Surface characterization of titania–silica composite oxides prepared by rapid hydrolysis

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Abstract

The surface structures of TiO_2–SiO_2 composite oxides prepared by rapid hydrolysis were characterized by an ESR technique. The g_{zz} value of O_2^- adsorbed on titanium oxides gave a good indication for discriminating between tetrahedral and octahedral Ti sites. The tetrahedral Ti sites which predominates on the surface of low-loaded TiO_2–SiO_2 is closely related to the selectivity in the epoxidation of 1-octene with *tert*-butyl hydroperoxide catalyzed by TiO_2–SiO_2 composite oxides. © 1998 Elsevier Science B.V.

1. Introduction

Selectivity in catalysis is closely related to the special structural sites of catalyst surfaces [1,2]. TiO_2–SiO_2 composite oxides and titanium silicalites have attracted much attention in terms of their selective oxidation activities [3–8]. Tetrahedral titanium sites in TiO_2–SiO_2 composite oxides and titanium silicalite are proposed to be active for epoxidation of olefins with *tert*-butyl hydroperoxide and hydrogen peroxide, respec-

tively, but octahedral ones are not [9]. There are many methods for the characterization of catalyst structures [10,11]. We have reported that XAFS of TiO_2 gave a clue to the elucidation of its local structure [8,12]. However, XAFS data include information of bulk and surface structures. We have tried to clarify the surface structures of TiO_2–SiO_2 composite oxides by an ESR technique. Some ESR studies on the adsorbed oxygen species on titania which were assigned as O_2^- [13–18] suggested that triplet *g* values of O_2^- were dependent on the structure of titania [13]. We have found that the g_{zz} value ranged from 2.021 to 2.018 is a reliable indication for the surface structure of TiO_2–SiO_2 composite oxides.

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2. Experimental

2.1. Preparation of TiO_2–SiO_2 composite oxides

The TiO_2–SiO_2 composite oxides (Ti/Si(mol ratio) = 5/95–75/25) were prepared by hydrolysis of $Ti(OPr^i)_4$ and $Si(OEt)_4$ with a mixture of ethanol–0.01 N aqueous acetic acid followed by calcination at 823 K as described in the previous paper [8].

2.2. ESR measurements

The composite oxide (ca. 100 mg) in an ESR tube was heated in an O_2 atmosphere (8 kPa) at 673 K for an hour followed by evacuation at the same temperature for 2 h. After cooling to room temperature oxygen (8 kPa) was admitted for 5 min. Oxygen was evacuated and an ESR measurement was carried out at room temperature with JEOL TE-300 and ES-PRIT 425 spectrometers equipped with an Mn^{2+} marker and a variable temperature equipment. Oxygen enriched to 85.4 at% of ^{17}O was obtained from Isotec.

2.3. Thermal stability of active oxygen species

After active oxygen species on TiO_2–SiO_2 were produced, an ESR tube kept in the ESR cavity was warmed to a fixed temperature. The tube was kept standing for 2 min and an ESR spectrum was obtained in situ at the temperature. Then heating and ESR measurement were successively continued in the cavity.

2.4. Oxidation of 1-octene with t-butyl hydroperoxide (TBHP) in the presence of TiO_2–SiO_2

Epoxidation of 1-octene was carried out under an N_2 atmosphere at 363 K. TiO_2–SiO_2 (0.2 g) was added to 1-octene (10 ml) in a 50 ml three-necked flask followed by addition of TBHP (10 mmol, 0.2 ml of a 50 wt%-benzene solution). The solution was stirred with a magnetic stirrer for 6 h. The concentrations of TBHP and 1,2-epoxyoctane were determined by the methods described earlier [8].

3. Results and discussion

3.1. ESR spectra of O_2^- adsorbed on TiO_2–SiO_2 composite oxides

The XAFS study has shown that main titanium sites in 5/95 (mol ratio) TiO_2–SiO_2 were tetrahedral, while those in 75/25 TiO_2–SiO_2
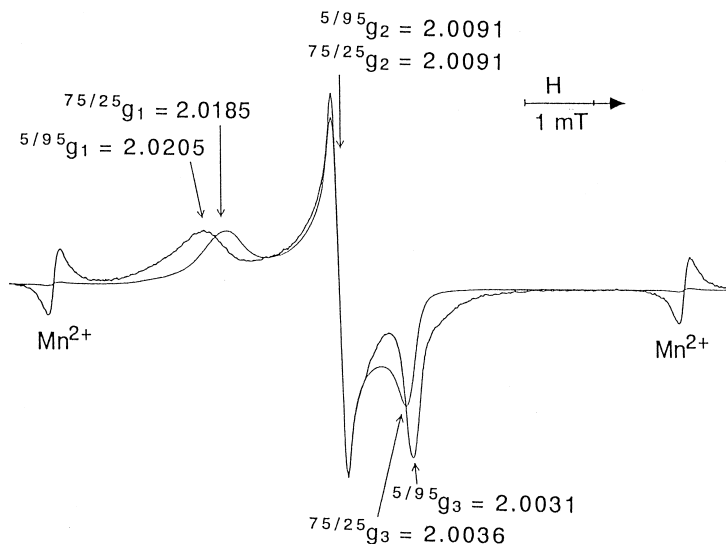

Fig. 1. ESR spectra of O_2^- adsorbed on 5/95 and 75/25 TiO_2–SiO_2 composite oxides at room temperature.

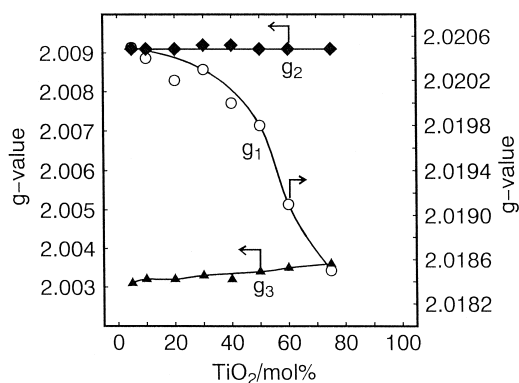Fig. 2. Plots of g values vs. Ti content.

were octahedral [8]. Titanium ions of TiO_2–SiO_2 oxides prepared by the modified sol–gel method are present on the surface and in the bulk. The exact structure of the surface is virtually different from that of the bulk [10,11]. Fluorescence XAFS is reflected not only from the surface structures but from those in the depth of hundreds nm from the surface. We want to know their exact surface structures in relevance to the catalysis. ESR technique is not everything for the surface characterization, but we have ob-

served that ESR active species, O_2^- on Ti sites, were taken as a probe for surface discrimination. There have been reported many preparation methods for O_2^- species, but we adopted the procedure as described in the literature [19]. When composite oxides were heated in vacuo at 673 K, no signals of Ti^{3+} species were observed at room temperature and 77 K. At 77 K a broad signal assigned to an F center was observed [20]. When these oxides were treated with oxygen at room temperature, triplet signals assigned to O_2^- species [13–17] were produced (Fig. 1). The g values are designated as g_1, g_2, and g_3 in the order of appearing from the low magnetic field. They are 2.0205, 2.0091, 2.0031 for 5/95 TiO_2–SiO_2, and 2.0185, 2.0091, 2.0036 for 75/25 TiO_2–SiO_2, respectively.

Each g value is plotted against titanium content (Fig. 2). No difference was observed between g_2 values. The g_3 value increases very slightly with an increase in Ti content. The g_1 value changes remarkably. They decrease monotonously with the increase in the Ti content. The g_1 and g_3 values are always repro-
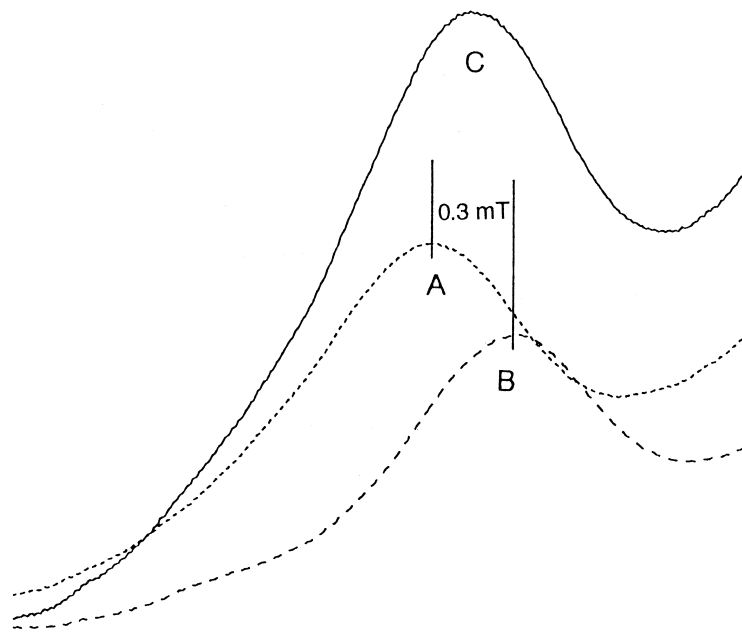

Fig. 3. ESR spectra of g_1 region. (A) 5/95 TiO_2–SiO_2, (B) 75/25 TiO_2–SiO_2, (C) (A) + (B).

ducible for each composite oxide. The tendency of the change in the g_1 value resembles the change of XANES pre-edge peak area in the low region of Ti content [8]. However, the areas above 50 mol% of Ti were estimated zero since bulk structures of anatase TiO_2 predominate to make the peak separation difficult.

There are some differences between g values, especially g_1 values measured at room temperature and 77 K [21]. Even at 77 K we only observed a set of g values for O_2^- species (2.0217, 2.0099, 2.0038 for 5/95 TiO_2–SiO_2, 2.0206, 2.0100, 2.0041 for 75/25 TiO_2–SiO_2). The tendency of the variation in g_1 values at 77

K with Ti content is parallel to that at room temperature.

The different g_1 value definitely indicates the different surface structure. The stable structure of TiO_2 is octahedral anatase or rutile [22]. It is reasonably assigned that the surface of 75/25 TiO_2–SiO_2 is composed of octahedral TiO_2 in accordance with the bulk structure. Taking into account the difference of g_1 values the surface structure of 5/95 TiO_2–SiO_2 should be tetrahedral. The g_1 value gives a good indication for the evaluation of the surface structure of titanium sites in TiO_2–SiO_2. The simulation gave a conclusion that a mixture of octahedral
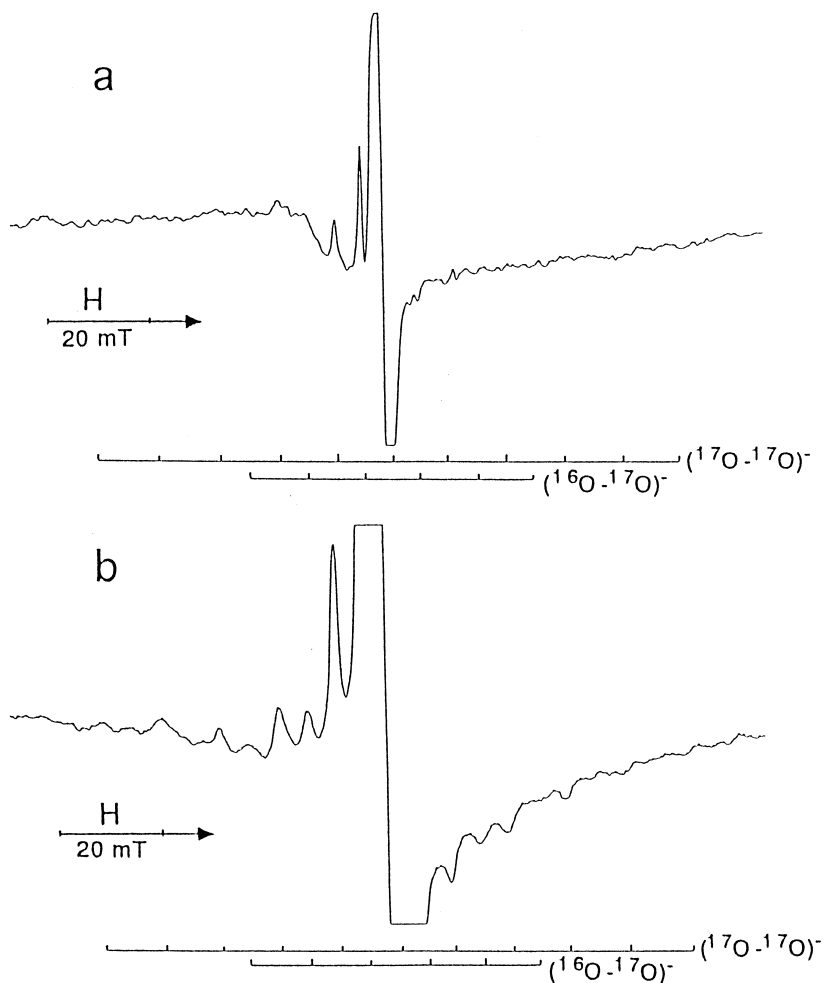

Fig. 4. ESR spectra of $^{17}O_2^-$ and $^{16}O^{17}O^-$ on 5/95 and 75/25 TiO_2–SiO_2 composite oxides at room temperature.

and tetrahedral TiO$_2$ makes the g_1 value into a weighted average since the line widths are too wide for the two species to be separated (Fig. 3). The intermediate g_1 values between 2.0185 and 2.0205 indicate the mixing of tetrahedral and octahedral structures of Ti sites.

Oxygen is adsorbed almost parallel but slightly tilted to the surface of TiO$_2$ [21] which we have confirmed by using $^{17}O_2$ as was shown by Naccache et al. [23] (Fig. 4). Thus the hyperfine pattern consists of six and eleven lines centered at $g_3 = 2.003$ with a hyperfine splitting equal to 7.71 (7.46) and 7.32 (6.80) mT for $^{17}O_2^-$ ($^{16}O^{17}O^-$) on tetrahedral and octahedral TiO$_2$, respectively. Thus, total spin density of oxygen on tetrahedral TiO$_2$ is higher than that on octahedral TiO$_2$. This result coincides with the order in spin density by molecular orbital calculation [24].

Kanzig and Cohen expressed g values assuming an ionic model as follows [25]:

$$g_{xx} = g_e \tag{1}$$

$$g_{yy} = g_e + 2\lambda/E \tag{2}$$

$$g_{zz} = g_e + 2\lambda/\Delta \tag{3}$$

where λ is the spin–orbit coupling constant of oxygen usually taken as 135 cm^{-1}, and E the separation between the energies of σ_{gz} and π_{gx} anti-bonding orbitals, and Δ is that between two π_g anti-bonding orbitals split caused by the crystal field of Ti^{4+} ion onto which O$_2^-$ is
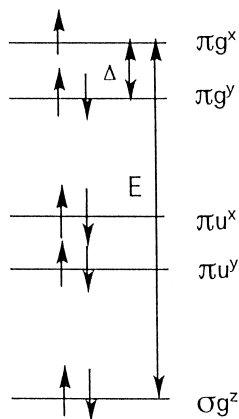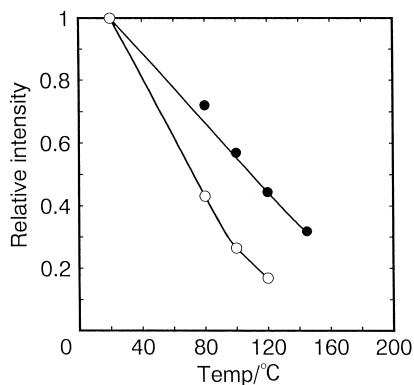

Fig. 5. Simplified energy level diagram for O$_2^-$.

Fig. 6. Change of ESR signal intensities of O$_2^-$ with heat-treatment. (●) 5/95 TiO$_2$–SiO$_2$, (○) 75/25 TiO$_2$–SiO$_2$.

adsorbed (Fig. 5). Therefore, the tentatively designated g_1, g_2, and g_3 correspond to g_{zz}, g_{yy}, and g_{xx}, respectively. Applying the experimental data at 77 K into Eq. (3), we evaluated Δ to be 1.66 and 1.83 eV for tetrahedral and octahedral TiO$_2$, respectively.

3.2. Reactivity of O$_2^-$ adsorbed on tetrahedral and octahedral TiO$_2$

The reactivity of O$_2^-$ was examined by heat treatment (Fig. 6) and reaction with CO. The O$_2^-$ species on 5/95 TiO$_2$–SiO$_2$ was gradually decayed with heat-treatment up to 145°C and those on 75/25 TiO$_2$–SiO$_2$ was rapidly decomposed. The thermal stability of O$_2^-$ on tetrahedral sites of TiO$_2$ is greater than that on octahedral ones. The tendency is parallel to the Δ values in Fig. 5: anti-bonding π_g^x energy level of O$_2^-$ on tetrahedral sites, singly occupied molecular orbital, might be lower than that on octahedral ones [24].

When heat-treatment was carried out in a CO atmosphere, no change was observed in the rate of disappearance of O$_2^-$ signals. No reaction of CO with O$_2^-$ occurred up to 180°C over tetrahedral and octahedral sites of Ti. Neither O$_2^-$ species on tetrahedral TiO$_2$ nor those on octahedral TiO$_2$ are active for CO oxidation. Antibonding π_g^x and π_g^y orbitals are degenerated. Once electron is introduced into O$_2$, the orbitals

are separated by Δ (Fig. 5). The larger the magnitude of Δ is, the stronger the interaction between O_2 and metal ions becomes. Their moderate stability O_2^- species on TiO_2 is led by their relatively large Δ due to the crystal field interaction.

With heat-treatment the g_1 values shift to higher values for 75/25 TiO_2–SiO_2, and to lower values for 5/95 TiO_2–SiO_2 (Fig. 7). The shift in 5/95 TiO_2–SiO_2 was found to be due to the measurement at high temperature. The re-measurement at room temperature gave the g_1 value of 2.021. The shift in 75/25 TiO_2–SiO_2 is based on the fact that O_2^- species on octahedral TiO_2 were decayed more rapidly than those on tetrahedral TiO_2. Thus, most titanium sites in 75/25 TiO_2–SiO_2 are octahedral ones mixed with a small amount of tetrahedral structure, which is supported by a break at 100°C in Fig. 6.

A good correlation is observed between the g_{zz} value and epoxidation selectivity of 1-octene (Fig. 8). The XANES pre-edge peak area is also plotted. Since pre-edge peak areas above 50 mol% of Ti are zero, the correlation between the XANES pre-edge peak area and epoxidation selectivity is worse at the high Ti content. Surface tetrahedral titanium sites in TiO_2–SiO_2 are surely active species for the epoxidation of 1-octene with *tert*-butyl hydroperoxide. Photooxi-
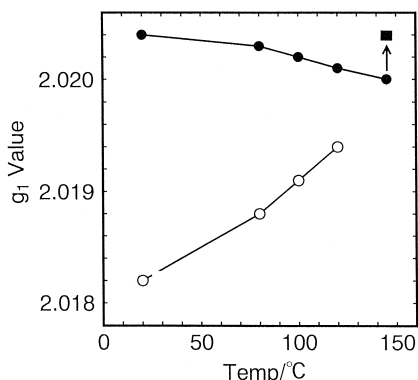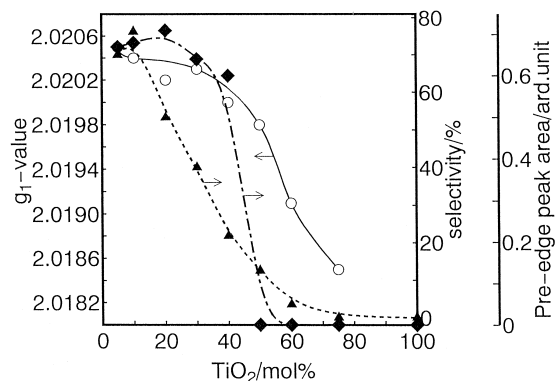
Fig. 8. Plots of g_1 value, XANES pre-edge peak area, and selectivity in the 1-octene epoxidation vs. Ti content. ($\bigcirc$) g_1 value, ($\blacklozenge$) pre-edge peak area, ($\blacktriangle$) selectivity.

dation of propene with oxygen over 5/95 TiO_2–SiO_2 gave propene oxide, but no propene oxide was formed over 75/25 TiO_2–SiO_2 [26]. It can be deduced that active sites in TiO_2 for epoxidation are tetrahedral ones.

Synchrotron radiation is not freely available at present, but ESR spectrometers are commonly used in laboratories. We have demonstrated that O_2^- species formed on the surfaces of TiO_2–SiO_2 can be a probe for surface characterization and selectivity in catalysis. Anpo et al. proposed that g values of Ti^{3+} ions in titania gave a suitable indication for discriminating tetrahedral and octahedral Ti sites [27]. We recommend that ESR signals of O_2^- produced by O_2 adsorption on heat-treated TiO_2 are also a good measure for discriminating them.

Fig. 7. Change of g_1 values with heat-treatment. ($\bullet$) 5/95 TiO_2–SiO_2, ($\bigcirc$) 75/25 Ti_O2–SiO_2. ($\blacksquare$) Measured after cooling to room temperature.

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