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Surface and Catalytic Properties of TiO_2–Al_2O_3

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Titania–aluminas of various compositions (atomic ratios: 1/9, 1/1, 9/1) were prepared from the sulfates by coprecipitation with aqueous ammonia or urea. The XPS study with sputteretching by Ar ions revealed that the composition of the surface layer was the same as that of the bulk for the sample coprecipitated with ammonia, whereas the Al atoms were enriched in the surface layer for the sample coprecipitated with urea. An acidity maximum was observed for TiO_2–Al_2O_3 (1/9) prepared with ammonia (TiO_2–Al_2O_3 (1/9)-A), while no acid sites were found for TiO_2–Al_2O_3 (1/9) prepared with urea (TiO_2–Al_2O_3 (1/9)-U). Basic property appeared only for TiO_2–Al_2O_3 (1/1)-A when it was exposed to water vapor. A maximum in oxidizing property was observed for TiO_2–Al_2O_3 (1/1)-U but not for TiO_2–Al_2O_3 (1/1)-A. On the other hand, reducing property decreased with the increase of TiO_2 content for both TiO_2–Al_2O_3-A and TiO_2–Al_2O_3-U. The maximum activities were observed on TiO_2–Al_2O_3 (1/9, 1/1)-A for the isomerization of 1-butene and on TiO_2–Al_2O_3 (1/9)-A for the dehydration of 2-butanol, respectively. A good correlation was found between the acidity and the activity for the dehydration. In the case of the isomerization, it has been concluded from the results of coisomerization of 1-butene-d_0/d_8 that the reaction proceeds by the alkyl cation mechanism involving intermolecular hydrogen transfer on TiO_2–Al_2O_3 (1/9)-A, but the contribution of the carbanion mechanism caused by the action of basic sites becomes greater as the content of TiO_2 becomes higher. The active sites for the alkyl cation mechanism have been inferred to be the protons supplied from butene molecules adsorbed on the surface.

INTRODUCTION

The comprehensive work on surface and catalytic properties of binary oxides of TiO_2 with MgO (*1*), SiO_2 (*2*), ZrO_2 (*3*), SnO_2 (*4*), MoO_3 (*5*), or WO_3 (*6*) have been reported recently. As for TiO_2–Al_2O_3, only the acidic property of the binary oxide prepared from $TiCl_4$ and $AlCl_3$ by hydrolysis with aqueous ammonia was measured (*7*). The present paper deals with the detailed surface and catalytic properties of TiO_2–Al_2O_3 of various compositions, which were prepared from coprecipitation of $Ti(SO_4)_2$ and $Al_2(SO_4)_3$ with urea as well as with aqueous ammonia. The effects of the preparation method on the difference in composition between the surface layer and the bulk, and on the acid–base and oxidizing–reducing properties and catalytic activities for 1-butene isomerization and 2-butanol dehydration have been examined.

EXPERIMENTAL METHODS

Preparation of Catalyst

Titania–alumina catalysts with different atomic ratios of Ti to Al were prepared by coprecipitation of a mixed solution of $Ti(SO_4)_2$ and $Al_2(SO_4)_3$. Ammonia and urea were used as precipitation reagents. For precipitation with ammonia, aqueous ammonia was added to the mixed aqueous solution which was kept cooling in an ice bath. The final pH was 9.5. The precipitate was aged for 1 h in a water bath at 100°C, filtered, washed with hot deionized water until no SO_4^{2-} ions were detected with Ba^{2+} in a filtrate, and dried at 100°C. For precipitation with urea, a mixed aqueous solution of $Ti(SO_4)_2$, $Al_2(SO_4)_3$, and urea was heated at 100°C. In the initial few hours, precipitation gradually occurred. In about 5 h, as decomposition of urea progressed to a certain extent, the formation of precipitate was suddenly accelerated and the pH value of the solution increased. The precipitate was

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heated for five more hours to facilitate aging, then filtered, washed, and dried as above.

Titanium oxide and Al_2O_3 were similarly prepared from $Ti(SO_4)_2$ and $Al_2(SO_4)_3$, respectively, by precipitations both with aqueous ammonia and with urea. Henceforth, the notation A and U will be used to specify the precipitation method; for instance, TiO_2–Al_2O_3-U shows the catalyst sample being prepared by using urea as a precipitation reagent. All samples were calcined at 500°C in air for 3 h before further treatments. The amounts of the reagent used for preparation of the samples, the compositions, the SO_4^{2-} contents, and the specific surface areas of the resulting samples are summarized in Table 1.

The composition of a resulting binary oxide was determined by X-ray fluorescence analysis. The amount of SO_4^{2-} ions contained in the sample was analyzed with Ba^{2+} ions after dissolving the samples into oxalic acid.

X-Ray Analysis and DTA-TG

X-Ray diffraction pattern was recorded on a Toshiba ADG-301 diffractometer for the powdered sample that had been calcined at 500 and 700°C in air. DTA-TG was measured in air, the heating rate being 20°C/min.

Acidity and Basicity Measurement

Acidity was measured by titration with butylamine according to Benesi's method (*8*). The indicators used were methyl red ($pK_a = 4.8$), phenylazonaphthylamine (4.0), dimethyl yellow (3.3), *p*-(phenylazo)diphenylamine (1.5), dicinnamilideneacetone (−3.0), benzalacetophenone (−5.6), and anthraquinone (−8.2). Basicity was measured by titration with benzoic acid, bromothymol blue ($pK_a = 7.1$) being used as an indicator (*9*). Basicity was measured both for the sample calcined at 500°C in air and for the sample which was exposed to water vapor for various periods at room temperature. For

TABLE 1

Amounts of Reagents for Preparation of Samples and Analysis of Resulting Samples

Catalyst nomenclature	Starting Materials				Resulting Materials			
	$Ti(SO_4)_2$ 30% soln (ml)	$Al_2(SO_4)_3 \cdot 17H_2O$ (g)	Ti/Al ratio	Precipitation reagent	Ti/Al ratio	mol% Al_2O_3	Specific surface area ($m^2 \cdot g^{-1}$)	SO_4^{2-} content mol%
TiO_2–A	776	0	∞	ammonia	∞	0	173	
TiO_2–Al_2O_3 (9/1)-A	650	78.3	9/1	ammonia	7.1	7	305	
TiO_2–Al_2O_3 (1/1)-A	341	356	1/1	ammonia	0.73	41	316	
TiO_2–Al_2O_3 (1/9)-A	62	583	1/9	ammonia	0.074	86	100	11.5
Al_2O_3–A	0	636	0	ammonia	0	100	250	3.5
TiO_2–U	388	0	∞	urea 1000 g	∞	0	212	
TiO_2–Al_2O_3 (9/1)-U	650	78.3	9/1	urea 1000 g	7.9	6	249	
TiO_2–Al_2O_3 (1/1)-U	341	356	1/1	urea 1000 g	0.73	41	180	
TiO_2–Al_2O_3 (1/9)-U	62	583	1/9	urea 1000 g	0.072	87	96	4.2
Al_2O_3–U	0	318	0	urea 1000 g	0	100	134	1.2

the exposure procedure, the samples in small test tubes were placed in a desiccator in which water was put at the bottom. The samples were periodically taken out from the desiccator and subjected to basicity measurement.

Infrared Measurement

The infrared spectrum of pyridine adsorbed on the sample was measured to distinguish the types of acid sites (*10*). The sample was pressed into a disk and outgassed at 500°C for 3 h in an *in situ* cell. After cooling to room temperature, the sample was exposed to pyridine at 10 Torr for 10 min followed by outgassing at 100 and 200°C. In some experiments, water vapor was admitted to the sample that had been exposed to pyridine and outgassed at 200°C.

ESR Spectroscopy

For measurement of oxidizing sites, the sample in an ESR cell was outgassed at 500°C for 3 h and exposed to perylene vapor through a breakable seal at 100°C for 2 days. The perylene cation radicals were measured by ESR. For measurement of reducing sites, the sample that had been outgassed at 500°C for 3 h was exposed to nitrobenzene at room temperature for 1 day. The ESR spectrum of nitrobenzene anion radicals was measured after excess nitrobenzene adsorbed on the sample was removed from the sample by condensing into a liquid nitrogen trap attached to the ESR cell.

XPS

For XPS measurement, the powdered sample was pressed onto the Au net spot-welded to the sample holder and then outgassed at 500°C for 2 h. The experiments were performed on a VG ESCA 3 spectrometer equipped with a sputter-etching ion gun. The spectra were measured with Al$K\alpha$ and/or Mg$K\alpha$ radiation. The base pressure of the spectrometer was usually below 10^{-8} Torr during the experiments. Sputter-etching was generally performed at an Ar pressure of 5×10^{-6} Torr and the voltages of 2 and 3 kV for 30 min each. After each treatment, the spectrum was recorded.

Catalytic Reaction

To test the catalytic properties, 1-butene isomerization and dehydration of 2-butanol were chosen as test reactions. The reactions were carried out in a recirculation reactor having a volume of about 400 ml. For 1-butene isomerization, 98 Torr of 1-butene was allowed to react over 100 mg of catalyst at 100°C. The reaction mixture was periodically withdrawn from the reaction system and subjected to gas chromatographic analysis, a 5-m column packed with propylene carbonate on Celite 545 being operated at 0°C. For 2-butanol dehydration, 8 Torr of 2-butanol was allowed to react over 25–100 mg of catalyst at 150°C. Products were analyzed by gas chromatography. A column packed with propylene carbonate on Celite 545 was used for separation of butene isomers, and a 1-m column of DOP was used for separation of 2-butanol and butenes.

Coisomerization of 1-butene- d_0/d_8 (*11*) was carried out in a microcatalytic pulse reactor. A mixture containing equal amounts of nondeutero-1-butene and perdeutero-1-butene was injected in a He stream ahead of the catalyst. Products were separated by a gas chromatographic column and collected in a liquid nitrogen trap. The collected products were subjected to mass spectrometric analysis. For the poisoning experiment with ammonia, TiO_2–Al_2O_3 (9/1)-A was outgassed at 500°C for 3 h. After cooling to 100°C, the catalyst was exposed to 1 Torr of ammonia for 10 min followed by outgassing at 115°C for 1 h.

RESULTS AND DISCUSSION

PHYSICAL CHARACTERS OF BULK MIXED OXIDE

In precipitation with urea, the pH value in the supernatant increased by two steps for all samples. Although a small amount of precipitate was formed on the first step (0–5 h), most of the precipitate was formed when the second sharp increase in pH value occurred in about 6 h. This does not necessarily mean that only titanic acid was separately precipitated in the first stage and $Al(OH)_3$ was precipitated in the second stage, since, after calcination, neither TiO_2 crystallites nor Al_2O_3 crystallites were detected by X-ray diffraction analysis for TiO_2–Al_2O_3 (1/1)-U and TiO_2–Al_2O_3 (1/9)-U. A weak pattern that shows anatase was observed only for TiO_2–Al_2O_3 (9/1)-U. Similar X-ray patterns were observed for the samples prepared by coprecipitation with ammonia. These indicate that the binary metal oxides are not simply mechanical mixtures of TiO_2 and Al_2O_3, but consist of new complex oxides which are not indentified by X-ray diffraction.

The DTA-TG curves are shown in Fig. 1a for the samples precipitated with ammonia and in Fig. 1b for the samples precipitated with urea. The curves for the samples precipitated with urea were similar. All these show two endothermic peaks at about 100 and 200°C. However, the curves for the samples precipitated with ammonia were different from each other. The endothermic peaks observed at lower temperature correspond to the elimination of physically adsorbed water and those at higher temperature to the dehydration of hydroxyl group. The differences in DTA curves between TiO_2–Al_2O_3-U and TiO_2–Al_2O_3-A suggest that the physicochemical nature of the former complex oxide is different from that of the latter one.

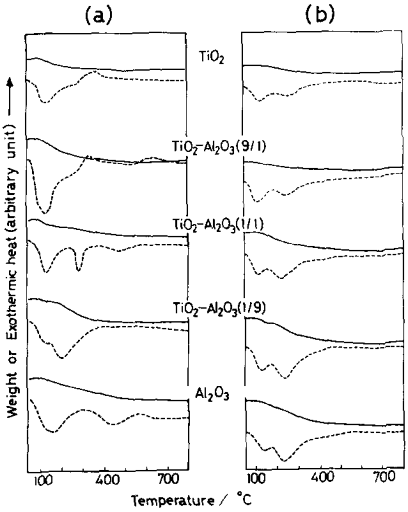


FIG. 1. DTA (– – –) and TG (———) curves for the samples precipitated with ammonia (a) and with urea (b).

SURFACE CHARACTERISTICS

(i) *Surface Composition*

The XPS spectra of Al_{2s} and Ti_{2p} levels for TiO_2–Al_2O_3 (1/1)-A and TiO_2–Al_2O_3 (1/1)-U before and after sputter-etching are shown in Fig. 2. Before sputter-etching, the binding energies of Al_{2s}, $Ti_{2p_{1/2}}$, $Ti_{2p_{3/2}}$, and O_{1s}, which were referred to C_{1s} (284 eV) on the sample, were 118.4, 463.9, 458.2, and 530.4 eV, respectively. These values were the same for the two samples within an experimental error. Therefore, the valence state of each component atom should be the

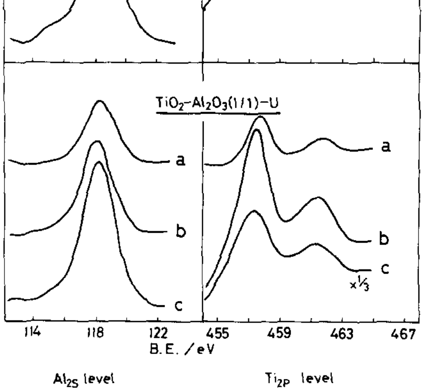


FIG. 2. XPS spectra of Al_{2s} and Ti_{2p} levels. a, before sputter-etching; b, after sputter-etching by 2-kV Ar^+ ion; c, after sputter-etching by 3-kV Ar^+ ion.

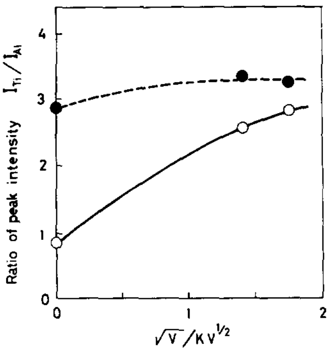


FIG. 3. Variations of peak intensity ratio of $Ti_{2p_{1/2}}$ + $Ti_{2p_{3/2}}$ to Al_{2s}. ●, TiO_2–Al_2O_3 (1/1)-A; ○, TiO_2–Al_2O_3 (1/1)-U.

same for the two samples. By sputter-etching, the intensities of all bands were increased, and the binding energies of the Ti_{2p} levels were shifted to the lower binding energy side. The shift may be due to partial reduction of Ti^{4+} to Ti^{3+} by sputter-etching (*12–14*). The binding energy of Al_{2s} was not shifted by sputter-etching.

The intensity ratios of $Ti_{2p_{1/2}}$ + $Ti_{2p_{3/2}}$ to Al_{2s} are plotted against the square root of the sputter-etching voltage, *V*, in Fig. 3. Since the amount of the material removed from the surface by sputter-etching is proportional to the square root of the voltage applied to sputter-etching, the abscissa is proportional to the in-depth distance from the surface (*15*). The ratio of $Ti_{2p_{1/2}}$ + $Ti_{2p_{3/2}}$ to Al_{2s} for the TiO_2–Al_2O_3 (1/1)-A sample remained constant, whereas the ratio for the TiO_2–Al_2O_3 (1/1)-U sample increased with an increase in the sputter-etching voltage. This indicates that the composition of the surface layer was the same as that of the bulk for the sample precipitated with ammonia, and that the Al atoms were enriched in the surface layer for the sample precipitated with urea. The concentration of Al atoms in the surface layer is considered due to very slow coprecipitation with urea.

(*ii*) *Acidic and Basic Properties*

The amounts of acid sites at different acid strengths on unit surface area are shown in Fig. 4A for the TiO_2–Al_2O_3-A samples, and in Fig. 4B for the TiO_2–Al_2O_3-U samples. For the TiO_2–Al_2O_3-A samples, a maximum amount of acid sites was observed at any strengths for the TiO_2–Al_2O_3 (1/9) sample. A similar trend was also observed for TiO_2–Al_2O_3 which was prepared from $TiCl_4$ and $AlCl_3$ by coprecipitation with aqueous ammonia (*7*), except that the acidity of Al_2O_3 is lower than that of Al_2O_3 prepared from the sulfate. The amount of acid sites stronger than $H_0 = -8.2$ on the TiO_2–Al_2O_3 (1/9) sample is comparable to that of SiO_2–Al_2O_3. It is interesting, however, that no acid sites were observed for the TiO_2–Al_2O_3 (1/9)-U sample. The difference in the dependencies of acidities on TiO_2/Al_2O_3 ratio is difficult to interpret. A speculative interpretation may be that the high acidity of TiO_2–Al_2O_3 (1/9)-A is due to the high content of SO_4^{2-}, since TiO_2 is reported to increase its acidity on the addition of SO_4^{2-} (*16*), while the low acidity of TiO_2–Al_2O_3 (1/9)-U is not only due to the relatively low content of SO_4^{2-}, but also due to the high content of Al_2O_3 *on the surface*, as evidenced by XPS. The reason why the acidity of TiO_2–Al_2O_3 (1/9)-U is lowest is probably due

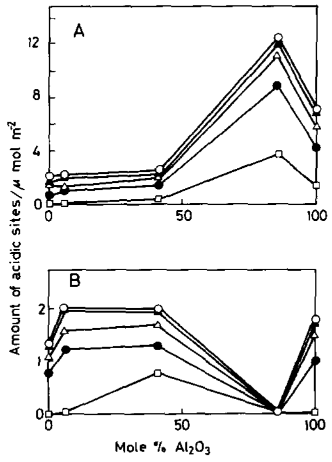


FIG. 4. Amounts of acid sites at different strengths. (A) precipitated with ammonia; (B) precipitated with urea; ○, $H_0 \leq 3.3$; ▲, $H_0 \leq 1.5$; △, $H_0 \leq -3.0$; ●, $H_0 \leq -5.6$; □, $H_0 \leq -8.2$.

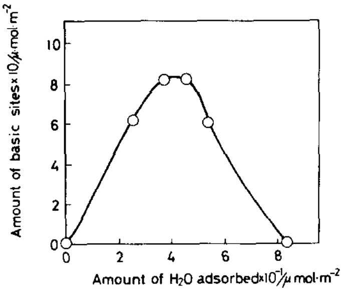


FIG. 5. Amounts of basic sites appeared on addition of water for TiO_2–Al_2O_3 (1/1)-A.

to the mixed effects of three factors; surface composition, SO_4^{2-} content, and the other unknown factor caused by urea coprecipitation.

Basic sites were not observed for all samples that had been calcined at 500°C. However, basic sites appeared only on the TiO_2–Al_2O_3 (1/1)-A sample after admission of a certain amount of water vapor. The amount of basic sites is plotted against the amount of water adsorbed in Fig. 5. The maximum amount of basic sites was observed when 40 μmol H_2O/m^2 was adsorbed. Exposure to an excess amount of water resulted in elimination of basic sites. Although an appearance of basic sites on exposure to water vapor has been reported for Al_2O_3 (*17*), this is the first such observation for a binary oxide. The appearance of basic sites on the addition of water vapor is probably due to the increase in negative charge of the oxygen ions adjacent to Lewis acid sites, since the electron attracting force of Lewis acid sites is weakened by the adsorption of water vapor on Lewis sites.

The ir spectra of adsorbed pyridine showed that most of the acid sites present on the samples were of Lewis type, since the bands at 1440–1448 cm^{-1}, which are characteristic of pyridine coordinatively bonded to Lewis acid sites were observed, while the bands at around 1540 cm^{-1} indicating the presence of Brönsted acid sites could not be observed. Traces of Brönsted acid sites were observed only on the TiO_2–Al_2O_3 (1/9)-A sample. Exposure to water vapor did not convert Lewis acid sites into Brönsted acid sites.

(*iii*) *Oxidizing and Reducing Properties*

The relative amounts of the cation radicals of perylene and the anion radicals of nitrobenzene produced on the samples are shown in Fig. 6 and Fig. 7, respectively. The number of oxidizing sites increased on mixing the two component oxides for the samples precipitated with urea and the maximum amount was observed for the TiO_2–Al_2O_3 (1/1)-U sample. However, the amount did not change much with mixing the two component oxides for the samples precipitated with ammonia. The number of reducing sites of the samples precipitated with ammonia decreased as the amount of Al_2O_3 added to TiO_2 increased. The decrease in the reducing site of TiO_2 by addition of a foreign oxide was observed for

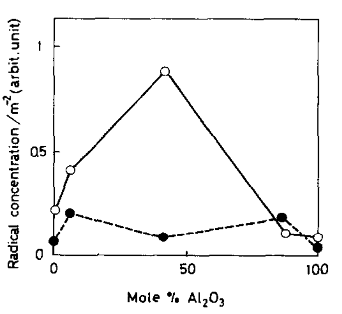


FIG. 6. Relative amounts of perylene cation radicals ●, precipitated with ammonia; ○, precipitated with urea.

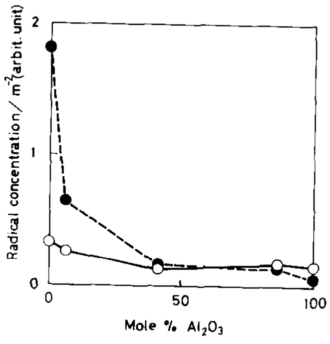


FIG. 7. Relative amounts of nitrobenzene anion radicals. ●, precipitated with ammonia; ○, precipitated with urea.

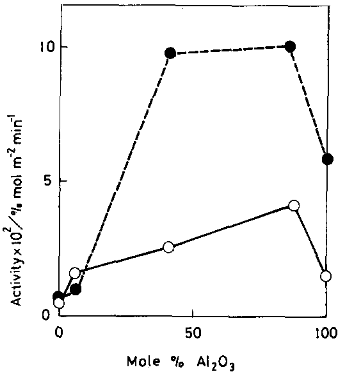


FIG. 8. Variations of activity for 1-butene isomerization with composition of catalyst. ●, precipitated with ammonia; ○, precipitated with urea.

TiO_2–SiO_2 (*18*) and TiO_2–SnO_2 (*4*). The reducing sites of the binary oxides containing TiO_2 were ascribed to partially reduced TiO_2 component, and TiO_2 became difficult to reduce when a foreign oxide was mixed in. Addition of Al_2O_3 seems to bring about the same effect on the reducibility of TiO_2.

CATALYTIC PROPERTIES

(*i*) *1-Butene Isomerization*

The variations of the activity and the *cis/trans* ratio for 1-butene isomerization as a function of change in composition are shown in Fig. 8 and Fig. 9, respectively. The *cis/trans* ratios were obtained by extrapolation to zero conversion. The activity was higher for binary oxides than for single-component oxides. The maximum activity was observed with the 1 : 9 mixture for the two preparation methods. The *cis/trans* ratio in the products decreased from 10 for TiO_2 to 2 for Al_2O_3 as the composition of Al_2O_3 was increased. A high *cis/trans* ratio is generally observed when the reaction intermediate is carbanion (*19–23*). The high *cis/trans* ratio was reported for TiO_2 that was prepared from $TiCl_4$ and was also interpreted by an anionic mechanism (*4, 24*). Though the present TiO_2 samples were prepared from $Ti(SO_4)_2$, the *cis/trans* ratios were also high. Thus, it is suggested that the isomerization proceeds via anionic intermediates over TiO_2, whatever starting material TiO_2 was prepared from. Since the *cis/trans* ratio is generally low when the reaction proceeds via *s*-butyl cation (*11, 19*), the decrease in the *cis/trans* ratio as Al_2O_3 was added suggests a change in mechanism to the alkyl cation mechanism.

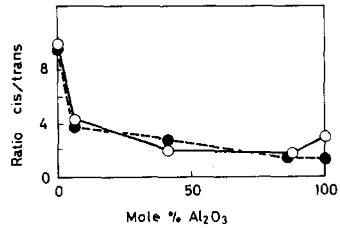


FIG. 9. Ratios of *cis*-2-butene/*trans*-2-butene produced in 1-butene isomerization. ●, precipitated with ammonia; ○, precipitated with urea.

The isotopic distributions of the products in the coisomerization of 1-butene d_0/d_8 over TiO_2–Al_2O_3 (1/9, 1/1, 9/1)-A samples are given in Table 2. From the distribution, it is possible to know whether the reaction involves an intermolecular H transfer or an intramolecular H transfer as well as an isotope effect (*11*). If the reaction involves an intermolecular H transfer, the difference in the number of H (or D) atoms exchanged per molecule (AEM value) between the reactant and the product would be close to 0.5. If the reaction involves an intramolecular H transfer, the difference in the AEM value would be close to 0. The differences in the AEM value were about 0.65 for the TiO_2–Al_2O_3 (1/9)-A and about 0.3 for the TiO_2–Al_2O_3 (1/1)-A and TiO_2–Al_2O_3 (9/1)-A. These suggest that an intermolecular H transfer is involved in the reaction over the TiO_2–Al_2O_3 (1/9)-A, while both an intermolecular H transfer and an intramolecular H transfer are involved in the reaction over the TiO_2–Al_2O_3 (9/1)-A and the TiO_2–Al_2O_3 (1/1)-A.

Since the alkyl cation mechanism should result in an intermolecular H transfer (*11, 25, 26*) and, in most cases, gives the *cis/trans* ratio of about 1 in 1-butene isomerization (*13, 25–27*), it is suggested that the active sites of the TiO_2–Al_2O_3 (1/9)-A

TABLE 2

Isotopic Distribution of Products in Coisomerization of 1-Butene d_0/d_8 at 100°C[a]

Catalyst	Flow rate ($ml \cdot min^{-1}$)	Product	Percentage each product	Percentage each isotopic species									AEM[b]	IE[c]
				d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8		
None		1-B[d]	100	50.3							1.0	48.7	0.01	1.01
TiO_2–Al_2O_3	100	1-B	55.6	47.3	2.4	0.7	0	0	0.3	1.8	8.0	39.6	0.163	1.01
(1/9)-A		*trans*	25.9	23.7	19.7	5.4	1.2	0.6	2.3	9.3	25.1	12.7	0.871	1.01
0.100 g		*cis*	18.5	26.8	19.2	4.6	0.9	0.5	1.8	8.1	25.4	14.5	0.801	1.03
	140	1-B	79.1	50.6	1.0	0.2	0	0	0.2	1.2	6.9	39.9	0.113	1.07
		trans	9.4	26.4	20.0	3.9	0.9	0.5	1.6	7.0	25.4	14.4	0.767	1.06
		cis	11.5	28.2	20.1	3.0	0.6	0.3	1.2	6.1	26.3	14.4	0.712	1.08
TiO_2–Al_2O_3	55	1-B	61.5	25.4	11.3	3.6	1.0	0.5	1.3	6.0	18.3	32.7	0.587	0.71
(1/1)-A		*trans*	18.8	38.6	19.8	8.5	2.6	1.7	3.4	7.1	10.0	8.4	0.858	2.36
0.100 g		*cis*	19.6	40.9	18.9	6.7	2.1	1.3	1.6	6.9	11.2	10.4	0.848	2.25
	140	1-B	80.0	40.1	6.9	1.5	0.4	0.3	0.8	2.9	11.7	35.3	0.322	0.96
		trans	9.7	49.2	16.0	5.1	1.9	1.2	2.3	5.3	9.0	10.0	0.632	2.68
		cis	10.3	52.5	13.9	3.8	1.4	1.0	1.7	4.4	9.2	12.0	0.528	2.59
TiO_2–Al_2O_3	60	1-B	84.6	46.9	1.5	0	0	0	0	1.2	7.5	42.8	0.114	0.94
(9/1)-A		*trans*	6.6	51.7	13.4	2.0	0	0	0.6	4.3	15.0	12.9	0.428	2.04
0.100 g		*cis*	8.8	52.4	11.8	1.6	0	0	0.4	4.4	15.1	14.3	0.401	1.92
TiO_2–Al_2O_3	60	1-B	96.6	41.0	2.0	0	0	0	0	0.2	4.0	53.8	0.064	0.75
(9/1)-A		*trans*	1.2	72.9	10.4	0.5	0	0	0	0.5	3.8	11.9	0.162	5.17
0.500 g poisoned by NH_3		*cis*	2.4	76.2	4.9	1.8	0	0	0	0.3	3.6	13.2	0.127	4.85
TiO_2–Al_2O_3[e]	15	1-B	93.7	49.2	3.4	0.1	0	0	0	0.2	3.7	43.4	0.077	1.11
(9/1)-A		*trans*	2.1	75.4	5.0	0.5	0	0	0	0.3	4.6	14.2	0.112	4.24
0.500 g poisoned by NH_3		*cis*	4.2	75.5	4.5	0.5	0	0	0	0.3	5.0	14.2	0.111	4.13

[a] Each pulse contained 3.4×10^{-5} mol of a mixture of 1-butene-d_0 and 1-butene-d_8.

[b] Number of H (or D) atoms exchanged per molecule, calculated from $\sum_{i=1}^{4} \cdot N_i + \sum_{i=5}^{8} (8 - i) \cdot N_i$, where N_i represents fraction of the isotopic species containing i D atoms.

[c] $\mathrm{IE} = \left(\sum_{i=0}^{3} N_i + \frac{1}{2}N_4\right) \Big/ \left(\sum_{i=5}^{8} N_i + \frac{1}{2}N_4\right)$.

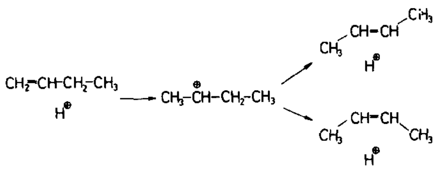
[d] Reactant.

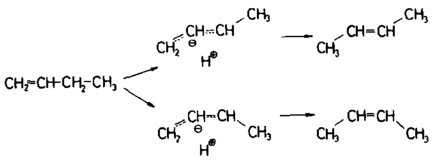
[e] Reaction temperature: 120°C.

sample are acidic. The presence of acid sites detected by Benesi's method also supports that the active sites are acidic. On the other hand, the carbanion mechanism often results in an intramolecular H transfer (*24, 28–34*) and gives a high *cis/trans* ratio in 1-butene isomerization (*19–24*). The *cis/trans* ratios were 3.8 and 2.7 for the TiO_2–Al_2O_3 (9/1)-A and the TiO_2–Al_2O_3 (1/1)-A, respectively. Therefore, it is suggested that, over these catalysts, the carbanion mechanism is partly operating, in addition to the alkyl cation mechanism. Both acidic and basic sites seem to be acting as active sites. Poisoning TiO_2–Al_2O_3 (9/1)-A by ammonia resulted in a considerable decrease in the AEM values. The reaction involved almost entirely an intramolecular H transfer. If ammonia was dissociated to NH_2^- and H^+ to poison both acidic and basic sites, the deuterium distribution characteristic of base-catalyzed reactions would not have been observed. Thus, the data with ammonia poisoning in Table 2 indicate that acidic sites are poisoned selectively by ammonia. Therefore, basic sites on TiO_2–Al_2O_3 (9/1)-A are considered to act as active sites.

In our previous paper (*18, 24*), it was reported that TiO_2 outgassed at high temperature catalyzed butene isomerization by carbanion mechanism and the active sites were considered to be associated with Ti^{3+} ions, which were produced on the surface of TiO_2 by outgassing at a high temperature. Probably the O^{2-} ions adjacent to Ti^{3+} ion act as basic sites by abstraction of an H^+ from the butene molecule. Although the presence of basic sites could not be detected by the indicator method, partly reduced TiO_2 component may exist on the surface of the TiO_2–Al_2O_3 (9/1)-A and the TiO_2–Al_2O_3 (1/1)-A, and act as basic sites. It seems reasonable to assume that the contribution of carbanion mechanism to the isomerization becomes greater as the TiO_2 content is higher. The assumption explains the higher *cis*/*trans* ratio for the higher TiO_2 content.

Isotope effects were small for the formation of *cis*- and *trans*-2-butenes over the TiO_2–Al_2O_3 (1/9)-A, whereas considerable isotope effects were observed over both TiO_2–Al_2O_3 (1/1)-A and TiO_2–Al_2O_3 (9/1)-A. In the alkyl cation mechanism, if the addition of an H^+ to the reactant is a slow step, no isotope effect would be observed, while, if the abstraction of an H^+ from the *s*-butyl cation is a slow step, the isotope effect would be large. In the case of the carbanion mechanism, a considerable isotope effect would be expected in the cases where a slow step is involved either in the abstraction of an H^+ from the reactant or in the addition of an H^+ to the carbanion. The observed isotope effects suggest that the slow step in the alkyl cation mechanism, which mainly occurs on TiO_2–Al_2O_3 (1/9)-A and partly on TiO_2–Al_2O_3 (1/1)-A and TiO_2–Al_2O_3 (9/1)-A, is involved in the addition of an H^+ to the reactant. Considerable isotope effects observed for TiO_2–Al_2O_3 (1/1)-A and TiO_2–Al_2O_3 (9/1)-A support the idea that the carbanion mechanism is partly operating on these catalysts.





In order to see how the surface OH groups participate in the reaction, the following experiment was undertaken on the TiO_2–Al_2O_3 (1/1)-A. The OH groups were replaced with OD groups by repeated exposure to D_2O vapor followed by evacuation and finally outgassed at 500°C. In the first pulse, nondeutero-1-butene was reacted over the catalyst. In the second pulse, perdeutero-1-butene was reacted. The isotopic distributions of the products in these experiments are given in Table 3. In the first pulse, only small amounts of D atoms

TABLE 3

Isotopic Distribution of Products over D Exchanged TiO_2–Al_2O_3 (1/1)-A(0.100 g) at 100°C

Pulse No.	Reactant	Product	Percentage each product	Percentage each isotopic species						
				d_0	d_1	d_2	$d_3 \sim d_5$	d_6	d_7	d_8
1	1-Butene-d_0	1-B	93.8	99.4	0.6	0	0	0	0	0
	3.4×10^{-5} mol	*trans*	2.3	98.3	1.7	0	0	0	0	0
		cis	3.9	98.8	1.2	0	0	0	0	0
2	1-Butene-d_8	1-B	98.6	0	0	0	0	0	5.2	94.8
	2.5×10^{-5} mol	*trans*	0.5	8.4	3.4	0.6	0	0.7	8.6	78.2
		cis	0.9	9.5	3.8	0.4	0	0.8	10.0	75.5

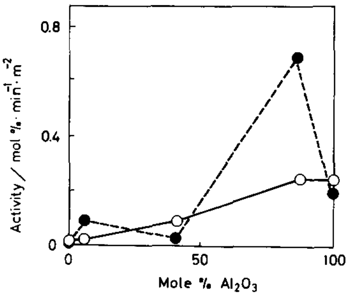


FIG. 10. Variations of activity for dehydration of 2-butanol with composition of catalyst. ●, precipitated with ammonia; ○, precipitated with urea.

were incorporated into the products. The number of D atoms picked up by three butenes was 4.2×10^{11} atoms/cm^2. In the second pulse, considerable amounts of d_7 isotopic species were found in the products. In addition, more than 10% of the light molecules ($d_0 - d_4$) were contained in the products. It seems likely that considerable amounts of butene were absorbed on the surface and that these supplied protons to the butene molecules to be isomerized via alkyl cation mechanism.

Ozaki and Kimura (*34*) investigated butene isomerization over SiO_2–Al_2O_3 and concluded that Brönsted acidity was somehow generated from the olefin molecules chemisorbed on the surface and acted as proton donors to butene molecules to form *s*-butyl cations as intermediates. They assumed that the proton donors were produced by the interaction of olefin molecules with Lewis sites. Hightower and Hall (*25*) observed that the residues on the surface provided with protons the butene molecules to be isomerized, and suggested that the residues were formed by the interaction of butene molecules with small amounts of surface protons.

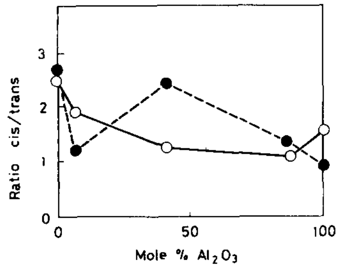


FIG. 11. Ratios of *cis*-2-butene/*trans*-2-butene produced in dehydration of 2-butanol. ●, precipitated with ammonia; ○, precipitated with urea.

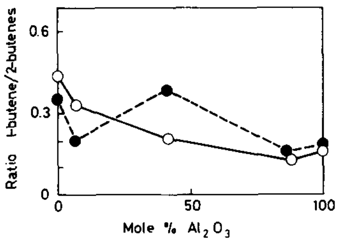


FIG. 12. Ratios of 1-butene/2-butenes produced in dehydration of 2-butanol. ●, precipitated with ammonia; ○, precipitated with urea.

Although only 4.2×10^{11} surface D atoms/cm^2 were incorporated into butene molecules at one pulse, and although no Brönsted acid sites could be detected by ir spectroscopy except for TiO_2–Al_2O_3 (1/9-A), it may be possible that the proton donors are formed by the interaction of butene molecules with surface OH groups.

(*ii*) *Dehydration of 2-butanol*

In the dehydration of 2-butanol, the *cis*/*trans* ratio in the produced 2-butenes and the 1-butene/2-butenes ratio in the products were nearly constant up to the conversion level 60%. The conversion rate was zero order in 2-butanol. The activity is plotted against the composition in Fig. 10. The ratios of the *cis*/*trans* and 1-butene/2-butene, which were extrapolated to zero conversion, are shown in Fig. 11 and Fig. 12, respectively. The variation of the activity for the dehydration was different from that for 1-butene isomerization. A maximum activity was observed for the TiO_2–Al_2O_3 (1/9)-A catalyst.

It is reported that the 1-butene/2-butenes and *cis*/*trans* ratios in the products reflects the acid–base property of catalyst and that as basic property becomes dominant over acidic property, the ratios become higher (*35*). The 1-butene/2-butenes ratios were less than unity for all catalysts and the *cis/trans* ratios were not so high as those in 1-butene isomerization. Therefore, acid-catalyzed dehydration was dominant for TiO_2–Al_2O_3 catalysts. However, it is notable that the TiO_2–Al_2O_3 (1/1)-A exhibited basic property on addition of water and showed the highest 1-butene/2-butenes ratio. Production of water during the reaction may enhance the basic property which takes a part of active sites. A relatively high *cis/trans* ratio observed for the TiO_2–Al_2O_3 (1/1)-A catalyst also supports the possibility that a carbanion mechanism is partly involved in the reaction.

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