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The Nature of Active Sites on TiO_2 and TiO_2–SiO_2 for the Isomerization of Butenes

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The isomerization of 1-butene and *cis*-2-butene was studied over TiO_2 and TiO_2–SiO_2 having different mole ratios with various treatments on the surface. The activity decreased with increasing the evacuation temperature on both catalysts. The ratio of *cis*/*trans*-2-butene from 1-butene increased when TiO_2 and TiO_2–SiO_2 were evacuated above 400 and 500°C, respectively. Oxygen treatment of the catalysts evacuated at 450°C decreased the activity of TiO_2 but increased that of TiO_2–SiO_2. Hydrogen treatment showed the opposite effect to that of oxygen.

Ti^{3+} were produced on the surface by the evacuation above 300 and 400°C on TiO_2 and TiO_2–SiO_2, respectively. On these surfaces the nitrobenzene anion radicals were formed by electron transfer to nitrobenzene from Ti^{3+} and Ti^{2+}.

The change in nature of active sites after several treatments was discussed in terms of surface acidity and electron donating property.

INTRODUCTION

In previous papers (*1,2*), the surface and catalytic properties of TiO_2 and TiO_2–SiO_2 were reported. The catalytic property of TiO_2–SiO_2 was quite different from that of TiO_2. For instance, TiO_2–SiO_2 showed high activity for the amination of phenol with ammonia, which was higher than that of SiO_2–Al_2O_3, whereas TiO_2 was almost inactive for this reaction. The difference was attributed to the strong acid sites on TiO_2–SiO_2, which was generated by mixing of two oxides (*3,4*).

For the isomerization of butenes, TiO_2 calcined in air was less active than TiO_2–SiO_2, but the selectivity of *cis*/*trans*-2-butene from 1-butene was higher than that of TiO_2–SiO_2 (*1*). Shannon *et al.* (*5*) have also reported the isomerization of butenes over TiO_2 of rutile type and suggested that more than one kind of sites participated in the reaction. However, the nature of active sites was not examined so extensively.

On the surface properties of TiO_2–SiO_2, Karakchiev (*6*) investigated its oxidative and structural aspects. The existence of electron donating sites on TiO_2 was revealed by Che *et al.* (*7*), and the number of the sites was reported to be decreased remarkably by the addition of SiO_2 (*8*).

The present paper attempts to elucidate the nature of active sites on TiO_2 and TiO_2–SiO_2 for the isomerization of butenes by measuring the changes of the surface property with various treatments of the catalyst combined with the kinetic measurement.

EXPERIMENTAL METHODS

Catalyst Preparation

TiO_2–SiO_2 was obtained from the mixed solution of ethyl orthosilicate and titanium tetrachloride by coprecipitation with aqueous ammonia at pH 7.5. The precipitate was aged over water bath for 2 hr and washed with distilled water until no chloride ions were detected and dried at 100°C for 20 hr.

TiO_2(I) was prepared by the hydrolysis of titanium tetrachloride followed by aging, washing and drying as above. TiO_2(II) and

TiO_2(III) were "Titanox" AWD and RA-10 from Titanium Pigment Co. which had structure of anatase and rutile, respectively.

Reaction Procedure

A closed circulation reactor having a volume of about 900 ml was used for the kinetic measurement. A 50 mg of the catalyst was placed in a reactor with quartz tips and evacuated for 3 hr at various temperatures. After cooling to 200°C, 200 Torr (1 Torr = 133.3 N m^{-2}) of the reactant were introduced and the reaction products were analyzed periodically by gas chromatography. The analysis was carried out at 0°C on a 4 m column (4 mm diam Cu tubing) containing 30% propylene carbonate on 30–60 mesh Uniport C. In poisoning experiments, 1 Torr of NH_3 or 3 Torr of CO_2 were mixed with 200 Torr of butene and served to the reaction. To examine the effect of the treatment with H_2 or O_2, the catalyst evacuated at 450°C was exposed to H_2 of 23 Torr at 450°C or to O_2 of 38 Torr at 200°C followed by the evacuation at the same temperatures. The activity was expressed by the initial conversion per minute per unit weight of catalyst. The ratios of *cis*/*trans*-2-butene and 1-/*trans*-2-butene were obtained by extrapolation to zero conversion.

Butenes were purified by passing through the zeolum F-9 (synthetic zeolite from Tekko-sha, structure and composition are identical to 13-X) kept at dry ice temperature and distilled before use.

ESR Measurement

Samples of 20 mg in the ESR cells which were attached to the same vacuum line were first evacuated at 200°C for 1.5 hr. One of them was taken off from the system by sealing the upper part of the cell. Then, the other samples were heated up to 300°C under vacuum and continued to evacuate for 1.5 hr at this temperature. The second sample was taken off as above. These procedures were repeated every 100°C increment until the last sample was evacuated at 700°C. These samples were subjected to ESR measurement. After recording the spectra, the samples were exposed to nitrobenzene vapor through breakable seals for 2 days at room temperature. Then, excess nitrobenzene was trapped by liquid nitrogen and subjected to ESR measurement again. In some experiments, the sample was treated with O_2 or H_2. ESR spectrum was measured both at room temperature and at −195°C.

RESULTS

Butene Isomerization

The activities and the selectivities (the ratios of two products) for the isomerizations of 1-butene and *cis*-2-butene over the catalysts having different composition and evacuated at 450°C are shown in Figs. 1 and 2. A big difference in the selectivity was observed between TiO_2(I) and the mixed oxides. Over TiO_2(I), the ratios of *cis*/*trans* and 1-/*trans* were much higher. The selectivity difference was more prominent compared with the case where the catalysts calcined *in air* were used as in our previous paper (*1*). The difference in the activity between TiO_2 and TiO_2–SiO_2 was not so large in the present case where

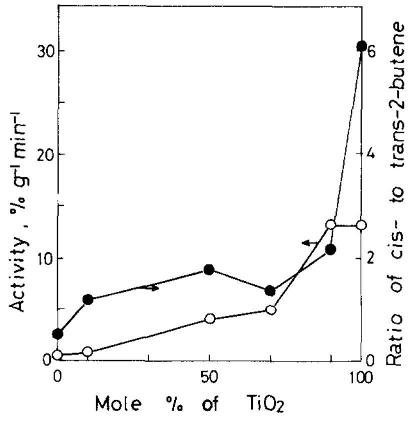

FIG. 1. Activities (○—) and selectivities (ratios of *cis*/*trans*-2-butene) (●—) over TiO_2–SiO_2 of different compositions.

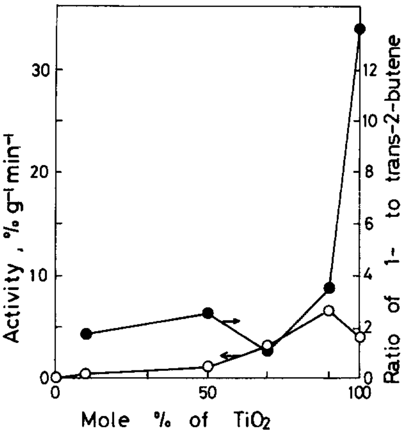

FIG. 2. Activities (O—) and selectivities (ratio of 1-/*trans*-2-butene) (●—) over TiO_2–SiO_2 of different compositions.

the catalysts calcined *in vacuo* were used, though it was very big in our previous study (*1*).

The activities and the selectivities of TiO_2(I) and TiO_2–SiO_2 (9:1) for the isomerization of 1-butene were quite dependent on the evacuation temperature as shown in Figs. 3 and 4. Over TiO_2(I), the activity decreased with increasing the evacuation temperature. The activity curve has a shoulder around 500°C. Remarkable change in selectivity was observed at 400°C. The formation of *cis*-2-butene became preferential at higher evacuation temperature.

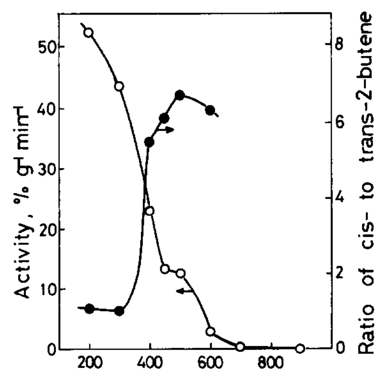

FIG. 3. Dependencies of the activity and the selectivity on the evacuation temperature in the isomerization of 1-butene over TiO_2(I).

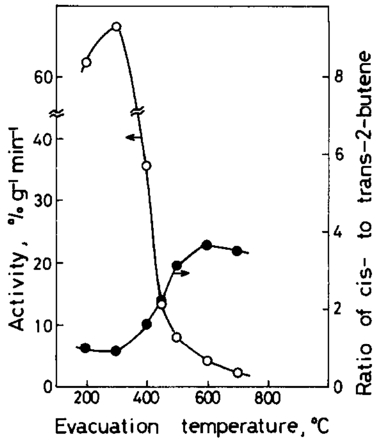

FIG. 4. Dependencies of the activity and the selectivity on the evacuation temperature in the isomerization of 1-butene over TiO_2–SiO_2 (9:1).

Substantially the same dependencies of the activity and the selectivity on the evacuation temperature were observed over TiO_2–SiO_2 (9:1). The different features from those of TiO_2(I) are as follows. The temperature which gives the maximum selectivity is higher in TiO_2–SiO_2 (9:1) by about 100°C. The activity still remained on TiO_2–SiO_2 (9:1) after severe evacuation at 700°C, whereas it diminished completely on TiO_2(I).

TiO_2(II) and TiO_2(III) did not show any measurable activity when evacuated at 500 or 700°C. TiO_2(I) which had been calcined in air at 700°C and evacuated at 200°C also showed no activity.

The results of various treatments of catalysts evacuated at 450°C are listed in Table 1. These treatments or poisoning resulted in different selectivities over TiO_2(I), but brought about little change over TiO_2–SiO_2 (9:1). This suggests that only one kind of active sites is operative on TiO_2–SiO_2 (9:1), but more than one kind on TiO_2(I) after the evacuation at 450°C.

The change in activity over TiO_2(I) with various treatments also differed from that of TiO_2–SiO_2 (9:1). The difference was prominent when treated with O_2. This treatment for TiO_2–SiO_2 (9:1) enhanced

TABLE 1

CHANGES IN THE ACTIVITY AND THE RATIO OF *cis/trans*-2-BUTENE IN THE ISOMERIZATION OF 1-BUTENE WITH VARIOUS TREATMENTS AND POISONINGS AFTER EVACUATION AT 450°C

	TiO_2(I)		TiO_2–SiO_2 (9:1)	
	Activity (% min^{-1} g^{-1})	Ratio of *cis/trans*-2-butene	Activity (% min^{-1} g^{-1})	Ratio of *cis/trans*-2-butene
Untreated	13.3	6.1	13.2	2.2
Poisoned with NH_3	3.0	9.0	2.8	2.2
Poisoned with CO_2	14.2	6.8	14.9	2.3
Treated with O_2	7.0	2.9	27.7	1.9
Treated with H_2	15.8	11.0	11.2	3.2

the activity twice as much as the original one, but did not change the *cis/trans* ratio. For TiO_2(I), it decreased the activity to a half of its original one and decreased the *cis/trans* ratio.

H_2 treatment had opposite effect on the selectivity and the activity to that of O_2 treatment. It increased the selectivity and the activity of TiO_2(I), but decreased the activity of TiO_2–SiO_2 (9:1).

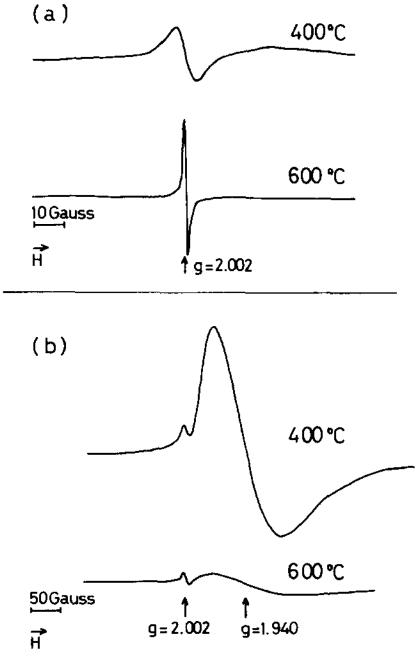

FIG. 5. ESR signals of TiO_2 evacuated at 400 and 600°C measured at room temperature (a) and −195°C (b).

With NH_3 adsorption, TiO_2(I) and TiO_2–SiO_2 (9:1) were decreased in activity. The selectivity of TiO_2(I) increased, whereas that of TiO_2–SiO_2 (9:1) was unchanged. CO_2 adsorption had no effect on two catalysts.

ESR Spectra

TiO_2(I) showed only sharp signal of $g = 2.002$ at room temperature as shown in Fig. 5a. The width of the signal varied with the evacuation temperature. These were 6.5 G for the samples pretreated at 300–500°C and 1.5 G for those at 600–700°C. Peak height of this signal increased up to 600°C, but decreased considerably at 700°C. This sharp signal was also observed on TiO_2(II) and TiO_2(III). Peak heights were the same order of magnitude for TiO_2(I), (II), and (III) when evacuated at 500°C.

As the measurement temperature was reduced to −195°C, the broad signal of $g = 1.940$ appeared in addition to the sharp signal as shown in Fig. 5b. The broad signal was assigned to Ti^{3+} (*9,10*). With TiO_2–SiO_2 (9:1), the sharp signal was very small. The broad signal was detectable at room temperature and developed greatly at −195°C.

On exposure to nitrobenzene, strong signal developed on TiO_2 and TiO_2–SiO_2 (9:1) at room temperature. An example is shown in Fig. 6. This signal can be as-

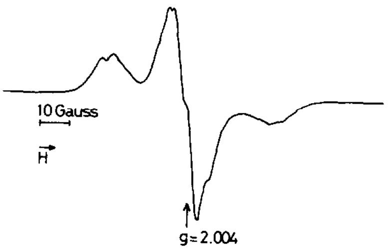

FIG. 6. ESR signal of nitrobenzene on TiO_2 evacuated at 500°C, measured at room temperature.

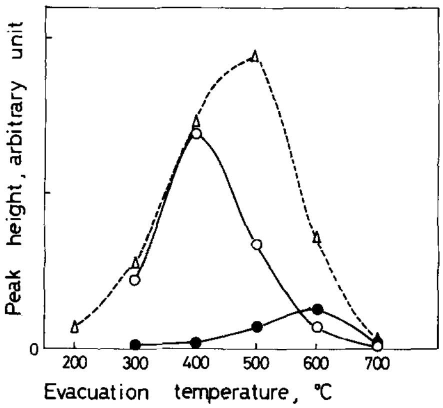

FIG. 7. Amounts of nitrobenzene anion radicals and Ti^{3+} of TiO_2 evacuated at various temperatures. (Δ---) nitrobenzene anion radical, Ti^{3+} before (○—) and after (●—) exposure to nitrobenzene.

signed to the nitrobenzene anion radical (*11*).

The ESR peak intensities of the nitrobenzene anion radical at room temperature and Ti^{3+} at −195°C before and after the exposure to nitrobenzene are plotted against evacuation temperatures in Figs. 7 and 8. The maximum amounts of Ti^{3+} were observed at 400 and 500°C for TiO_2(I) and TiO_2–SiO_2 (9:1), respectively.

In the lower pretreatment range, the amount of Ti^{3+} decreased on exposure to nitrobenzene to produce the anion radical, Ti^{3+} itself being oxidized into Ti^{4+}. This indicates that electron donating sites are Ti^{3+}, most of which are located on the surface. In the higher pretreatment range, the amount of Ti^{3+} increased on the contrary. As the pretreatment temperature becomes higher, the reduction of the surface seems to proceed further to form a small amount of Ti^{2+}. Therefore, a part of the anion radicals is considered to be formed on Ti^{2+} to oxidize it into Ti^{3+}, which caused to increase the amount of Ti^{3+} at higher evacuation temperature.

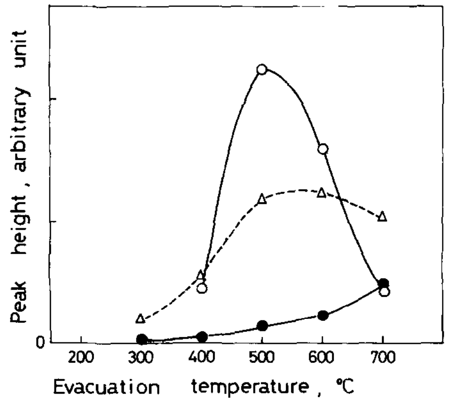

FIG. 8. Amounts of nitrobenzene anion radicals and Ti^{3+} of TiO_2–SiO_2 (9:1) evacuated at various temperatures. (Δ---) nitrobenzene anion radical, Ti^{3+} before (○—) and after (●—) exposure to nitrobenzene.

Both TiO_2(II) and TiO_2(III) did not show any detectable signal of Ti^{3+} after evacuated at 500°C. The amount of nitrobenzene anion radical on TiO_2(II) or TiO_2(III) was less than 1/50 of that on TiO_2(I).

H_2 treatment at 450°C for TiO_2(I) and TiO_2–SiO_2 (9:1) which had been evacuated at 500°C resulted in great increase in the amount of Ti^{3+}, whereas O_2 treatment at 200°C eliminated Ti^{3+}. TiO_2(I) which was calcined at 700°C in air followed by evacuation at 500°C showed a small signal of Ti^{3+}. H_2 treatment of TiO_2(II) and TiO_2(III) at 500°C generated Ti^{3+} whose shape was much more symmetrical than those on TiO_2(I) or TiO_2–SiO_2 (9:1). The exposure of these surfaces to nitrobenzene, however, did not result in the formation of the anion radical or the decrease of Ti^{3+}. Most of Ti^{3+} are considered to be inside of the solid and are not accessible to nitrobenzene molecule.

DISCUSSION

As mentioned in the foregoing section, the formation of nitrobenzene anion radical on the surface may be caused by surface Ti^{3+} and Ti^{2+} as follows:

$$\text{nitrobenzene} + Ti^{3+} = \text{nitrobenzene anion radical} + Ti^{4+},$$

$$\text{nitrobenzene} + Ti^{2+} = \text{nitrobenzene anion radical} + Ti^{3+}.$$

The changes in the number of the anion radical with the evacuation temperature on

TiO_2(I) and TiO_2–SiO_2 (9 : 1) are similar to the selectivity changes for 1-butene isomerization. Therefore, one of the possible active sites for the isomerization is Ti^{3+} on the surface.

Shannon *et al.* (5) denied the possibility of Ti^{3+} as active sites on TiO_2 for the isomerization of butene from the fact that O_2 did not affect the activity. However, the activity of TiO_2(I) evacuated at 450°C was certainly affected by O_2 treatment. As the production of Ti^{3+} on the surface depends on the way of the preparation and the pretreatment condition, there might be no Ti^{3+} on the surface of their TiO_2, whose activity was not affected by O_2 treatment.

The centers which gave the sharp signal (Fig. 5a) were called "paramagnetic defect" by Hasegawa and Kawaguchi (*12*) and reported to be active sites for the condensation reaction of acetaldehyde. The possibility of the centers being active for the isomerization of butene is not plausible, because three kinds of TiO_2 used here showed almost the same amount of these centers, but only one of them was active.

The *cis*/*trans* ratio from 1-butene isomerization over solid acids, where the reaction proceeds via butyl carbonium ion, is generally 1–2 (*13,14*). The ratio of 1-/*trans* is less than 1 in the isomerization of *cis*-2-butene. Over solid bases where π-allyl carbanion is considered as an intermediate, both ratios of *cis*/*trans* and 1-/*trans* are much higher than 1 (*14–19*). From the value of the ratio (Figs. 1 and 2), it is suggested that the isomerizations occur through π-allyl carbanion over TiO_2(I) evacuated above 400°C and TiO_2–SiO_2 (9 : 1) above 500°C. Below these evacuation temperatures, carbonium ion mechanism seems to operate.

In the previous paper (*1*), the mechanism of the generation of acid sites by mixing of two oxides, TiO_2 and SiO_2, was proposed. The acid sites of the mixed oxide in which the major component oxide is TiO_2 are caused by the excess positive charge on Si^{4+}. On these acid sites, the isomerization may proceed via carbonium ion to give *cis*/*trans* ratio around 1. When evacuated at high temperature, Ti^{4+} in TiO_2–SiO_2 are reduced into Ti^{3+} by releasing one of the oxygen atoms. Hence, the positive charge on Si^{4+} is reduced by the transfer of negative charge to Si^{4+} through oxygen bridge, which results in the elimination of acid sites. Ti^{3+} thus produced would act as electron donating centers and become the active sites for the isomerization of 1-butene over which the reaction proceeds via π-allyl carbanion to give high *cis*/*trans* ratio.

As TiO_2(I) is reported to have weak Brönsted acid sites when pretreated at lower temperature (*20*), the active sites of TiO_2(I) evacuated below 400°C are possibly acidic sites over which the reaction proceeds via carbonium ion. When evacuated above 400°C, some fraction of Ti^{4+} are reduced to Ti^{3+} which become the active sites for the isomerization over which π-allyl carbanion mechanism is operative to give high *cis*/*trans* ratio.

Since Ti^{3+} began to appear at lower temperature in the case of TiO_2(I), Ti^{4+} of TiO_2(I) is considered to be reduced much easier than that in TiO_2–SiO_2 (9 : 1). The evacuation at 450°C may result in the production of the active center of electron donating property by reducing a large part of Ti^{4+} of TiO_2(I), but may not be sufficient to reduce a large part of Ti^{4+} in TiO_2–SiO_2 (9 : 1), as judged from the selectivity changes with various treatments and poisonings shown in Table 1. Since the activity decreased with the increase of the evacuation temperature (Figs. 3 and 4), the activity of acidic site is considered to be higher than that of Ti^{3+}. Thus, the reaction proceeds mainly on acid sites until a large part of Ti^{4+} converts to Ti^{3+}. On exposure to O_2, Ti^{3+} is expected to be oxidized to Ti^{4+}, which regenerates acid sites on TiO_2–SiO_2 (9 : 1) and the activity increases as shown in Table 1. Ti^{3+} of TiO_2(I) is also oxidized, but it does not seem to regenerate acid sites. The change in nature of active sites on two catalysts with evacuation temperature and O_2 treatment could be explained as follows.

In the case of TiO_2(I) evacuated below 400°C, Brönsted acid sites (surface OH groups on Ti^{4+}) are active. By evacuation at 450°C, the dehydration of OH groups and the reduction of Ti^{4+} proceed, which cause the generation of Ti^{3+}. Thus, the surface has both Brönsted acid sites and the electron donating centers. On exposure to O_2, Ti^{3+} oxidizes to Ti^{4+}, but Brönsted acid sites are not reproduced as H_2O might be necessary to produce OH group. Raising the evacuation temperature above 450°C causes further reduction and Ti^{2+} begins to appear.

In the case of TiO_2–SiO_2 (9:1) evacuated below 450°C, Brönsted and/or Lewis acid sites of Si^{4+} induced by Ti^{4+} are present. By the evacuation at 450°C, a part of Ti^{4+} are reduced to Ti^{3+} which results in the decrease of acid sites and the appearance of the electron donating sites. On exposing to O_2, Ti^{3+} changes to Ti^{4+} which reproduces acid sites of Si^{4+}. As a result, the activity for the isomerization of 1-butene increases. The evacuation above 450°C gives rise to the reduction of Ti^{4+} to Ti^{3+} and further to Ti^{2+}. The higher temperature is required for TiO_2–SiO_2 (9:1) to reduce the surface to the same extent as that of TiO_2(I). After complete reduction of Ti^{4+}, the surface shows only electron donating property. Since the selectivities of all the mixed oxides were substantially the same, the other mixed oxides having different molar ratios of Ti/Si probably have similar properties as those of TiO_2–SiO_2 (9:1).

It should be noted that the above discussion on the nature of TiO_2 can be applied only to the TiO_2 prepared by the present method. When the TiO_2 was calcined once in air at 700°C, it showed different property from untreated TiO_2; no activity was observed with the catalyst evacuated at 200°C.

Since TiO_2(II) and TiO_2(III) also showed different property, the nature of TiO_2 after certain treatment depends strongly on the preparation method of TiO_2.

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