loading of titanium was adjusted to 0.6 wt % TiO₂. The samples will be referred to LD-TiO₂/SiO₂, LA-TiO₂/SiO₂ and LI-TiO₂/SiO₂, respectively. The titanium complexes react with the surface hydroxyl groups of silica and are expected to be fixed in an atomically dispersed state on the silica. By calcination in air, the complexes will decompose to form titanate species of a some aggregated state. However, the degree of aggregation is expected to be low. In fact, the BET surface area are found to be 626, 610 and 612 m² g⁻¹, for LD-TiO₂/SiO₂, LA-TiO₂/SiO₂ and LI-TiO₂/SiO₂, respectively. The small reduction of surface area by the loading indicates an ultrahigh dispersion of the titanium species. As a reference, bulk TiO₂ (Degussa, P25; BET surface area = 50 m² g⁻¹) was used.

2.2 Characterization

For characterization of the catalysts, diffuse reflectance UV spectra and X-ray absorption (XAFS) spectra at the Ti K-edge were recorded. The X-ray absorption experiment was carried out at station BL-7C with a Si(111) two-crystal monochromator in Photon Factory, National Laboratory for High Energy Physics, Tsukuba, Japan. The higher harmonics were eliminated by a focusing double mirror and the energy resolution at the Ti K-edge was about 0.4 eV. The data collection was done in the X-ray fluorescence mode except for P25 (transmission mode) at room temperature under the following SR ring operation conditions; ring energy = 2.5 GeV, ring current = 280 - 330 mA.

2.3 Reaction

The photooxidation of propane over the catalysts was carried out with a conventional low-pressure gas-circulation system with a quartz reactor (dead volume = 277 ml) and a 250 W ultrahigh pressure mercury lamp as light source. The catalyst was irradiated for a given time at room temperature under an atmosphere of propane and oxygen and the products were analyzed by g.l.c. No products were formed without catalysts and/or irradiation.

3. Characterization

3.1 UV spectra

Figure 1 shows diffuse reflectance spectra of the catalysts. The general feature of LI-TiO₂/SiO₂ is similar to that of P25, except for a blue shift in the threshold. On the other hand, the spectra of LD-TiO₂/SiO₂ and LA-TiO₂/SiO₂ are composed of narrow peaks which are assignable to ligand to metal charge transfer bands. This suggests that the titanium species in LD-TiO₂/SiO₂ and LA-TiO₂/SiO₂ has a molecular nature; the species is a cluster of TiO_x.

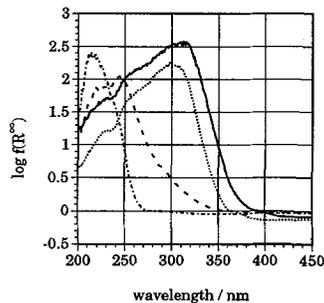


Fig. 1 Diffuse reflectance spectra of P25(—), LI-TiO₂/SiO₂(.....), LA-TiO₂/SiO₂(- - -), and LD-TiO₂/SiO₂(- · - ·).

3.2 XANES

The local structure of the titanium oxide on silica was investigated by XAFS. Figure 2 shows the XANES spectra of the samples and reference compounds. The spectrum of LI-TiO₂/SiO₂ resembles that of rutile, suggesting an octahedral structure. On the other hand, a fairly strong pre-edge peak is observed in the spectra of LD-TiO₂/SiO₂ and LA-TiO₂/SiO₂. A strong pre-edge peak is expected for a titanium ion in a low coordination symmetry without inversion center. Referring to a report by Bordiga et al. [4], the species in these catalysts would be tetra- or penta-fold-coordinated.

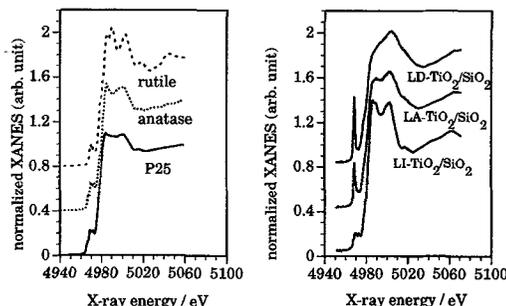


Fig.2 XANES of TiO₂ and Catalysts

3.3 EXAFS

The k³-weighted Fourier transformation (FT) was carried out on the EXAFS of catalysts in the k range of 3.2 - 13 Å⁻¹. The results are shown in Fig. 3. Only one meaningful peak is observable for LD-TiO₂/SiO₂ and LA-TiO₂/SiO₂ indicating mononuclear titanium species. The FT of LI-TiO₂/SiO₂ is composed of a couple of peaks ranging in 0.7 - 3.7 Å, indicating an aggregated state of titanium species. The structural parameters were obtained by a curve fitting analysis described in a previous work [5]. The equation used for the fitting is

$$\chi(k) = \sum_j \frac{N_j}{kR_j^2} f_j(k) \exp(-2\sigma_j^2 k^2) S_j(k) \sin(2kr_j + \delta_j(k))$$

where $S_j(k)$ is the damping factor and $f_j(k)$ is the backscattering amplitude. In the present analysis, the product of $S_j(k) \cdot f_j(k)$ was treated as a single function. The product function and phase shift function, $\delta_j(k)$, were deduced from the EXAFS of reference compounds using the above equation. For the Ti-O pair, the functions deduced from the EXAFS of Na₂VO₄ ($N_1 = 4$, $R_1 = 1.937$ Å, $N_2 = 2$, $R_2 = 1.964$ Å; best fit: $N_1 = 4.0$, $R_1 = 1.937$ Å, $N_2 = 2.0$, $R_2 = 1.977$ Å) and rutile (crystal data: $N_1 = 4$, $R_1 = 1.944$ Å, $N_2 = 2$, $R_2 = 1.988$ Å; best fit: $N_1 = 4.0$, $R_1 = 1.948$ Å, $N_2 = 2.0$, $R_2 = 1.983$ Å).

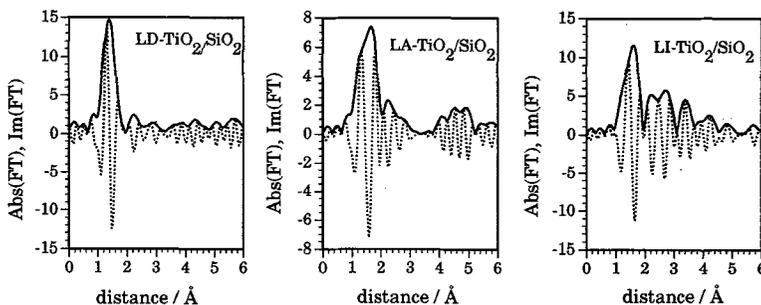


Fig. 3 k³-weighted Fourier transforms of catalysts. Solid line: absolute value, dotted line: imaginary part.

The validity for using the functions were verified by curve fitting to the Ti-O peak in FT of EXAFS of anatase (crystal data: $N_1 = 4$, $R_1 = 1.937$ Å, $N_2 = 2$, $R_2 = 1.964$ Å; best fit: $N_1 = 4.0$, $R_1 = 1.937$ Å, $N_2 = 2.0$, $R_2 = 1.977$ Å) and rutile (crystal data: $N_1 = 4$, $R_1 = 1.944$ Å, $N_2 = 2$, $R_2 = 1.988$ Å; best fit: $N_1 = 4.0$, $R_1 = 1.948$ Å, $N_2 = 2.0$, $R_2 = 1.983$ Å). For the Ti-Ti pair, the functions

were deduced from the second peak of the FT in EXAFS of anatase ($N=4$, $R=3.04$ Å). The reliability of the functions are verified by curve fitting to the second peak in FT of EXAFS of rutile (crystal data: $N(\text{Ti})=2$, $R(\text{Ti})=2.958$ Å, $N(\text{O})=4$, $R(\text{O})=3.218$ Å; best fit: $N(\text{Ti})=2.2$, $R(\text{Ti})=2.93$ Å, $N(\text{O})=3.8$, $R(\text{O})=3.20$ Å).

The results are shown in Table 1 for LD- $\text{TiO}_2/\text{SiO}_2$ and LA- $\text{TiO}_2/\text{SiO}_2$ and in Table 2 for LI- $\text{TiO}_2/\text{SiO}_2$. The structural parameters indicate that the titanium species in LD- $\text{TiO}_2/\text{SiO}_2$ is a mononuclear species of an almost regular tetrahedral TiO_4 and the species in LA- $\text{TiO}_2/\text{SiO}_2$ is also mononuclear but the titanium ion is coordinated by five oxygen atoms as suggested by XANES. On the other hand, the parameters for LI- $\text{TiO}_2/\text{SiO}_2$ suggest a linear chain of TiO_6 unit which has a distorted octahedral structure similar to that in rutile.

Table 1 Structural parameters for LD- $\text{TiO}_2/\text{SiO}_2$ and LA- $\text{TiO}_2/\text{SiO}_2$

LD- $\text{TiO}_2/\text{SiO}_2$				LA- $\text{TiO}_2/\text{SiO}_2$			
scatterer	N	R(Å)	$\Delta\sigma^2$	scatterer	N	R(Å)	$\Delta\sigma^2$
O	4.1	1.79	-1.57×10^{-3}	O	4.0	1.89	1.43×10^{-3}
				O	1.0	1.99	-6.37×10^{-3}
R factor = 7.5 %				R factor = 2.3 %			

N: coordination number. R: distance from the central Ti atom. $\Delta\sigma^2$: Debye-Waller factor deviation from that of the reference compounds. R factor is defined as $\sqrt{\sum(\text{exp-theo.})^2/\sum \text{exp.}^2}$

Table 2 Structural parameters for LI- $\text{TiO}_2/\text{SiO}_2$

scatterer	N	R(Å)	$\Delta\sigma^2$	scatterer	N	R(Å)	$\Delta\sigma^2$	scatterer	N	R(Å)	$\Delta\sigma^2$
O	4.0	1.88	-1.69×10^{-3}	O	1.9	2.61	1.32×10^{-3}	Ti	2.0	3.61	1.69×10^{-3}
O	2.0	2.01	-1.69×10^{-3}	O	1.9	3.03	-1.04×10^{-2}	O	2.0	3.70	-5.76×10^{-3}
								O	2.0	4.20	1.80×10^{-2}
R factor = 8.4 %				R factor = 10.1 %				R factor = 9.5 %			

See footnote to Table 1 for N, R and $\Delta\sigma^2$.

4. Photooxidation of propane

The results of photooxidation of propane over the catalysts are shown in Table 3. The reaction time was controlled to achieve the same conversion level. For comparison, the results over high loading catalysts (HD-, HA-, HI- $\text{TiO}_2/\text{SiO}_2$) reported previously [2] are also included. Generally speaking, the selectivity to partial oxidation increased by reducing the loading of titanate from 4.5 to 0.6 wt %. The effect is especially remarkable for A- $\text{TiO}_2/\text{SiO}_2$ and I- $\text{TiO}_2/\text{SiO}_2$. Almost qualitative conversion to acetone over LI- $\text{TiO}_2/\text{SiO}_2$ is noticeable at such a considerable high level of conversion. From the structural chemistry point of view as clarified in the present study, a suitable aggregation of TiO_6 clusters results in the formation of highly active species for partial photooxidation of propane. It seems that mononuclear species are not suitable, although the TS-1 catalyst which contains a mononuclear TiO_4 unit in a zeolite framework is known as a good catalysts for the epoxidation of olefins in a thermal reaction.

Table 3 Photooxidation of propane over bulk TiO_2 (P25) and $\text{TiO}_2/\text{SiO}_2$ catalysts

Catalyst	Time / min	Conv. / %	Selectivity / %					
			C_3H_6	C_2H_4	CH_3CHO	$\text{C}_2\text{H}_5\text{CHO}$	$(\text{CH}_3)_2\text{CO}$	CO or CO_2
P25	10	12.1	2	1	tr	0	13	84
HD- $\text{TiO}_2/\text{SiO}_2$	30	11.1	9	3	12	1	26	46
LD- $\text{TiO}_2/\text{SiO}_2$	30	11.1	9	7	31	5	28	18
HA- $\text{TiO}_2/\text{SiO}_2$	40	14.5	7	3	8	1	39	42
LA- $\text{TiO}_2/\text{SiO}_2$	45	12.9	4	5	19	5	67	0
HI- $\text{TiO}_2/\text{SiO}_2$	15	13.9	6	4	3	tr	57	30
LI- $\text{TiO}_2/\text{SiO}_2$	20	12.6	1	2	1	tr	95	0

Amount of catalysts: 200 mg of P25 and 500 mg of $\text{TiO}_2/\text{SiO}_2$. Each 70 μmol of propane and oxygen was introduced.

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