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NOTE

Epoxidation Activity of Coordinatively Unsaturated Titanium Oxide

Liquid-phase epoxidation of olefins proceeds on Ti catalysts with hydroperoxides as oxidizing reagents (1–4). In the case of heterogeneous Ti catalysts, however, the relationship between their configuration and the epoxidation activity is not well known (5). Previously we investigated the properties of the titania–silica-mixed oxide prepared by rapid hydrolysis of the mixture of tetraisopropyl titanate(IV) and tetraethyl orthosilicate (6, 7). The content of Ti in it affects the configuration of Ti: tetrahedral Ti is formed in the silica matrix at low Ti content, while octahedral Ti predominates at high Ti loading. Tetrahedral Ti is responsible for the Lewis acidity due to its coordinatively unsaturated state. It also catalyzes the epoxidation of olefins, in which hydroperoxides are accommodated in its coordination site in the first step of the reaction. Thus the tetrahedral Ti plays an important role in affecting the physical and catalytic properties of the titania–silica. Then a question arises whether the tetrahedral Ti without silica matrix also catalyzes epoxidation or not. This paper deals with the epoxidation activity of Ti's on alumina and in TiO_2 in relation to their configurations.

A known amount of tetraisopropyl titanate(IV) [$Ti(PrO^i)_4$] was dissolved in ethanol containing γ-alumina (TM-300: Taimei Chemical Co.). After ethanol was evaporated, the Ti-loaded alumina was dried at 80°C overnight and was calcined in air at 550°C for 3 h. Ultrafine TiO_2 (IT–S) was obtained from Idemitsu Kosan Co. Epoxidation of oct-1-ene was carried out at 90°C under a nitrogen atmosphere with *t*-butyl hydroperoxide (TBHP) as an oxidant. 1,2-Epoxyoctane was determined by the use of a Shimadzu 3BT gas chromatograph with a Chromosorb 102 column (3 m) at 120°C and, also, according to the hydrochloric acid–pyridine method (7). No other reaction product except for 1,2-epoxyoctane or *t*-butyl alcohol and acetone derived from TBHP was detected by the gas chromatograph. The acid strength of the catalysts was measured in dry benzene by using the following Hammett indicators: methyl red (pK_a 4.8), methyl yellow (pK_a 3.3), benzeneazodiphenylamine (pK_a 1.5), dicinnamalacetone (pK_a −3.0), and benzalacetophenone (pK_a −5.6). XANES spectra were obtained at the beam line 6B and 7C stations of the Photon Factory in the National Laboratory for High Energy Physics (Tsukuba). The details of the experimental procedure were described elsewhere (7).

Figure 1 shows the Ti K-edge XANES spectra of the standard samples. The configuration of the Ti in $Ti(PrO^i)_4$ and Ba_2TiO_4 (8) is tetrahedral, and their spectra have a sharp preedge peak. This peak is due to the forbidden transition from the 1*s* level to the 3*d* level of metal ions and, therefore, becomes stronger as the deviation of the configuration of metal ions from octahedral symmetry increases (9). The preedge peak of commercial TiO_2 (both anatase- and rutile-types) is very small and shows a triplet (10). Both TiO_2 are typical octahedral compounds. Ti in tetra-*n*-butyl titanate(IV) [$Ti(OBu^n)_4$] and $TiFe_2O_5$ is in a five-coordinated state (11, 12), and, thus, the intensity of

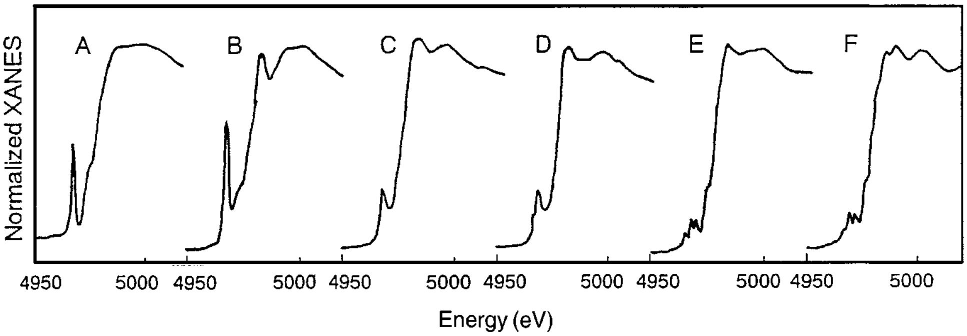

FIG. 1. XANES spectra of the standard samples. (A) Ti $(OPr^i)_4$; (B) Ba_2TiO_4; (C) $Ti(OBu^n)_4$; (D) $TiFe_2O_5$; (E) TiO_2 [anatase]; (F) TiO_2 [rutile].

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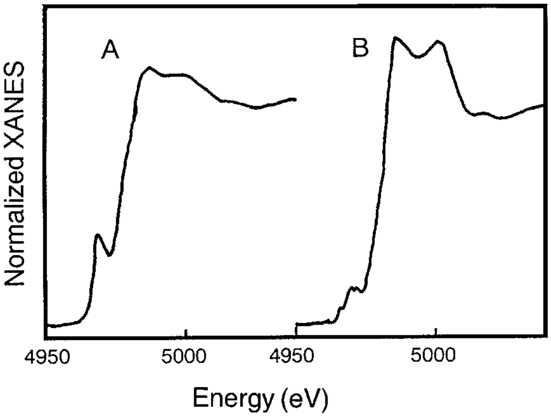

FIG. 2. XANES spectra of (A) ultrafine TiO_2 and (B) ultrafine TiO_2 after calcination at 400°C in air for 3 h.

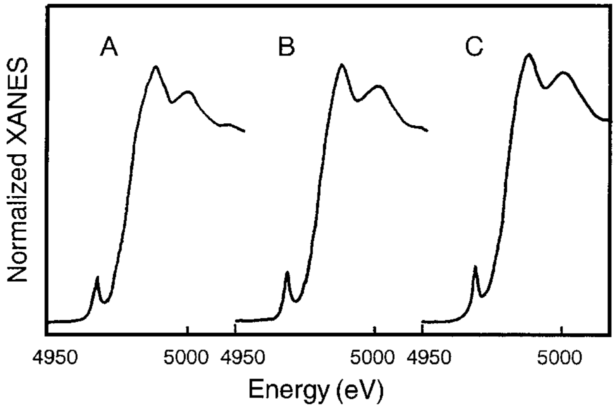

FIG. 3. XANES spectra of Ti supported on γ-Al_2O_3. Ti to Al molar ratio is (A) 2/98, (B) 5/95, and (C) 10/90.

their preedge peaks is between those of tetrahedral Ti and octahedral Ti.

XANES spectra of the ultrafine TiO_2 are shown in Fig. 2. The spectrum of the TiO_2 as obtained has a singlet preedge peak, while the preedge peak of the TiO_2 which was calcined at 400°C in air for 3 h shows a small triplet. The latter is an octahedral TiO_2, while the former has a structure deviated from octahedral symmetry. Ultrafine TiO_2 was prepared by vapor-phase hydrolysis of $Ti(PrO^i)_4$ without calcination at high temperatures (13). Therefore, it is amorphous and its structure will not be octahedral. It seems that the Ti's in ultrafine TiO_2 were mixed with four- and five-coordinated states. Table 1 shows the physical properties and epoxidation activity of ultrafine TiO_2 before and after calcination. The BET surface area decreased after heat treatment at 400°C, indicating that sintering occurred. The TiO_2 without heat treatment catalyzed epoxidation of oct-1-ene, while it lost epoxidation activity after calcination. Thus coordinative unsaturation of Ti is important for this reaction. The acid strength also decreased by heat treatment. Previously we deduced that an unsaturated Ti site which can accommodate an electron pair works as a Lewis acid site. The present result seems to be in accordance with the previous discussion.

XANES spectra of the Ti supported on γ-alumina (with varying Ti content) are shown in Fig. 3. All spectra have a sharp singlet preedge peak, indicating that the Ti is coordinatively unsaturated. The shapes of the XANES spectra resemble that of the five-coordinated Ti in $Ti(OBu^n)_4$ or $TiFe_2O_5$. Thus the Ti on γ-alumina may be five coordinated. All catalysts had epoxidation activity as shown in Table 2. The selectivities, however, were much lower than that with the titania–silica (7). As γ-alumina also has acid sites, the change in the acid nature with the change in the Ti content cannot be discussed now.

The conclusion is that the coordinatively unsaturated site of Ti, which can accommodate hydroperoxides, is responsible for epoxidation activity, irrespective of whether the Ti is combined with silica or other supports or is used alone. The reason why Ti is supported on silica gel in the practical application (14) will be that silica is the best support to maintain tetrahedral Ti with high epoxidation activity.

TABLE 1

Physical Properties and Epoxidation Activity[a] of Ultrafine TiO_2

Catalyst	S_w (m^2/g)	Acid strength	Selectivity[b] (%)	Yield[c] (%)
TiO_2 without calcination	112.2	$1.5 < H_0 \leq 3.3$	31.1	25.0
TiO_2 calcined at 400°C	73.4	$3.3 < H_0 \leq 4.8$	0	0

[a] Catalyst, 0.2 g; oct-1-ene, 10 ml; TBHP, 0.1 *M*, 90 °C; reaction time, 5 h.

[b] Selectivity is defined by the ratio of 1,2-epoxyoctane produced to TBHP decomposed.

[c] Yield is based on the amount of TBHP charged.

TABLE 2

Physical Properties and Epoxidation Activity of Ti-Loaded γ-Al_2O_3[a]

Ti/Al (molar ratio)	S_w (m^2/g)	Acid strength	Selectivity (%)	Yield (%)
2/98	100.6	$-3.0 < H_0 \leq 1.5$	18.9	8.2
5/95	99.8	$-5.6 < H_0 \leq -3.0$	24.3	19.2
10/90	104.5	$-5.6 < H_0 \leq -3.0$	42.8	28.7

[a] Conditions of the epoxidation and the definition of selectivity and yield are the same as described in Table 1.

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