Effect of the preparation condition on the properties of titania–silica derived from tetraisopropyl titanate(IV) and tetraethyl orthosilicate

Seiichiro Imamura [1], Tohru Nakai, Hiroyoshi Kanai [a], Takeshi Shiono and Kazunori Utani

Department of Chemistry, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606, Japan
[a] *Faculty of Life Science, Kyoto Prefectural University, Shimogamo, Sakyo-ku, Kyoto 606, Japan*

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Titania–silica mixed oxide was prepared by hydrolyzing tetraethyl orthosilicate and tetraisopropyl titanate(IV) with a mixture of ethanol and 0.01 N aqueous acetic acid. Surface Ti content, BET surface area, and the number of acid sites increased with an increase in 0.01 N aqueous acetic acid. Thus hydrolysis of both alkoxides occurred simultaneously with a large amount of the acetic acid solution, and there was extensive interaction between TiO_2 and SiO_2 phases. With small amount of 0.01 N aqueous acetic acid, however, titanium hydroxide was first formed and, then, it was covered with the silica phase produced in a later stage of the hydrolysis. Increase in the acetic acid solution also led to the formation of a large amount of tetrahedral Ti species, which were active for the epoxidation of oct-1-ene using *t*-butyl hydroperoxide as an oxidant.

Keywords: titania–silica; sol–gel method; hydrolysis condition, structure of Ti; epoxidation

1. Introduction

Titania–silica attracts attention both as a ceramic material with superior performance [1] and as a typical acid catalyst [2]. As titania–silica contains Ti, a transitional element, it also shows redox property; we investigated the action of titania–silica in the oxidative decomposition of halogenated organic compounds [3,4] as well as its acid property [5]. The ratio of Ti to Si affects the configuration of Ti in titania–silica prepared by hydrolysis of a mixture of tetraisopropyl titanate(IV) and tetraethyl orthosilicate [6,7]. Tetrahedrally coordinated Ti predominates in the low Ti content region, and it was responsible both for Lewis acidity and epoxidation activity. It is known that the properties of the oxides prepared by a sol–gel method are affected by the condition in which the starting metal alkoxides are hydrolyzed [8]. Thus we investigated the effect of the hydrolyzing condition of the mixture of tetraethyl orthosilicate and tetraisopropyl titanate(IV) on the physical and catalytic properties of the titania–silica produced.

2. Experimental

Titania–silica with 10 mol% of Ti ($Ti/(Ti + Si) = 0.1$ atomic ratio) was prepared as follows. 0.02 mol of tetraisopropyl titanate(IV) and 0.18 mol of tetraethyl orthosilicate were dissolved in 40 ml of ethanol and refluxed at 353 K for 30 min. After the solution was cooled to room temperature, 140 ml of a mixture of ethanol and 0.01 N aqueous acetic acid was added to this solution over ca. 5 min with vigorous stirring. The solution was again refluxed at 353 K for 1 h. The mixture was then kept standing at 353 K until no weight change was observed (ca. 1 week). The titania–silica obtained was calcined at 823 K in air for 3 h.

Epoxidation of oct-1-ene was carried out under a nitrogen atmosphere at 363 K using *t*-butyl hydroperoxide (TBHP) as an oxidant. Titania–silica (0.2 g) was added to 10 ml of oct-1-ene (0.064 mol) in a 50 ml three-necked flask immersed in an oil bath kept at 363 K. The flask was purged with nitrogen and 0.2 ml of a 50 wt% of benzene solution of TBHP was added (TBHP: 0.001 mol). The solution was stirred with a magnetic agitator, and the reaction was followed by analyzing the remaining TBHP and 1,2-epoxyoctane produced. As we wanted to clarify the efficiency of TBHP consumed in the epoxidation of oct-1-ene, the selectivity and yield were based upon TBHP: the selectivity of 1,2-epoxyoctane was defined by the ratio of the epoxide formed to TBHP decomposed, and the yield by the ratio of the epoxide to TBHP charged.

1,2-epoxyoctane was determined by a Shimadzu GC-3BT gas chromatograph with a column of 20% PEG 20 M plus 5% KOH on Celite 545 (3 m) at 393 K. It was also determined according to the hydrochloric acid–pyridine method based upon the amount of hydrochloric acid consumed [9].

The acid strength of titania–silica was measured in dry benzene by using the Hammett indicators: benzeneazodiphenylamine ($pK_a = 1.5$), dicinnamalacetone ($pK_a = -3.0$), and benzalacetophenone ($pK_a = -5.6$). The number of acid sites were determined by titration with *n*-butylamine.

Titania–silica was treated with 8 kPa of oxygen at

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[1] To whom correspondence should be addressed.

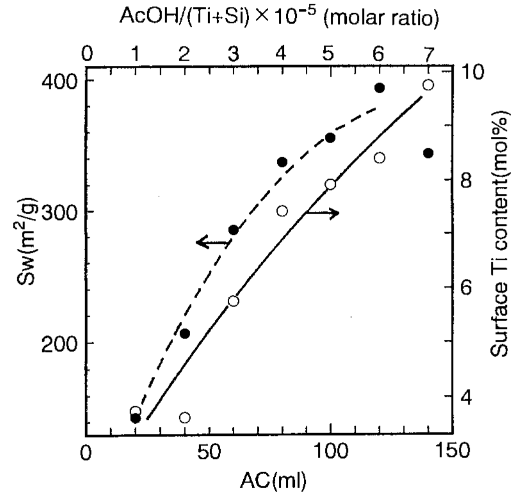

Fig. 1. Effect of the amount of 0.1 N aqueous acetic acid (AC) on the surface Ti-content (○) and BET surface area (●) of titania–silica.

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. ESCA analysis was carried out with a Shimadzu ESCA 750 spectrophotometer.

3. Results and discussion

All experiments described below were performed to explore the effect of the composition of the hydrolyzing agent (0.01 N aqueous acetic acid plus ethanol: total amount of 140 ml) in preparing titania–silica. The 0.01 N aqueous acetic acid is designated as AC hereafter. Fig. 1 exhibits the changes in the surface Ti content measured by an ESCA technique and the BET surface area of titania–silica as a function of the amount of AC. Although 10 mol% of Ti was charged, the surface Ti content was less than 4 mol% below 50 ml of AC (molar ratio of AcOH/(Ti + Si) of 2.5 × 10^{-5}). With an increase in AC, surface Ti increased and reached almost the theoretical value (10 mol%) with 140 ml of AC. The BET surface area also increased with an increment in AC. As alkoxides of Ti are hydrolyzed more easily than those of silicon [10], tetraisopropyl titanate(IV) is hydrolyzed in preference to tetraethyl orthosilicate when the amount of AC is small. Thus the hydrolyzed Ti will be covered with silica phase formed in the later stage, leading to the small surface Ti content. As almost simultaneous hydrolysis of tetraisopropyl titanate(IV) and tetraethyl orthosilicate will occur with a large amount of AC, Ti hydroxide and silicate polymer will be present as charged both in the bulk and at the surface. The SEM images of the titania–silica which were prepared with 20 ml (AcOH/(Ti + Si) = 1 × 10^{-5}) and 120 ml (AcOH/(Ti + Si) = 6 × 10^{-5}) of AC are shown in fig. 2. Fine primary particles aggregate to form secondary particles in the case of 120 ml of AC, while the size of the primary particles of the sample prepared with 20 ml of AC is almost of the same order of magnitude as that of the secondary particles of the former. Simultaneous hydrolysis of both alk-

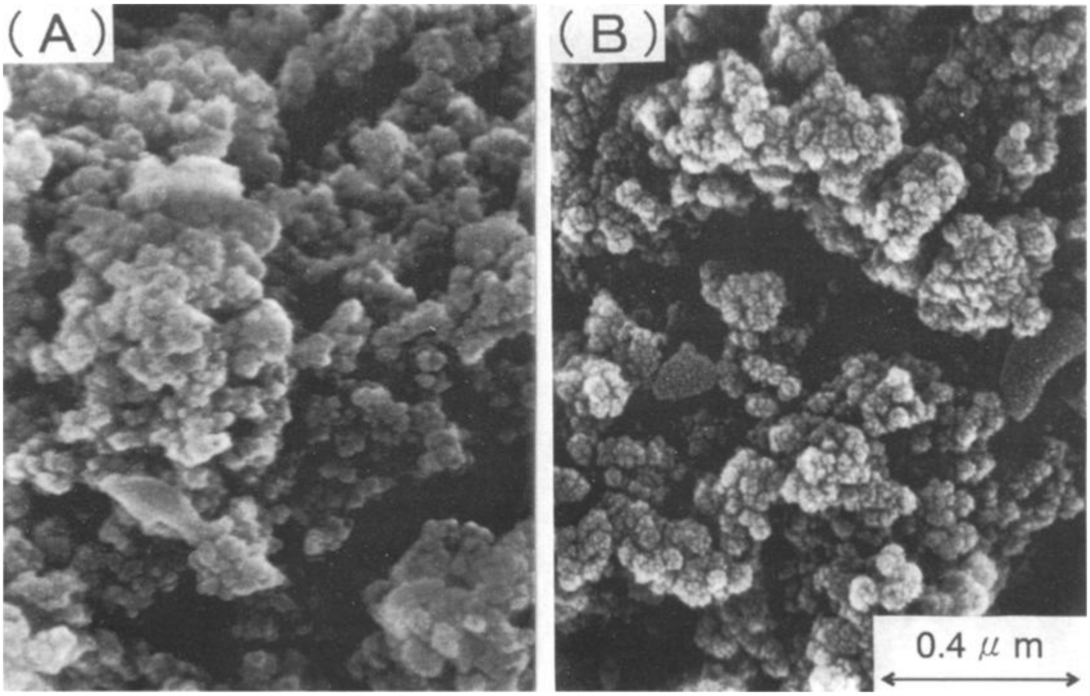

Fig. 2. SEM images of titania–silica prepared with 20 ml (AcOH/(Ti + Si) = 1 × 10^{-5} molar ratio) (A) and 120 ml (AcOH/(Ti + Si) = 6 × 10^{-5} molar ratio) (B) of AC.

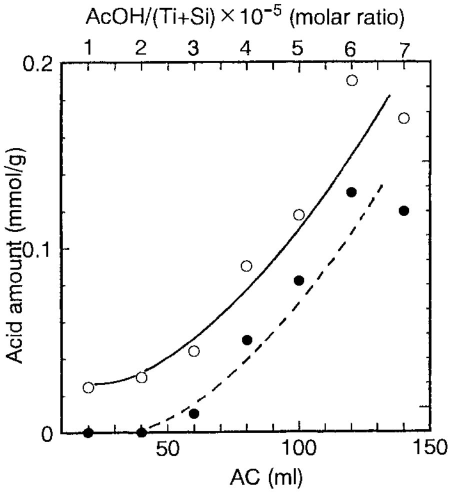

Fig. 3. Effect of the amount of AC on the amount of acid sites. (○) $H_0 \leqslant 1.5$, (●) $-5.6 < H_0 \leqslant -3.0$.

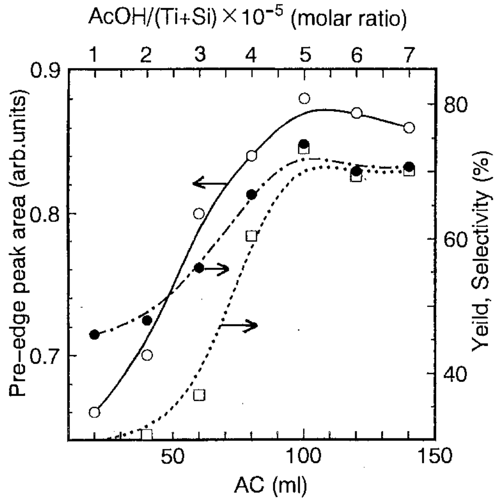

Fig. 5. Effect of the amount of AC on the Ti pre-edge peak intensity (area) and epoxidation activity. (○) Pre-edge peak intensity, (●) selectivity of 1,2-epoxyoctane, (□) yield of 1,2-epoxyoctane. The pre-edge peak intensity is the measure of the amount of tetrahedral Ti [6,7]. Reaction time is 3 h. Selectivity is defined by the ratio of 1,2-epoxyoctane produced to TBHP decomposed, and yield by the ratio of 1,2-epoxyoctane to TBHP charged (see experimental section).

oxides with a large amount of AC will lead to the extensive interaction between SiO_2 and TiO_2 throughout the mixed oxide, resulting in the formation of fine particles with large surface area. With a small amount of AC the silica phase will slowly grow over TiO_2 which is formed first, producing large particles.

The highest acid strength of the titania–silica as expressed by the Hammett acidity coefficient (H_0) was 1.5 for 20 and 40 ml of AC, and −3.0 for 60 ml of AC and above. The number of acid sites, as shown in fig. 3, increased with an increase in AC, which can be explained by the increased surface Ti content (fig. 1); the acid sites of mixed oxides are originated from the interaction between the different elements in the oxides [11].

XANES spectra of Ti K-edge of the titania–silica were observed (fig. 4). The noted feature is the change in the intensity of the pre-edge peak with the change in the amount of AC. This absorption peak is due to a transition from the 1s level to the 3d level of metal ions. Although the transition is formally forbidden, an asymmetrical configuration of metal ion allows it. Thus the intensity (area) of the peak increases with an increase in the deviation of the configuration of metal ions from octahedral symmetry [12]. Previously we found that the intensity of this pre-edge peak can be a measure of the amount of tetrahedrally coordinated Ti species [6,7]. Thus we measured the intensity of the pre-edge peak (amount of tetrahedral Ti) as a function of AC (fig. 5). Tetrahedral Ti increases with an increase in AC to 100 ml and becomes almost constant hereafter. Tetrahedral Ti is active for the epoxidation of olefins due to its unsaturated coordination sites which can accommodate hydroperoxides (oxidants) [7]. In fig. 5 is also shown the activity of the titania–silica in the epoxidation of oct-1-ene. Fair correlation exists between the amount of tetrahedral Ti and the epoxidation activity with respect to both yield and selectivity of 1,2-epoxyoctane.

The increase in the acid amount with an increase in AC was explained by the surface Ti increment as

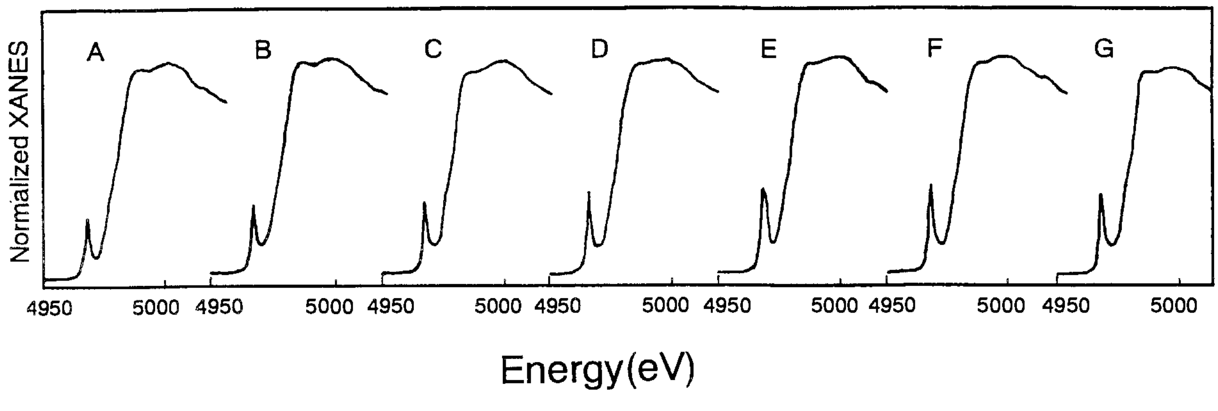

Fig. 4. Effect of the amount of AC on the XANES spectra of the Ti-K edge of titania–silica. Amount of AC (ml): (A) 20, (B) 40, (C) 60, (D) 80, (E) 100, (F) 120, and (G) 140.

described before. However, as tetrahedral Ti, which can accommodate an electron pair, functions as Lewis acid site [6,7], the acid site increment may be also explained by the increase in the amount of tetrahedral Ti.

In conclusion, rapid hydrolysis with a large amount of aqueous acetic acid is important to fully utilize the function of Ti in the titania–silica catalyst. This situation is different from the ordinary sol–gel procedure to obtain high performance titania–silica ceramic materials in which Ti and Si are homogeneously mixed at atomic levels.

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