Isomerization of Butenes over Thorium Dioxide

Yuzo Imizu, Tsutomu Yamaguchi, Hideshi Hattori, and Kozo Tanabe
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060

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The isomerization of butenes has been studied over four kinds of ThO_2 catalysts which differ in starting materials or preparative procedures. The selective ThO_2 catalysts for the formation of 1-olefin in the dehydration of 2-alkanol, which were prepared from nitrate and oxalate, were active and gave high *cis*/*trans* ratios in the isomerization of 1-butene, whereas the non-selective ThO_2 catalyst, which was prepared from chloride, was completely inactive. The isomerization reaction was poisoned by both CO_2 and NH_3. The activity was enhanced by the treatment with hydrogen, but was reduced by the treatment with oxygen, the selectivity being unchanged with both treatments. The coisomerization of *cis*-2-butene and *cis*-2-butene-d_8 showed that the isomerization involved an intramolecular hydrogen transfer, and a large isotope effect, 6.0, for the formation of 1-butene and a small isotope effect, 1.5, for the formation of *trans*-2-butene were observed. With these results, the nature of active sites on thorium oxide, and the reaction mechanism were discussed.

Thorium dioxide has been used as a catalyst for dehydration of alcohols.[1,2] In recent years, it has been recognized to be a selective catalyst for the dehydration of 2-alkanol to form 1-alkene when it is properly prepared.[3,4]

Davis and Brey reported that the selectivity of thorium dioxide in dehydration and dehydrogenation of alcohols strongly depended upon the preparative procedures of the catalyst.[5] The thorium dioxide prepared from nitrate shows a high selectivity for the formation of 1-octene in the dehydration of 2-octanol, whereas the thorium dioxide prepared from thorium chloride gives a considerable amount of 2-octenes. Besides the preparative procedure, the pretreatment condition is another major factor for determining selectivity. Thorium dioxide pretreated with hydrogen is a dehydration catalyst, while thorium dioxide pretreated with oxygen is a dehydrogenation catalyst.[5]

The nature of active sites on thorium dioxide which determines the selectivity, however, has not yet extensively been investigated. Yamaguchi *et al.* reported in the dehydration of alcohol over alumina[6] and zirconium dioxide[7,8] that the selectivity of the catalysts can be determined by surface acidic and basic properties. The isomerization of butenes is known to be a reaction suitable for testing the correlation of acidic and basic properties of catalysts with the activity and selectivity.[9—13] In the present work, the isomerization of butenes was carried out over several thorium dioxides to investigate the nature of active sites.

Experimental

Catalysts and Reactants. Four kinds of thorium dioxide were prepared, which differ in starting materials or in preparative procedures. ThO_2(I) and ThO_2(II) were obtained from oxalate and nitrate, respectively, by thermal decomposition in air at 500 °C for 6—8 h. ThO_2(III) was prepared from nitrate by the precipitation method as shown by Brey *et al.*[14] To 5000 ml aqueous solution of thorium nitrate (0.145 M), 500 ml aqueous ammonia (28%) was added. Precipitate was filtered, followed by washing with 1500 ml distilled water. The resulting thorium hydroxide was dried for 2 days and finally calcined at 500 °C in air for 6 h. ThO_2(IV) was prepared from thorium chloride by precipitation as follows. Aqueous ammonia (28%, 50 ml) was added to 500 ml aqueous solution of 50 g thorium chloride. Precipitate was washed, dried, and calcined as in the case of ThO_2(III). Those thorium salts were supplied from Wako Pure Chemical Co. All catalysts were evacuated at 500 °C for 3 h before use for the reaction.

Butenes (Takachiho pure grade) were purified by passage through a column of molecular sieves 3A or 4A maintained at the temperature of dry ice–acetone. 2-Butanol was obtained from Wako Pure Chemical Co. and purified by passage through molecular sieves 3A at room temperature.

Apparatus and Procedure. Dehydration of *s*-butyl alcohol and isomerization of butenes were carried out in two recirculation reactors whose volumes were 3000 ml for dehydration and 410 ml for isomerization. For dehydration, the initial pressure of *s*-butyl alcohol was 6 Torr and about 300 mg of a catalyst was used. Reaction temperature was 300 °C. Products were analyzed by gas chromatography. A 1 m column packed with TCP 30% on Celite 545 was operated at 100 °C. For isomerization of butenes, 88 Torr of butene and 50—150 mg of catalyst were used. Reaction temperature was 80 °C. Products were analyzed by gas chromatography with a 5 m column containing VZ-7, operating at room temperature.

For poisoning experiment with carbon dioxide or ammonia, the catalyst that had been evacuated at 500 °C was cooled to 100 °C and was exposed to 88 Torr of carbon dioxide or ammonia for 1 h. After evacuation at certain temperatures (200—500 °C) for 1 h, the catalyst was served for a reaction.

For hydrogen or oxygen treatment, the catalyst that had been evacuated at 500 °C was exposed to hydrogen or oxygen (60 Torr) at 500 °C or 300 °C for 2 h, followed by evacuation at various temperatures for 1 h.

For the coisomerization of non-deuterated and perdeuterated *cis*-2-butenes,[10,15] a mixture containing about equal amount of *cis*-2-butene-d_0 and *cis*-2-butene-d_8 was reacted at 80 °C.

Results

Specific surface areas, the activities, and the selectivities for the dehydration of 2-butanol and the isomerization of butenes are listed in Table 1. The catalysts showed a high selectivity for the formation of 1-alkene in the dehydration except for ThO_2(IV), over which considerable amounts of 2-alkenes were produced.[5] For the isomerization of butenes, the ThO_2(IV) was completely inactive. This was true even for the catalyst evacuated at 900 °C. The other thorium dioxides were active and gave high *cis*/*trans* and 1-/*trans* ratios in the isomerization of 1-butene and

Table 1. Catalytic activity and selectivity of ThO_2 for isomerization of butenes and dehydration of *s*-butyl alcohol

Catalyst	Surface area (m^2/g)	1-Butene		Activity[a]	2-Butanol composition of butenes[b]		
		Activity[a]	Ratio of *cis* to *trans*		1-butene	*trans*-2-butene	*cis*-butene
ThO_2(I)	59.1	29.8	3.4	1.87×10^{-1}	84.2	9.3	6.5
ThO_2(II)	62.3	22.9	3.1	2.36×10^{-1}	82.4	10.6	7.0
ThO_2(III)	41.7	10.8 (1.1)[c]	3.2 (3.3)[d]	0.74×10^{-1}	76.6	14.8	8.6
ThO_2(IV)	46.3	0.0	—	2.22×10^{-1}	39.8	26.8	33.4

a) Initial activity; $\%^{-1}\,\text{min}^{-1}$. b) Extrapolated to 0 conversion. c) Reactant; *cis*-2-butene. d) Ratio of 1- to *trans*-. Reaction temperature: 80 °C for isomerization; 300 °C for dehydration.

Table 2. Poisoning effects of CO_2 and NH_3 on the activity and selectivity for isomerization of 1-butene

Poison	Evacuation temp (°C)	k[a]	*cis-/trans-*
CO_2	300	0.02	4.1
CO_2	400	0.12	3.9
CO_2	450	0.28	3.5
CO_2	500	1.00	3.2
NH_3	200	0.35	3.8
NH_3	300	0.37	4.1
NH_3	350	0.73	3.5
NH_3	400	1.00	3.2

a) Ratio of the activity after poisoning to the original activity.

Table 3. Effect of oxygen or hydrogen treatment on the activity and selectivity for isomerization of 1-butene

Treatment gas	Treatment temp (°C)	Evacution temp (°C)	Relative activity[a]	Selectivity *cis-/trans-*
No treatment	—	—	1.00	3.2
Oxygen	500	200	0.48	3.4
Oxygen	300	300	0.74	3.5
Oxygen	80[b]	—	0.00	—
Hydrogen	500	500	3.52	3.3

a) Ratio of the activity after treatment to the original activity. b) Reaction was carried out in the presence of 5.6 Torr oxygen.

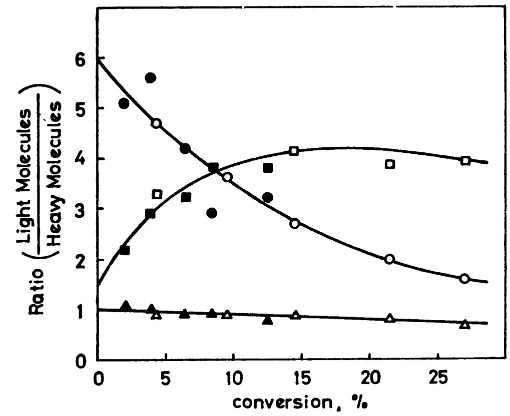

Fig. 1. The variations of the ratios of "*light molecules*" to "*heavy molecules*" with the conversion in the coisomerization of *cis*-2-butene d_0/d_8 over both untreated ThO_2 and hydrogen treated ThO_2. Reaction temperature; 80 °C, untreated ThO_2; (●) 1-butene, (■) *trans*-2-butene, (▲) *cis*-2-butene, treated ThO_2; (○) 1-butene, (□) *trans*-2-butene, (△) *cis*-2-butene.

cis-2-butene, respectively.

Poisoning effects of carbon dioxide and ammonia are given in Table 2. Both carbon dioxide and ammonia poisoned the active sits for isomerization. The catalyst regained the original activity by evacuation at 400 °C for ammonia poisoned catalyst and by evacuation at 500 °C for carbon dioxide poisoned catalyst. Poisoning with ammonia and carbon dioxide did not result in appreciable change in selectivity.

In Table 3 are listed the effects of oxygen or hydrogen treatment on the activity and selectivity in the isomerization. While hydrogen treatment resulted in an increase in the activity, oxygen treatment reduced the activity. The selectivity was almost unchanged with these treatments.

Isotopic distribution of butene isomers in the coisomerization of *cis*-2-butene d_0/d_8 are listed in Table 4. Since the numbers of hydrogen (or deuterium) atoms exchanged per molecule (AEM value) are much smaller than 0.5, the value of which is expected if the reaction involves an intermolecular hydrogen transfer, the reaction is suggested to involve an intramolecular hydrogen transfer. The ratios of "*light molecule*" to "*heavy molecule*" are plotted against isomerization conversion in Fig. 1 for both untreated and hydrogen treated catalysts. The plots are on the same lines for both untreated and hydrogen treated catalysts. The intercepts of the plots show the isotope effect. A large isotope effect, 6.0, for the formation of 1-butene and a small isotope effect, 1.5, for the formation of *trans*-2-butene were observed.

Discussion

As suggested by Davis and Brey, catalytic properties of thorium dioxide vary with both preparative procedure and pretreatment.[5] There seem to be different types of active sites on the surface of thorium dioxide.

In the isomerization of butenes, the selectivities did

TABLE 4. ISOTOPIC DISTRIBUTIONS OF BUTENE ISOMERS IN COISOMERIZATION OF *cis*-2-BUTENE d_0/d_8

Catalyst	Product	% each product	% Isotopic species						Atoms exchanged/ molecule[a)]	Ratio of *light molecule/ heavy molecule*[b)]
			d_0	d_1	d_2—d_5	d_6	d_7	d_8		
ThO_2(III)	*cis-*		47.8	0.1	0	0.9	2.9	48.3		0.9
	1-	1.2	81.6	1.9	0	0	3.6	12.9	0.055	5.1
	trans-	0.9	66.5	2.3	0	0	2.7	28.5	0.050	2.2
	cis-	97.9	50.9	0.4	0	0	3.1	45.6	0.035	1.1
	1-	3.9	77.0	3.8	0	0	4.4	14.8	0.082	4.2
	trans-	1.6	72.2	3.7	0	0	3.0	21.1	0.067	3.2
	cis-	93.5	46.6	0.4	0	0.9	3.4	48.7	0.056	0.9
	1-	6.1	72.3	4.0	0	0	5.7	18.0	0.097	3.2
	trans-	6.5	73.9	5.4	0	0	3.5	17.2	0.089	3.8
	cis-	87.4	44.2	1.1	0	0	4.4	50.3	0.055	0.8
ThO_2(III) treated with hydrogen at 500 °C	1-	2.2	79.9	2.7	0	0	3.4	14.0	0.061	4.7
	trans-	2.1	76.0	0.0	0	0	3.2	20.8	0.032	3.2
	cis-	95.7	46.9	0.6	0	0.5	3.6	48.3	0.052	0.9
	1-	6.0	67.0	5.0	0	1.0	5.7	20.2	0.150	2.7
	trans-	8.6	75.2	5.5	0	0.0	3.6	15.7	0.091	4.2
	cis-	85.4	44.4	1.9	0	1.2	4.9	47.6	0.092	0.9
	1-	8.2	53.8	7.6	0	2.1	8.4	28.1	0.202	1.6
	trans-	19.9	69.4	10.3	0	0.9	5.3	14.1	0.174	3.9
	cis-	71.9	36.6	4.2	0	1.7	8.2	49.3	0.159	0.7

a) Calculated from $\sum_{i=0}^{4} i\cdot N_i + \sum_{i=5}^{8} (8-i)\cdot N_i$, N_i; formation of isotopic species containing *i* deuterium atoms.

b) Calculated from $(\sum_{i=0}^{3} N_i + N_4/2)/(\sum_{i=5}^{8} N_i + N_4/2)$.

not substantially change with either pretreatment or poisoning. It appears that only one type of active sites is operative for the isomerization of butenes. One type of active sites on ThO_2(IV) which is non-selective for dehydration, is not active for isomerization of butenes. Oxygen treatment of ThO_2(III) resulted in the elimination of the active sites for the isomerization. By referring to the report that oxygen treatment enhances the active sites for dehydrogenation,[5)] the active sites for dehydrogenation are not considered to be active for the isomerization. On the other hand, hydrogen treatment was reported to produce the active sites for selective dehydration to 1-alkene. Since it actually increased the activity for the isomerization, it is suggested that the active sites for the isomerization are of a type of active sites which catalyze the selective dehydration.

The active sites for the isomerization were poisoned by both an acidic molecule, carbon dioxide, and a basic molecule, ammonia. It is plausible that the active site is an acid-base pair site. If either part of a pair site is blocked by a poison, the rest of the pair site may not show any activity. This interprets the observed selectivity which was unchanged by poisoning with both molecules.

Breysse has shown that the treatment of thorium dioxide with hydrogen or oxygen at 500 °C caused a slight deviation from stoichiometry.[16)] It is suggested that hydrogen treatment removes surface oxygen ion and provides a surface with excess thorium ions. The coordinatively unsaturated thorium ion is expected to be more strongly acidic than saturated thorium ion.[17)] There should be oxygen ions adjacent to the unsaturated thorium ion. These oxygen ions are expected to be more strongly basic than oxygen ion adjacent to saturated thorium ion.

Since the isomerization involves an intramolecular hydrogen transfer, the reaction may be initiated by the abstraction of a hydrogen atom (or ion) from a butene molecule. In the isomerization of 1-butene where a π-allyl carbanion is an intermediate, a preferential formation of *cis*-2-butene is generally observed[9,12,18,19)] which is attributed to a greater stability of a π-allyl carbanion in *cis*-form than in *trans*-form. A rotation of a C^2–C^3 bond within a π-allyl carbanion may not easily occur because of a double bond character of the bond. Therefore, if the reaction proceeds *via* a π-allyl carbanion intermediate, high raios of *cis*-2-butene to *trans*-2-butene and 1-butene to *trans*-2-butene are expected. This is the case observed. The reaction is considered to be initiated by the abstraction of a proton from butene to form a π-allyl carbanion. Oxygen ion may abstract a proton. A π-allyl carbanion may be adsorbed on the coordinatively unsaturated thorium ion.

In the isomerization of *cis*-2-butene, the abstraction of a proton may be common for both the formation of 1-butene and the formation of *trans*-2-butene. If the slow step were the abstraction of a proton, a large isotope effect would be observed for formation of both compounds. A small isotope effect for the formation of *trans*-2-butene indicates that the abstraction of a proton is not a slow step. A rotation of the C^2–C^3 bond within a π-allyl carbanion may be the slow step for the formation of *trans*-2-butene. A large isotope effect observed only for the formation of 1-butene suggests that a slow step is involved in a transfer of the adsorbed proton which had been abstracted from one of the terminal carbon atoms to the carbon atom 3 of a π-allyl carbanion.

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