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Active Sites on Barium Oxide for Isomerization of Butenes, Exchange of Butenes with D_2, and H_2–D_2 Equilibration

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The isomerization of 1-butene, the exchange reaction of butenes with D_2, and the H_2–D_2 equilibration were carried out over BaO evacuated at different temperatures. Activity for the isomerization appeared when BaO was evacuated at 450°C and reached a maximimum when evacuated at 800°C. The ratio of *cis*-2-butene to *trans*-2-butene was high ($\sim$5) over the BaO evacuated below 600°C and it became low ($\sim$1) when evacuated at higher temperatures. BaO evacuated at 550°C was not active for both the exchange reaction of butenes with D_2 and the H_2–D_2 equilibration, but BaO evacuated at 800°C showed high activity for these reactions.

Ammonia did not poison the active sites for the isomerization on BaO evacuated 550°C but strongly poisoned the active sites on BaO evacuated at 800°C.

The results of co-isomerization of *cis*-2-butene d_0–d_8 revealed that the isomerization involved intramolecular hydrogen transfer over BaO evacuated at 550°C. Over BaO evacuated at 800°C, the isomerization which was accompanied with a rapid hydrogen scrambling among butene molecules also occurred in addition to the isomerization with intramolecular hydrogen transfer.

INTRODUCTION

In recent years, alkaline earth metal oxides have been recognized to be solid base catalysts and to catalyze various kinds of reactions. These reactions include double bond and *cis–trans* isomerization of olefins (*1–6*), polymerization of styrene (*7*), conversion of benzaldehyde into benzyl benzoate (*8*), H_2–D_2 equilibration (*9, 10*), exchange reaction of olefin with D_2 (*11*), and hydrodenation of olefins (*1, 12, 13*). The activities and the selectivities for these reactions are quite dependent on the evacuation temperature of the oxides and their variations with the evacuation temperature are not the same for each reaction. For example, MgO shows its maximum activity for the isomerization of 1-butene when evacuated at 600°C (*4*) or 700°C (*3*), whereas the maximum activity for the hydrogenation of olefins is obtained by evacuation at 1100°C (*12, 13*). Therefore, there seems to exist more than a single kind of active sites on alkaline earth metal oxides. Among alkaline earth metal oxides, BaO is a catalyst on which only a few studies have been done notwithstanding that it is expected to have the strongest basic sites.

In this paper, isomerization of 1-butene, co-isomerization of *cis*-2-butene d_0/d_8, poisoning experiments for the isomerization, the exchange reaction of *cis*-2-butene with D_2, and H_2–D_2 equilibration have been studied over BaO which had been evacuated at different temperatures to characterize the nature of active sites. The existence of different kinds of active sites is demonstrated.

EXPERIMENTAL METHODS

BaO used as a starting material was obtained from E. Merck Company and had a purity of better than 98%. The starting material contained CO_2, H_2O and O_2 as forms of carbonate, hydroxide and peroxide, respectively. The amounts of CO_2, H_2O and O_2 which evolved on heating the starting material were measured as follows. The BaO was evacuated at 200°C in a system to which a trap and a manometer were attached. The sample was heated as desired temperature for 2 hr, evolving gas being trapped with liquid nitrogen. There remained a material in gas phase uptrapped with liquid nitrogen and it was analyzed by mass filter to be oxygen. The amount of gas evolved when liquid nitrogen was replaced by dry ice was taken as an amount of CO_2 and the amount of gas evolved when dry ice was removed was taken as an amount of H_2O. This procedure was repeated every 100°C increment of the temperature until 1000°C.

The isomerization was carried out at 0°C in a closed recirculation reactor having a volume of ca. 400 ml. Barium oxide (60–150 mg) was placed in a quartz reaction vessel after being sieved into 24–35 mesh and evacuated to 10^{-5} Torr (1 Torr $= 133.3\ \mathrm{N\ m^{-2}}$) at various temperatures for 2–3 hr. A fresh sample was used for each reaction. Butenes were purified by passing through molecular sieves 4A maintained at −78°C.

For poisoning experiments, NH_3, H_2O and CO_2 were used as poisons. After the evacuation at 550 or 800°C, a catalyst was exposed to a poison under a pressure of several torricellis at a certain temperature (primarily at room temperature) and evacuated at room temperature or sometimes at higher temperatures.

For the co-isomerization, a mixture containing about equal amounts of *cis*-2-butene and perdeuterated *cis*-2-butene was used as a reactant. An isotopic purity of the perdeuterated *cis*-2-butene was more than 99.6%. The products were analyzed by gas chromatography. A column containing propylene carbonate on Uniport C in 4 mm o.d. Cu tubing was operated at 0°C. The products in the co-isomerization were separated by preparative scale gas chromatographic column (10 m of propylene carbonate on Uniport C in 8 mm o.d. Cu tubing), collected at liquid nitrogen, and subjected to mass spectral analysis.

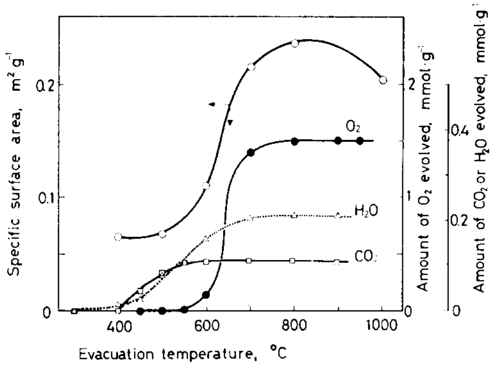

FIG. 1. Specific surface areas (○) and cumulative amounts of evolved H_2O (△), CO_2 (□), and O_2 (●) at various temperatures.

For the butene-D_2 exchange reaction, premixed gas of *cis*-2-butene and D_2 (1:1) was used as a reactant and the reaction was carried out at 0°C. The butenes were analyzed by gas chromatography and mass spectroscopy as in the case of co-isomerization.

The H_2–D_2 equilibration was carried out at 0°C over the catalyst which had been evacuated at 550 or 800°C. A 100 Torr of a mixture containing about equal amounts of H_2 and D_2 was used as a reactant and periodically analyzed by mass spectroscopy. A specific surface area was measured by the nitrogen adsorption at liquid nitrogen temperature.

RESULTS

In Fig. 1 are shown the specific surface areas and the amounts of evolved gases plotted against evacuation temperature. The evolutions of CO_2 and H_2O began at 400°C and continued up to 600 and 700°C, respectively. The evolution of O_2 occurred over the range of 600–750°C. Although the specific surface area may not be so

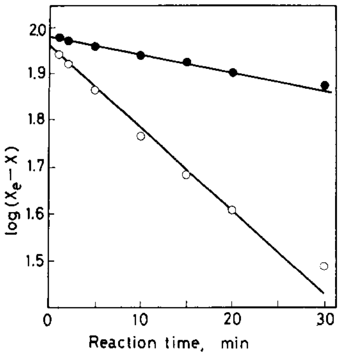

FIG. 2. First order plots for the isomerization of 1-butene over the BaO (550) 0.037 g (●) and the BaO (800) 0.060 g (○) at 0°C.

accurate because of a small value, it increased with the evolution of O_2.

The conversion rate of 1-butene was expressed by a first order equation with respect to a pressure of 1-butene. The first order plots are shown in Fig. 2, where X and X_e are percentage conversions of 1-butene at time t and at equilibrium, respectively. The activity was expressed by the rate constant, k, in the equation, $dX/dt = k(X_e - X)$.

The variations of the activity and the initial ratio of *cis*-2-butene to *trans*-2-butene in the isomerization of 1-butene are shown in Fig. 3. The activity appeared when the catalyst was evacuated at 450°C and attained a maximum when evacuated at 800°C. The ratio of *cis*-2-butene to *trans*-2-butene decreased remarkably when the catalyst was evacuated at 600–700°C.

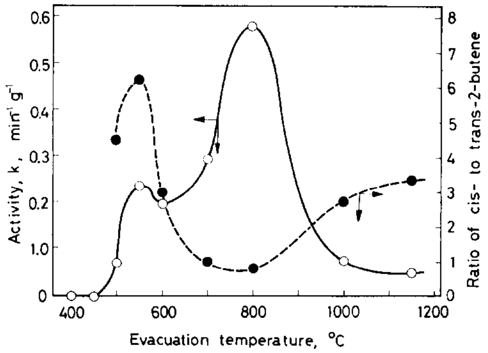

FIG. 3. Variation of the activity (○) and the ratio of *cis*-2-butene to *trans*-2-butene (●) with evacuation temperature at 0°C.

TABLE 1

Poisoning Effect with H_2O, CO_2, and NH_3

Catalyst	Poison	Activity ratio of poisoned to unpoisoned		
		Total	1- to *cis*-	1- to *trans*-
BaO(800)	H_2O	0	0	0
	CO_2	0	0	0
	NH_3	0.11	0.16	0.07
	O_2[a]	0.07	0.13	0.02
BaO(550)	H_2O	0	0	0
	CO_2	0	0	0
	NH_3	1.80	2.20	1.75

[a] BaO(800) was exposed to O_2 at 600°C and evacuated at 400°C. Reaction temperature: 0°C; initial pressure of 1-butene: 180 Torr; amount of catalyst: 0.150 g.

In Table 1 are given the poisoning effects with H_2O, CO_2, and NH_3 on the catalysts which had been evacuated at 550 and 800°C (which will be abbreviated to BaO(550) and BaO(800), respectively). Water and CO_2 completely poisoned both of the active sites of BaO(550) and the BaO(800). Poisoning with NH_3 produced a different effect on the BaO(550) than it did on the BaO(800). Ammonia strongly poisoned the active sites of the BaO(800), while it actually increased the activity of the BaO(550). When the BaO(800) was treated with 10 Torr of oxygen at 600°C followed by the evacuation at 400°C, which may produce barium peroxide, the activity decreased considerably, only 7% of its original activity being left.

The isotopic profiles of butenes in the co-isomerization over the BaO(550) and the BaO(800) are listed in Table 2. Over the BaO(550), the products consisted essentially of non-exchanged d_0 and d_8 isotopic species. The numbers of H (or D) atoms exchanged per molecule (AEM values) (*14*), extrapolated to zero con-

TABLE 2

Co-isomerization of *cis*-2-Butene d_0/d_8 over BaO(550) and BaO(800)

Catalyst	Product	% each product	% each isotopic species									AEM[a]	IE[a]
			d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8		
Non[b]	1-	0.1	65.0	0	0	0	0	0	0	0	35.0	—	—
	t-	0.6	47.2	0	0	0	0	0	0	2.5	50.3	—	—
	c-	99.4	48.9	0	0	0	0	0	0	2.9	48.2	—	—
BaO(550)	1-	2.3	76.0	2.9	0	0	0	0	0	0	21.1	0.03	3.8
(0.060 g)	*t*-	2.2	77.9	4.1	1.0	0	0	0	0	1.0	16.1	0.07	5.0
	c-	95.5	47.7	0.6	0	0	0	0	0	0.8	51.0	0.01	0.94
	1-	3.8	67.8	5.5	3.0	0	0	0	0.1	5.8	18.0	0.17	3.2
	t-	4.0	76.5	8.9	1.7	0	0	0	0	2.2	13.0	0.14	5.7
	c-	92.2	47.5	1.0	0	0	0	0	0	1.9	49.3	0.03	0.95
BaO(800)	1-	1.3	58.5	3.7	2.1	2.0	2.8	2.9	3.3	5.8	18.7	—	—
(0.060 g)	*t*-	7.0	23.0	8.8	9.8	11.7	12.7	10.8	7.5	4.6	11.0	—	—
	c-	91.7	48.8	0.8	0	0	0	0	0	2.5	47.9	—	—
	1-	2.5	36.8	5.9	5.3	6.9	8.8	8.8	7.8	7.5	10.5	—	—
	t-	23.0	8.3	7.7	10.5	18.0	20.0	16.8	9.9	4.1	3.0	—	—
	c-	74.5	38.7	3.1	2.1	2.6	3.0	2.6	2.5	4.3	40.7	—	—
	1-	2.6	16.8	7.8	7.9	12.8	15.9	15.0	10.6	6.4	6.6	—	—
	t-	34.4	2.9	5.4	11.9	20.1	23.9	19.3	10.5	3.7	2.3	—	—
	c-	63.0	34.2	2.8	3.4	5.0	6.1	5.2	4.0	3.9	35.4	—	—

[a] AEM $= \sum_{i=1}^{4} i \cdot N_i + \sum_{i=5}^{8} (8 - i)N_i$, IE $= (\sum_{i=0}^{3} N_i + \frac{1}{2}N_4)/(\sum_{i=5}^{8} N_i + \frac{1}{2}N_4)$, where N_i represents a fraction of isotopic species containing i D atoms.

[b] Starting mixture; reaction temperature: 0°C.

TABLE 3

Isotopic Profile of the "Non-exchanged Part" [a] in the Co-isomerization of *cis*-2-Butene d_0/d_8 over BaO(800)

Product	% each product	% each isotopic species									AEM	IE
		d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8		
1-	1.4	65.2	3.7	0.9	0	0	0.4	2.2	5.7	21.7	0.23	2.3
t-	3.3	42.8	13.5	8.6	2.8	0	1.0	4.4	5.7	21.1	0.62	2.1
c-	95.4	49.0	0.9	0	0	0	0	0	1.9	48.2	0.03	1.0
1-	2.4	54.0	7.2	2.6	0	0	2.3	6.2	9.6	17.8	0.41	1.8
t-	8.2	29.9	19.9	16.5	7.0	0	2.9	7.0	6.6	10.2	1.03	2.7
c-	98.4	43.8	2.8	1.1	0.2	0	0.2	1.6	3.9	46.2	0.14	0.92
1-	2.9	40.0	14.6	3.8	0	0	5.2	10.3	11.0	15.1	0.69	1.4
t-	14.4	22.2	21.3	18.2	6.3	0	2.0	8.7	9.5	12.7	1.10	2.0
c-	82.7	44.0	2.6	1.3	0.3	0	0.5	2.2	4.1	45.1	0.16	0.93

[a] For a calculation, see text. Reaction temperature: 0°C.

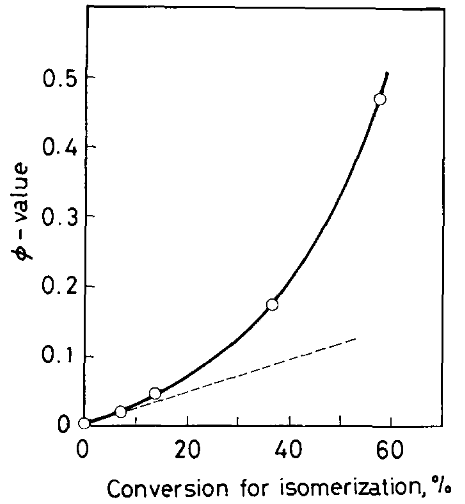

FIG. 4. ϕ-Value of a mixture of butenes vs conversion of the isomerization in the reaction of *cis*-2-butene with D_2 over the BaO (800). (— —). The initial gradient; reaction temperature: 0°C.

version were small (<0.1) for both *cis*-2-butene and *trans*-2-butene. This indicates that the reaction involves an intramolecular hydrogen transfer. The ratio of light molecules to heavy molecules represents the isotope effect (IE). Large isotope effects for the formations of 1-butene and *trans*-2-butene indicate that the slow step is the cleavage of a C–H bond.

Over the BaO(800), large amounts of exchanged isotopic species were produced. The isotopic profile showed triple peaks at d_0, d_4 and d_8 isotopic species which could be divided into two parts. One part consists of a binomial distribution with a maximum at the d_4 species. The other part consists essentially of non-exchanged isotopic species. The latter part can be calculated by the subtraction of the former part from whole part on the assumption that all d_4 species belong to the former part. The isotopic profiles of the latter part are listed in Table 3. The isotopic profile of the latter part resembles that produced over the BaO(550). The AEM values extrapolated to zero conversion were close to zero. The relative amounts of 1-butene, *trans*-2-butene and *cis*-2-butene in a former part were 1, 21, and 10, respectively, at the conversion of 25.5%. These amounts are close to thermodynamic equilibrium values, 1:27:5.

For the exchange reaction of *cis*-2-butene with D_2, the BaO(550) did not show any activity but the BaO(800) was active. The average number of D atoms in a molecule, the "ϕ-value," for a mixture of three butenes is plotted against isomerization conversion in Fig. 4. The initial gradient shows the relative values of the isomerization rate to the equilibrium rate. If the exchange rate is equal to the isomerization rate, the gradient should be $1/100\%^{-1}$. As the observed gradient was $0.0023\%^{-1}$, the exchange rate is slower than the isomerization rate under the reaction condition employed.

In Table 4 are listed the activities for the H_2–D_2 equilibration over the catalysts evacuated at different temperatures. The BaO(550) was inactive for the reaction, but the BaO(800) and the catalysts evacuated at higher temperatures were active.

DISCUSSION

The coincidence of the temperature at which the activity appeared with the temperature at which H_2O and CO_2 evolved suggests that the active sites are generated by removing H_2O and/or CO_2 which were contained in the starting material as impurities. The generation of the active sites in this way is common to other alkaline earth metal oxides such as MgO(4), CaO(4), and SrO(6).

TABLE 4

Activity for H_2–D_2 Equilibration over BaO at 0°C

Evacuation temp (°C)	Activity HD (%/min/g)
550	0
800	8.1
1000	8.9
1150	9.2

The distinct differences in the catalytic activity were observed between the BaO(550) and the BaO(800). These are summarized qualitatively in Table 5. Besides these differences, the BaO(550) was not poisoned with NH_3 for the isomerization, whereas the BaO(800) was strongly poisoned by NH_3 for the isomerization. Furthermore, the isotopic profiles in the co-isomerization were quite different for the two catalysts.

In general, preferential formation of *cis*-2-butene from 1-butene was observed over basic catalysts (*15–18*). The BaO(550) showed a high ratio of *cis*-2-butene to *trans*-2-butene in the isomerization of 1-butene and was not poisoned with NH_3. Therefore, the active sites of the BaO(550) are suggested to be basic sites. Over the BaO(550), it is likely that H^+ is abstracted from 1-butene at the allyl position to form the π-allyl carbanion. The same H^+ transfers to the terminal carbon to complete the formation of 2-butenes in an intramolecular hydrogen transfer. The amount of O_2 evolved between 550 and 800°C was so large that a considerable fraction of the surface of the BaO(550) was probably in a form of barium peroxide. However, barium peroxide does not seem to be active for the isomerization, because the isomerization hardly occurred over the catalyst obtained by the treatment of the BaO(800) with O_2 at 600°C. The O^{2-} which appeared on the surface by evolving H_2O and CO_2 may be a main active site on the BaO(550) and acts as a basic site.

The active sites of the BaO(800) are quite complex. The isotopic profile, which could be divided into two parts, suggests the existence of two kinds of sites; one kind produces the "non-exchanged part" and the other produces the "binomial part." Although the binomial distribution of the isotopic species with a maximum at the d_4 species is only an assumption, the latter kind of sites should be highly active for the hydrogen scrambling among olefin molecules. Since the binomial parts consists almost entirely of an equilibrium mixture of *n*-butenes, the isomerization of butenes should take place very fast on the sites of this kind. The butene-D_2 exchange reaction and the H_2–D_2 equilibration may occur on the same kind of the sites as well as hydrogen scrambling among olefin molecules.

TABLE 5

Comparison of BaO(550) with BaO(800)[a]

Reaction	BaO(550)	BaO(800)
Butene isomerization	+	+
H exchange between C_4H_8 and C_4D_8	−	+
Exchange of butene with D_2	−	+
H_2–D_2 equilibration	−	+

[a] +: active, −: inactive. Reaction temperatures are 0°C for all reactions.

From the similarity of the isotopic profile of the "non-exchanged part" over the BaO(800) to that obtained over the BaO(550), one kind of active sites on the BaO(800), over which the isomerization proceeds with intramolecular hydrogen transfer, seems to be the same kind as that on the BaO(550).

The other kind of the active sites on the BaO(800) is strongly poisoned with NH_3. Since oxygen deficient sites or incompletely coordinated barium ions which will be formed on the surface by evacuation at 800°C are considered to be very accessible to NH_3, the active sites probably include incompletely coordinated barium ions on the surface. There should be O^{2-} adjacent to the incompletely coordinated barium ion. Although the reaction mechanisms of the exchange reaction and the isomerization over the sites are unknown, D_2 molecules should at least dissociate on the sites in order to cause the exchange reaction. It seems more likely to postulate a pair containing an incompletely coordinated barium ion and an adjacent O^{2-}

than to postulate a barium ion acting alone as an active site.

The catalytic properties of BaO are similar to those of Al_2O_3 in several points. Alumina, when properly activated, has different types of active sites. One of which is active for double bond isomerization of olefins and the other is active for exchange of olefins with D_2. These sites are independent of each other (*19*). One of the similarities between Al_2O_3 and BaO is that both of them have a type of sites over which olefins undergo double bond isomerization with intramolecular hydrogen transfer and do not exchange with D_2 (*20, 21*). Another similarity is that both of the "exchange sites" on Al_2O_3 and BaO are associated with metal ions exposed on the surface (*23*). A properly high activation temperature may be required for the generation of this type of site on both catalysts.

There are also distinct differences between Al_2O_3 and BaO. The "exchange sites" on Al_2O_3 are not active for the isomerization of butenes, while the "exchange sites" on BaO are active for the isomerization of butenes. The position of a H atom in an olefin which undergoes exchange reaction might be different for Al_2O_3 and BaO. While exchange occurs only with an olefinic hydrogen over Al_2O_3 (*23*), an allylic hydrogen seems to be activated over BaO as the exchange reaction is accompanied by a fast isomerization.

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