Titanium sites of titania–silica mixed oxides for epoxidation activity and Lewis acidity

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Titania–silica was synthesized by rapid hydrolysis of $Ti(OPr^i)_4$ and $Si(OEt)_4$, and the state of titanium and epoxidation activity of this mixed oxide were investigated. XANES analysis showed that the amount of tetrahedrally coordinated titanium increased with a decrease in the titanium content. The epoxidation activity increased in accordance with the decreased amount of tetrahedral titanium sites. The amount of Lewis acid sites also increased with the decrease in titanium content. Thus the tetrahedral titanium was responsible both for the epoxidation acitivity and the Lewis acidity due to its coordinatively unsaturated nature.

Keywords: titania–silica; tetrahedral Ti; epoxidation; Lewis acidity

1. Introduction

Recently, much attention has been focused on titanium–silicon mixed oxides such as titania–silica and zeolite derivatives containing Ti (titanium silicalite: TS-1 and TS-2). The former is useful as ceramics with high performance and, at the same time, acts as a catalyst having acidic nature and redox property [1–4]. The latter shows interesting catalytic action in oxidation reactions involving hydrogen peroxide [5,6]. Although many works have been carried out to elucidate the microstructure of these titanium–silicon mixed oxides, there still remains ambiguity about the state of Ti [7–11]. Examples of the proposed Ti states for titanium silicalite are isolated Ti with Ti=O bonding [5], tetrahedrally coordinated Ti and octahedral Ti [12], and those for titania–silica are tetrahedral Ti [13], segregated TiO_2 [14], and so on. The cause for the formation of acid sites in titania–silica is also

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controversial. Tanabe et al. proposed that the acidity is produced by a charge imbalance resulting from the difference in the coordination states of Ti^{4+} and Si^{4+} [15], while Nishiwaki et al. reported that decreasing the particle size of TiO_2 resulted in charge imbalance and produced acid sites even in the absence of silica [16].

In this work, the effect of the content of Ti in titania–silica on the state of Ti was investigated in relation to its epoxidation activity and acid property.

2. Experimental

Titania–silica with a known Ti content was prepared by a rapid hydrolysis from a mixture of tetraisopropyl titanate(IV) and tetraethyl orthosilicate. The details of the procedure were described elsewhere [4].

Epoxidation of 1-octene and cyclohexene was carried out under a nitrogen atmosphere at 363 K with *t*-butyl hydroperoxide (TBHP) as an oxidant. Titania–silica (0.2 g) was added to 10 ml of chlorobenzene containing cyclohexene (0.2 M) and TBHP (0.1 M). No solvent was used for the epoxidation of 1-octene (10 ml). 1,2-epoxyoctane was determined with a Shimadzu GC-3BT gas chromatograph (column: Chromosorb 102, 3 m) at 393 K. 1,2-epoxycyclohexane was similarly determined with a column of 20% PEG 20M plus 5% KOH on Celite 545 (3 m). Both epoxides were also determined according to a hydrochloric acid–pyridine method on the basis of the amount of hydrochloric acid consumed by the epoxides [17].

Titania–silica was oxidized with 8 kPa of oxygen at 673 K for 2 h and was sealed into a Q-pack pouch in a dry box for the X-ray absorption measurements on the beam line 6B and 7C stations of the Photon Factory in the National Laboratory for High Energy Physics (Tsukuba). The ring energy and ring current were 2.5 GeV and 150–250 mA, respectively. IR analysis of NH_3 adsorbed on the titania–silica was carried out with a Nihon Denshi JIR-6500W spectrophotometer with a diffuse reflectance attachment. Since no NH_3 adsorption was observed on KBr, titania–silica was diluted with KBr to 5 wt% content for the IR measurements.

3. Results and discussion

Fig. 1 shows the XANES spectra of Ti in titania–silica along with the spectra of standard compounds, tetraisopropyl titanate(IV) and Ba_2TiO_4 (both with tetrahedrally coordinated Ti), and of anatase and rutile TiO_2 (with octahedral Ti). The measurements were carried out by fluorescence mode. A big pre-edge peak appeared for tetrahedral Ti species. The pre-edge feature suggests that titania–silica with a Ti content below 40 mol% mainly contains Ti species with tetrahedral

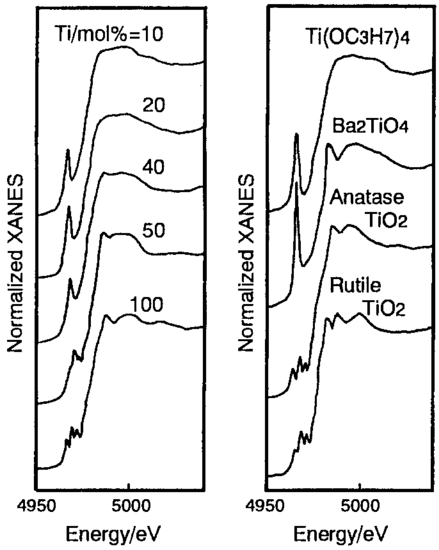

Fig. 1. XANES spectra of titania–silica with different Ti contents (left) and standard compounds (right) measured by fluorescence mode at room temperature. [a]Tetraisopropyl titanate(IV).

configuration, whereas octahedral Ti species predominates above 50 mol% of Ti. The area of pre-edge peak can be a measure for tetrahedral Ti species [1].

Ammonia (3 Torr) was adsorbed on the titania–silica pretreated at 373 K in vacuo to see the nature of its acid site by using an IR technique (fig. 2). No absorp-

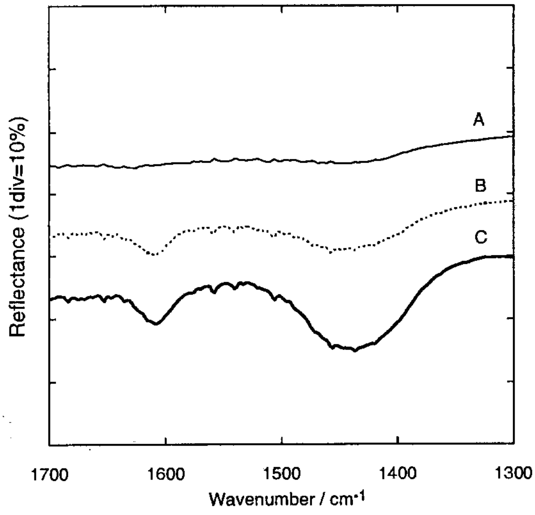

Fig. 2. IR spectra of NH_3 on (A) SiO_2, (B) titania–silica (Ti = 10 mol%) and (C) titania–silica (Ti = 40 mol%) measured at 373 K. Samples (diluted to 5 wt% with KBr) were pre-treated at 373 K under evacuation for 15 min followed by an introduction of 3 Torr of NH_3.

tion band due to NH_3 was observed on SiO_2 itself (fig. 2A), while two bands appeared on the titania–silica. The intensity of these bands increased with an increase in Ti content (compare spectra B and C in fig. 2). The band at 1420 cm^{-1} was ascribed to NH_4^+ species formed from the interaction between NH_3 and Brønsted acid sites [18]. The absorption band at 1605 cm^{-1} may be due to either NH_3 bonded to surface OH groups with hydrogen bonding or NH_3 species adsorbed on Lewis acid sites [19]. As the intensity of this band was found to increase with an increase in the pretreatment temperature (up to 673 K; though not shown in the figure), this band was deduced to be due to NH_3 adsorbed on Lewis acid sites.

Fig. 3 shows the effect of Ti content in the titania–silica on the amounts of tetrahedral Ti species and of Lewis acid sites, and epoxidation selectivity. As the Lewis acidity originated from Ti species, the amount of the Lewis acid sites was reduced per unit amount of surface Ti: the area of the absorption band at 1605 cm^{-1} was divided by the surface amount of Ti measured by an ESCA technique [4]. Thus $Area_{L\,acid}$ (in arbitrary unit) on the ordinate indicates the ratio of the amount of Ti species with Lewis acidity to the total amount of the surface Ti. Epoxidation selectivity was defined by the ratio of the amount of 1,2-epoxyoctane or 1,2-epoxycyclohexane produced to the total amount of TBHP decomposed.

As the Ti content decreases, the amount of tetrahedral Ti species increases and takes a maximum at about 20 mol% of Ti. Greegor et al. reported that Ti ions are located in the octahedral holes produced in the matrix of SiO_2 when the concentration of Ti is very low [1]. This may explain the decrease in the tetrahedral Ti species

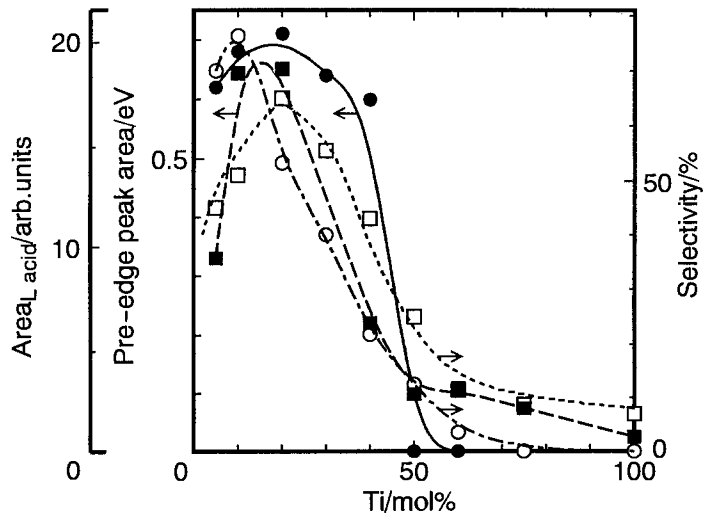

Fig. 3. Effect of Ti content on the physical and catalytic properties of titania–silica. (—●—) amount of tetrahedral Ti species, (— — ■ — —) amount of Lewis acid sites [$Area_{L\,acid}$], (- -□- -) selectivity of 1,2-epoxycyclohexane, (—○—) selectivity of 1,2-epoxyoctane.

at low Ti content (5 mol%). However, details are not known now. Pre-edge peaks of tetrahedral and octahedral Ti could not be separated clearly for 50 mol% of Ti. The amount of tetrahedral Ti species was expediently set as zero for the titania–silica with a Ti content of 50 mol% and above since these XANES spectra were similar to that of anatase TiO_2. Epoxidation selectivities also increase with a decrease in Ti content and take maxima. Especially the maximum point for the selectivity of 1,2-epoxycyclohexane coincides well with that for the amount of tetrahedral Ti species. Epoxidation of olefins proceeds via coordination of hydroperoxides to the vacant sites of metal ions such as W, Mo, V, and Ti in the initial step [20]. Thus the titania–silica with high Ti content in which Ti species has coordinatively saturated octahedral configuration cannot catalyze epoxidation; tetrahedral Ti species in the titania–silica is responsible for the epoxidation reaction.

The amount of Lewis acid sites increases with decreasing Ti content and also takes a maximum in accordance with the curve for the amount of tetrahedral Ti species. This seems to show that Lewis acidity of the titania–silica is also related to the tetrahedral Ti species; coordinatively unsaturated tetrahedral Ti acts as a Lewis acid site. Odenbrand et al. also reported that the tetrahedral Ti species is the site for the Lewis acidity [21]. The cause for the Brønsted acidity is not known. It may be produced by a charge imbalance inside the titania–silica as described before [15]. As moisture seems to remain even after evacuation at 673 K, the Brønsted acid sites (shown by the absorption band at 1420 cm^{-1} in fig. 2) may be partly produced by coordination of water to the tetrahedral Ti species.

In conclusion, both high epoxidation selectivity and Lewis acidity of the titania–silica with low Ti contents are well explained by the presence of tetrahedral Ti species which is of coordinatively unsaturated nature.

The catalytic behavior of titania–silica is different from that of titanium silicalite although they have identical constituents. For example, the latter catalyzes various oxidation reactions in an aqueous phase using hydrogen peroxide as an oxidant, while the former shows no activity in these reactions [22]. The characteristic feature of titanium silicalite may be based on its peculiar Ti–O bonds which reside in the supercage of the zeolitic structure. We are now further investigating the nature of the Ti species in titania–silica in relation to those in titanium silicalite.

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