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Catalytic Sites on SnO_2 and TiO_2–SnO_2 for the Isomerization of 1-Butene

MASAYOSHI ITOH, HIDESHI HATTORI, AND KOZO TANABE

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060, Japan

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The nature of active sites for the isomerization of 1-butene on SnO_2 and TiO_2–SnO_2 with various treatments has been studied.

Over SnO_2 evacuated at 400–600°C, a highly selective isomerization of 1-butene to *cis*-2-butene was observed (*cis-/trans*-2-butene ≈ 19). Paramagnetic centers having a g value of 1.900 (probably Sn^{3+}) observed on the surface are capable of transferring an electron to O_2 or nitrobenzene to form anion radicals. The changes in the isomerization activity, the number of paramagnetic centers, and the electron conductivity vs evacuation temperature were similar to one another. In addition, all of them were decreased by the treatment with O_2 or nitrobenzene. It is suggested that the selective isomerization of 1-butene to *cis*-2-butene takes place on the paramagnetic centers of $g = 1.900$ which have reducing character.

No paramagnetic centers of $g = 1.900$ or $g = 1.940$ (Ti^{3+}) were observed on TiO_2–SnO_2 which had been evacuated at 500°C, whereas strong acid sites of $H_0 \leqq -3.0$ were generated. The ratio of *cis*- to *trans*-2-butene in the isomerization of 1-butene over TiO_2–SnO_2 of compositions (9:1) or (1:9) was smaller than that for TiO_2 or SnO_2, respectively. It is presumed that the acid sites take part in the isomerization of 1-butene over TiO_2–SnO_2.

INTRODUCTION

Studies on the isomerization of butenes over TiO_2 (*1, 2*) and ZrO_2 (*3*), which are oxides of the elements in group IVb, have been previously reported from our laboratory. These oxides showed high ratios of *cis*-2-butene to *trans*-2-butene in the isomerization of 1-butene; the initial ratios of *cis-/trans*-2-butene were much higher than 1. In the case of TiO_2, Ti^{3+} with an electron donating character was created by a reduction of the surface and the amount of Ti^{3+} was well correlated with the isomerization activity against the evacuation temperature. Recently, a similar correlation has been found to exist between the concentration of electron donors and the 1-butene isomerization rate over MgO (*4*), and amorphous Al_2O_3 (*5*).

The isomerization and the dehydrogenation of butenes over SnO_2 which is an oxide of the element in group IVa have been studied by some investigators. Kemball *et al.* (*6*) reported, in a study of the interaction of *n*-butenes with SnO_2 prepared from reaction of tin with nitric acid, that the isomerization of 1-butene occurred readily at ca. 30°C (with a *cis–trans* product ratio of 1–2) and a large amount of 1,3-butadiene was formed. In the isomerization of *cis*-2-butene, exclusive *cis–trans* isomerization was observed with no detectable formation of 1-butene or 1,3-butadiene. Other workers (*7–9*) have also investigated the dehydrogenation of 1-butene to 1,3-butadiene and the isomerization of 1-butene (*cis-/trans-* = 1–2) over SnO_2. However, the nature of active sites has not been examined so extensively.

In the present work we have attempted to elucidate the nature of active sites for the isomerization of 1-butene over SnO_2 by measuring the changes in the surface properties with various treatments of the catalyst combined with the kinetic measurements. The 1-butene isomerization has also been studied over TiO_2–SnO_2 having different molar ratios of Ti/Sn.

EXPERIMENTAL METHODS

Catalyst Preparation

SnO_2(I) was obtained by drying the precipitate of stannic hydroxide at 100°C for 2 days in air. The precipitate was prepared by adding aqueous ammonia to aqueous solution of stannic chloride, followed by aging at 100°C over a water bath for 2 hr and washing with distilled water until no chloride ion was detected. SnO_2(II) was commercial SnO_2 from Kanto Chemical Co. SnO was prepared from stannous chloride by the same way as in SnO_2(I), except that the precipitate was dried at room temperature.

The TiO_2–SnO_2 with different molar ratios of Ti to Si were obtained by drying the coprecipitated mixtures of titanic acid and stannic hydroxide at 100°C for 2 days. The coprecipitated mixtures were prepared by hydrolysis of the mixed solution of titanium tetrachloride and stannic chloride with aqueous ammonia, followed by aging and washing similarly as in SnO_2(I). TiO_2 was prepared from titanium tetrachloride, which was named TiO_2(I) in the previous paper (*1*).

These catalysts were evacuated at 200–800°C for 3 hr or treated with various gases after evacuation at 500°C prior to the reaction or measurements of surface properties.

Surface Area and X-Ray Analysis

A specific surface area was determined by applying BET equation to the adsorption isotherm of nitrogen at −196°C. X-Ray diffraction patterns were measured over the range of $2\theta = 20$–$70°$ for the powdered samples of SnO_2(I) evacuated at various temperatures and TiO_2–SnO_2 calcined in air at 500°C.

Acidic Property Measurement

Acidic properties of TiO_2–SnO_2, SnO_2(I) and TiO_2 calcined in air at 500°C for 3 hr were measured by titration with *n*-butylamine in benzene according to the Johnson's method (*10*), the indicators of different pK_a values being used.

Reaction Procedure

A closed recirculation reactor having a volume of about 850 ml was used for kinetic measurement. A 0.5 g of catalyst was placed in a reactor with quartz tips and evacuated for 3 hr at various temperatures. A fresh sample was used for each run. After cooling to 200°C, 100 Torr (1 Torr = 133.3 N m^{-2}) of 1-butene was introduced and the reaction products were analyzed periodically by gas chromatography. Propylene carbonate (30 wt%) on 30–60 mesh Uniport C was used for the packing in a 4-m chromatographic column which was maintained at 0°C.

In poisoning experiments, the catalyst was evacuated at 500°C and exposed to NH_3, CO_2, H_2O, 1,3-butadiene or nitrobenzene at reaction temperature for 30 min except for nitrobenzene (at room temperature), and then evacuated at the same temperature for 30 min. In some experiments, the catalyst which had been evacuated at 500°C was exposed to 93 Torr of H_2 at 500°C or to 53 Torr of O_2 at 200°C followed by evacuation at the same temperatures.

1-Butene was purified by passing through a zeolum F-9 (synthetic zeolite from Tekkosha; its structure and composition are the same as 13X) kept at dry ice temperature and distilled before use.

An activity was expressed by mole percentage of the product at 2 min of a reaction time per unit weight of catalyst (g^{-1}) per unit time (min^{-1}).

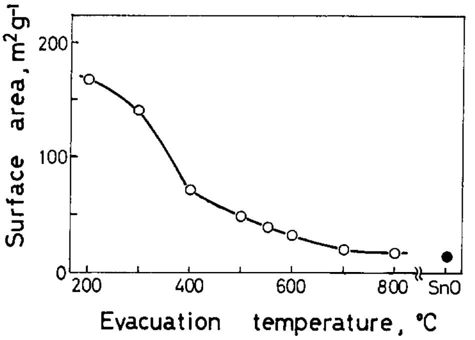

FIG. 1. Specific surface areas of SnO_2(I) (○—) evacuated at various temperatures and SnO (●—) evacuated at 500°C.

ESR Measurement

Each 50 mg of samples in ESR cells was evacuated at various temperatures for 3 hr. ESR spectra of these samples were measured at both room temperature and −196°C, and then the samples were exposed to O_2 or nitrobenzene vapor through breakable seals for 10 min or 2 days, respectively, at room temperature. Excess nitrobenzene was trapped by liquid nitrogen. These samples were subjected to ESR measurement at room temperature again. In some experiments, the sample which had been evacuated at 500°C was treated with 1-butene, 1,3-butadiene or H_2O at 200°C.

All ESR measurements were performed on a Japan Electron Optics X-band spectrometer (JES-ME-3X). A g value and relative amount of radicals were determined by referring to the signal of Mn^{2+} as a standard.

Conductivity Measurements

Electrical resistance was measured for a circular pellet of 11 mm in diameter and 1–2 mm in thickness. The pellet held by compression between two platinum electrodes was evacuated for 3 hr at 200°C and a resistance was measured in a vacuum at 200°C on a 1.5–8 Vdc bridge with a detector consisting of an amplifier. Then, the same pellet was heated up to 300°C in a vacuum and kept at this temperature for 3 hr. After cooling to 200°C, a resistance was measured. These procedures were repeated every 100°C increment up to 800°C. In some experiments, the conductivity was measured after the admission of O_2 or nitrobenzene at room temperature to the catalyst which had been evacuated at 500°C.

RESULTS

(A) SnO_2

Surface Area and X-Ray Analysis

Specific surface areas of SnO_2(I) evacuated at various temperatures and SnO evacuated at 500°C are shown in Fig. 1. The value decreased gradually with the rise of evacuating temperature.

The X-ray diffraction pattern of SnO_2(I) evacuated at 200–1000°C was assigned to be only that of tetragonal SnO_2. The peak intensity increased and peak narrowing occurred concurrently as the pretreatment temperature was raised. Any diffraction pattern of SnO or Sn was not detected even when SnO_2(I) was evacuated at 1000°C.

Isomerization of 1-*Butene*

Mole percentages of the reaction products over SnO_2(I) evacuated at 500°C vs reaction time are shown in Fig. 2. The variations of the activities for the isomerization and the formation of 1,3-butadiene and the ratio of *cis*-2-butene to *trans*-2-butene over SnO_2(I) are plotted as a function of evacuation temperature in Fig. 3. When the catalyst was evacuated at 400–600°C, the activity and the ratio of *cis*-2-butene to *trans*-2-butene were high; the activity for the isomerization to *cis*-2-butene was greatly increased in that range, though the amount of *trans*-2-butene was almost constant over the all range of evacuation temperature. Since the *cis*-/*trans*- ratio increased progressively at the initial stage of the reaction and then decreased as the reaction proceeded over SnO_2(I) which had been evacuated at 400–600°C, the maximum values of the ratios were plotted in Fig. 3. Below 600°C, a small amount of 1,3-butadiene was detected in addition to *cis*-2-butene and *trans*-2-butene. In this region, the reaction rate decreased considerably after 2–5 min of the reaction time, as is shown in Fig. 2.

The results of various treatments of the catalyst evacuated at 500°C are listed in Table 1. Treatment with O_2, nitrobenzene, 1,3-butadiene, H_2O or NH_3 caused decreases in the activity for the isomerization, the ratio of *cis*-2-butene to *trans*-2-butene, and the activity for the formation of 1,3-butadiene. The adsorption of CO_2 did not affect the activities. When SnO_2(I) was exposed to H_2 at 500°C, a great decrease in pressure of H_2 was observed, which was caused by reduction of SnO_2(I) to SnO. Two kinds of SnO, which were obtained from reduction of SnO_2(I) by H_2 and prepared from $SnCl_2$, had little catalytic activity for the isomerization and no activity for the formation of 1,3-butadiene.

The activities of SnO_2(II) evacuated at 500°C and SnO_2(I) calcined in air at 500°C before being evacuated at 500°C were much less than that of SnO_2(I) evacuated at 500°C.

ESR Spectra

SnO_2(I) evacuated at 500°C showed a broad signal (6×10^{17} spins g^{-1}, $g = 1.900$) at room temperature as shown in Fig. 4. As a small g value of this signal compared to that of free electron indicates a strong spin–orbit coupling, the paramagnetic centers are probably Sn^{3+} ions ($4d^{10}5s^1 \rightarrow 4d^9 5s^2$) (*7*).

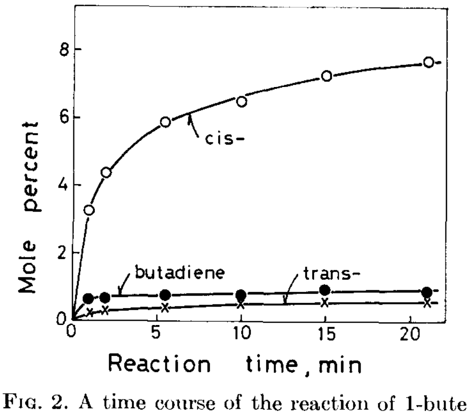

FIG. 2. A time course of the reaction of 1-butene over SnO_2(I) evacuated at 500°C.

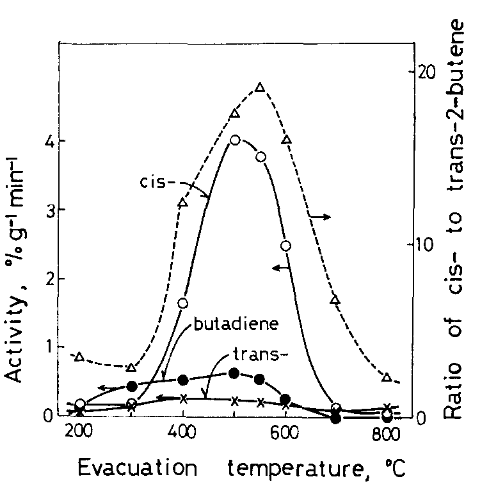

FIG. 3. Dependencies of the activity and the ratio of *cis-/trans*-2-butene on the evacuation temperature in the isomerization and the dehydrogenation of 1-butene over SnO_2(I).

On exposure to O_2, the intensity of the signal at $g = 1.900$ decreased, and a strong signal of O_2^- (*11–13*) appeared simultaneously. On exposure to nitrobenzene, nitrobenzene anion radicals (*14*) were produced and the signal at $g = 1.900$ disappeared. These facts indicate that the paramagnetic centers are electron donating sites and most of them are located on the surface of SnO_2(I).

The relative signal intensities of O_2^-, nitrobenzene anion radicals and the paramagnetic centers before and after the exposure to O_2 or nitrobenzene are plotted against evacuation temperatures in Fig. 5. A good correlation is observed between the amount of the paramagnetic centers before the exposure to O_2 or nitrobenzene and the activity for the isomerization of 1-butene to *cis*-2-butene. The amounts of radicals on SnO evacuated at 500°C are also shown in Fig. 5. On exposure to 1,3-butadiene or H_2O, the signal at $g = 1.900$ almost disappeared.

TABLE 1

Changes in the Activity and the Selectivity for the Isomerization and the Dehydrogenation of 1-Butene with Various Treatments[a]

Catalyst	Treating material	Treating temp (°C)	Desorption temp (°C)	Activity for isomerization (% g^{-1} min^{-1})	Ratio of *cis/trans*	Activity for formation of 1,3-butadiene (% g^{-1} min^{-1})
SnO_2 (I)	Untreated	—	—	4.25	17.5	0.61
	O_2	200	200	0.96	8.9	0.32
	Nitrobenzene	25	25	0	—	0
	1,3-Butadiene	200	200	0.46	7.0	0.13
	H_2O	200	200	0.19	5.0	0
	NH_3	200	200	0.21	2.7	0.14
	CO_2	200	200	3.91	16.3	0.61
	H_2	500	500	0.09	—	0
	Air	500	500	1.50	20	0.21
SnO_2 (II)	Untreated	—	—	1.61	20	0.43
SnO	Untreated	—	—	0.03	—	0

[a] All catalysts (except one which was treated with air) had been evacuated at 500°C.

When SnO_2(I) evacuated at 500°C was exposed to 1-butene at 200°C, the paramagnetic centers disappeared after 15 min of contact time, at which the formation of *cis*-2-butene almost stopped (see Fig. 2). This also indicates that the paramagnetic centers participate in the isomerization to *cis*-2-butene. On exposure to 1-butene, a new symmetrical ESR signal ($g = 2.002$, line width 8 G) appeared with disappearance of the signal at $g = 1.900$. As any hyperfine structure was not observed, this signal can not be assigned to butyl radical (*15*). The similar disappearance and appearance of these signals were observed by the addition of 1,3-butadiene, propylene or ethylene. This radical could not be removed by evacuation.

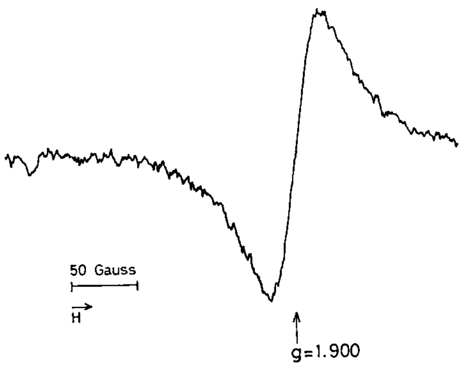

FIG. 4. ESR signal of SnO_2(I) evacuated at 500°C, measured at room temperature.

SnO_2(II) evacuated at 500°C and SnO_2(I) which had been calcined in air at 500°C before being evacuated at 500°C showed no signal at $g = 1.900$.

Conductivity

The change in conductivity with evacuation temperature is shown in Fig. 6. It is quite similar to the change in the activity for the isomerization of 1-butene to *cis*-2-butene and to the change in the amount of surface paramagnetic centers. On exposure to O_2 or nitrobenzene, the conductivity became almost zero. This seems to indicate that the thermal dissociation of SnO_2(I) occurred only on the surface layer and not in the bulk of the solid when evacuated at elevated temperatures.

(B) TiO_2–SnO_2

According to X-ray diffraction patterns, mixing of TiO_2 and SnO_2 decreased the peak intensities of TiO_2 (anatase) and SnO_2(I), and broadened the line width.

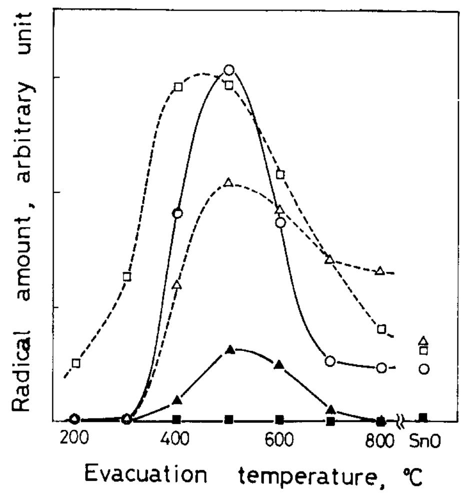

FIG. 5. Amounts of O_2^- (△— —), nitrobenzene anion radicals (□— —) and the radicals of $g = 1.900$ (○—) of SnO_2(I) evacuated at various temperatures, the radicals of $g = 1.900$ after the exposure to O_2 (▲—) and nitrobenzene (■—).

Acid amounts at various acid strengths of TiO_2-SnO_2 calcined in air at 500°C and the amounts of paramagnetic centers of TiO_2-SnO_2 evacuated at 500°C are shown in Fig. 7. High acidity (a large number of acid sites) including strong acid sites of $H_0 \leqq -3.0$ was generated by mixing SnO_2 with TiO_2. However, TiO_2-SnO_2 did not show the ESR signal either at $g = 1.940$ (Ti^{3+}) (*1*), which was observed on TiO_2 evacuated at 500°C, or at $g = 1.900$.

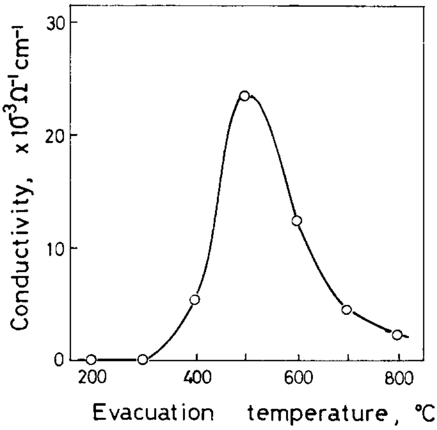

FIG. 6. Variation in conductivity of SnO_2(I) with evacuation temperature, measured at 200°C.

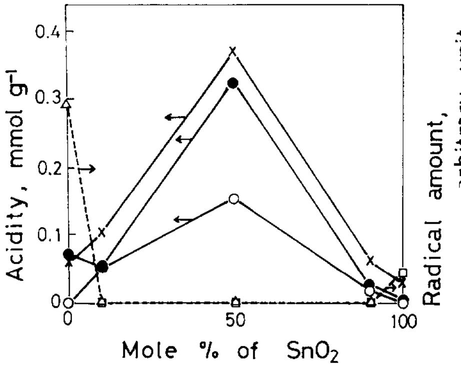

FIG. 7. Acidities of TiO_2-SnO_2 of different compositions calcined in air at 500°C: (×—) acidity at $H_0 \leqq 3.3$, (●—) $H_0 \leqq 1.5$, (○—) $H_0 \leqq -3.0$, and amounts of paramagnetic centers of TiO_2-SnO_2 evacuated at 500°C: (△— — —) $g = 1.940$ (Ti^{3+}), (□— — —) $g = 1.900$.

The result on the isomerization of 1-butene is shown in Fig. 8. The catalytic activity of TiO_2-SnO_2 (9:1) was less than a quarter of that of TiO_2, and the *cis-/trans-* ratio of TiO_2-SnO_2 (9:1) or (1:9) was less than that of TiO_2 or SnO_2, respectively.

DISCUSSION

A. SnO_2

SnO_2 is known to be a *n*-type semiconductor and its conductivity is due to

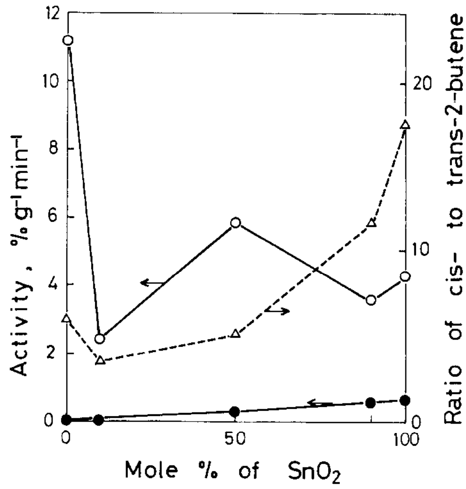

FIG. 8. Isomerization and dehydrogenation of 1-butene over TiO_2-SnO_2 of different compositions evacuated at 500°C: activity for the isomerization (○—) and dehydrogenation (●—), the ratio of *cis-* to *trans-*2-butene (△— —).

the donor levels which arise from Sn^{3+} (*16*, *17*). The evacuation of SnO_2(I) at 400–600°C resulted in the parallel appearances of a high electron conductivity and the paramagnetic centers. Since both of them are ascribed to Sn^{3+}, a part of the surface was reduced to form Sn^{3+} by evacuation at 400–600°C. The formations of O_2^- and nitrobenzene anion radical on the surface may be caused by the surface paramagnetic centers; an electron is transferred from a paramagnetic center to an O_2 or a nitrobenzene to form each anion, and at the same time the paramagnetic center disappears. The oxidation of the surface by O_2 or nitrobenzene lowered the electron conductivity. On this partially reduced surface, 1-butene was isomerized to *cis*-2-butene exclusively.

As mentioned in the foregoing section, a good correlation was observed between the activity for the selective isomerization of 1-butene to *cis*-2-butene and the amount of the paramagnetic centers against evacuation temperature. In addition, both of above values greatly decreased on admission of O_2, nitrobenzene, butadiene or H_2O. Therefore, the active sites for the selective isomerization are associated with the paramagnetic centers ($g = 1.900$) which show an electron donating character.

Since the signal at $g = 1.900$ disappeared and a new signal at $g = 2.002$ appeared by the admission of 1-butene or 1,3-butadiene to SnO_2(I) at a reaction temperature, an irreversible reaction of 1-butene or 1,3-butadiene with the paramagnetic centers is considered to occur during the isomerization of 1-butene. This interprets the great decrease in the reaction rate as the reaction proceeds (see Fig. 2).

The active sites for the formation of butadiene may be different from those for the isomerization, because, over SnO_2(I) evacuated at 300°C, 1,3-butadiene was formed to considerable extent, though no paramagnetic centers and very low activity for the isomerization were observed (see Fig. 3).

The *cis-/trans-* ratio in the isomerization of 1-butene over solid bases is generally much higher than 1, and π-allyl carbanion is considered as an intermediate (*18–21*). Over SnO_2(I) evacuated at 400–600°C, the observed high value of the ratio suggests that the isomerization to *cis*-2-butene occurs through π-allyl carbanion at the paramagnetic centers with electron donating character.

The high ratio of *cis*-2-butene to *trans*-2-butene is quite different from those of other reports (*6–9*), in which the ratios of *cis-* to *trans*-2-butene were 1–2. When SnO_2(I) was calcined in air at 500°C before being evacuated at 500°C, it showed no signal at $g = 1.900$ and a very low activity for the isomerization to *cis*-2-butene. SnO_2(II) also showed no signal at $g = 1.900$ and a low activity (see Table 1). There might be no paramagnetic centers on their SnO_2. Therefore, the formation of the paramagnetic centers depends on the way of the preparation and the pretreatment condition.

As SnO was not active both for isomerization or dehydrogenation, and showed a very small signal at $g = 1.900$ (see Fig. 5), evacuation of SnO_2(I) above 700°C may result in further reduction to form Sn^{2+}, which causes a decrease in the amount of the paramagnetic centers. Since SnO_2(I) evacuated at 1000°C showed only the X-ray diffraction pattern of SnO_2, the reduction of SnO_2(I) would be confined to the surface by the evacuation above 700°C.

B. TiO_2–SnO_2

In the present and previous papers (*1*, *2*), it has been elucidated that the selective isomerization of 1-butene to *cis*-2-butene over SnO_2(I) and TiO_2 is due to the paramagnetic centers with a reducing character of $g = 1.900$ and $g = 1.940$ (Ti^{3+}), respectively. A small *cis-/trans-* ratio of TiO_2–SnO_2 (1:9) and (9:1) compared to SnO_2(I) and TiO_2, respectively, may be caused by the complete absence of the paramagnetic centers on those TiO_2–SnO_2. Much lower activity for the isomerization over TiO_2–SnO_2 (9:1) than over TiO_2 may also be caused by the absence of Ti^{3+} on the surface.

The *cis-/trans-* ratio in the isomerization of 1-butene over solid acids is generally 1–2, and a butyl carbenium ion is considered as an intermediate (*18*, *22*). From a small *cis-/trans-* ratio and from the generation of strong acid sites, it is presumed that the acid sites take part in the isomerization of 1-butene over TiO_2–SnO_2.

The absence of paramagnetic centers of $g = 1.940$ and $g = 1.900$ on TiO_2–SnO_2 indicates that the reduction of TiO_2 or SnO_2 surface is retarded by the addition of a small amount of SnO_2 to TiO_2 or TiO_2 to SnO_2, respectively. As previously reported (*1*), the addition of SiO_2 to TiO_2 also retarded the reduction of TiO_2 surface; a higher evacuation temperature by about 100°C was required for TiO_2–SiO_2 (9:1) to reduce the surface to the same extent as TiO_2. Since no radicals were detected on TiO_2–SnO_2 (9:1) after evacuation at 700°C, the addition of SnO_2 is more effective than that of SiO_2 in retarding the reduction of TiO_2 surface.

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