Active Sites on CaO and BaO for Isomerization of Butenes and Exchange of Butenes with Deuterium: Selective Poisoning of the Exchange Sites with Oxygen

HIDESHI HATTORI AND AKIKO SATOH

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

The reactions of cis-2-butene, ethylene, and propylene with D_2, and coisomerization of cis-2-butene d_0/d_8 were carried out over CaO and BaO evacuated at different temperatures, and the effects of poisoning with oxygen were examined. Over CaO evacuated at 500, 600, or 1038°C, the exchange of butene with D_2 did not substantially occur but the isomerization occurred. Over CaO evacuated at 700 or 800°C, and BaO evacuated at 600 or 800°C, both the exchange and isomerization reactions occurred. The exchange rate of ethylene with D_2 was much slower than that of propylene or butene. Oxygen poisoned the exchange reaction of butene more selectively than it did the isomerization. Results of the coisomerization of cis-2-butene d_0/d_8 over BaO evacuated at 600°C showed that rapid hydrogen scrambling among butene molecules, which accompanied the isomerization, occurred in addition to the isomerization which involved an intramolecular hydrogen transfer. Poisoning with oxygen resulted in an elimination only of the hydrogen scrambling. Oxygen did not poison the isomerization reaction which involved an intramolecular hydrogen transfer. Two types of active sites are proposed on CaO and BaO, whose appearances are quite dependent on the evacuation temperature. One of them (Site I) is active only for the isomerization that involves intramolecular hydrogen transfer, and the other (Site II) is active both for the isomerization and exchange reactions. The nature of these sites and the reaction mechanisms over these sites are discussed.

INTRODUCTION

Catalytic activity and selectivity of alkaline earth metal oxides are quite dependent upon the pretreatment temperature (1–7). For the isomerization of butene, MgO (3, 4), CaO (4), SrO (5), and BaO (7) show similar dependencies of the activity and selectivity on the evacuation temperature. They become active by evacuation at the temperature where H_2O and/or CO_2 begin to be removed from the surfaces, and they show a high ratio of cis-2-butene to $trans$-2-butene in the isomerization of 1-butene. On evacuation at higher temperatures, the ratio of cis-2-butene to $trans$-2-butene decreases. With further rise of

evacuation temperatures, the activity gradually decreases.

In a previous paper (7), the nature of active sites on BaO was studied for the isomerization of butene, butene–D_2 exchange reaction, and H_2–D_2 equilibration. BaO that had been evacuated at 550°C was active for the isomerization of butene, in which an intramolecular hydrogen transfer was involved, but it showed no activity for the butene–D_2 exchange reaction and the H_2–D_2 equilibration. On the other hand, BaO that had been evacuated at 800°C was active for all the reactions described above. It was suggested that one type of active site exists on the BaO evacuated at 550°C and that more than one type of

32

active site exists on BaO evacuated at 800°C. It now appears that the alkaline earth metal oxides other than BaO show such dual sites when they are properly pretreated. If a certain molecule poisons one of the dual sites selectively, the existence of two types of sites on alkaline earth metal oxides and their natures will be distinguished by referring to the nature of a poison.

In the present paper, poisoning experiments with oxygen for the isomerization of butenes and the exchange of butenes with D$_2$ were carried out over BaO and CaO.

EXPERIMENTAL METHODS

Catalysts

The calcium oxide and BaO catalysts were prepared from calcium hydroxide (Kanto Chemical Co.) and from granular BaO (E. Merck Co.) by evacuation at various temperatures for about 3 hr.

For poisoning experiments with oxygen, three different methods were employed. (A) The CaO that had been evacuated at 700°C was exposed to 4.0×10^{13} molecules O$_2$/cm^2 at room temperature and served for a reaction without further evacuation. (B) The CaO that had been evacuated at 700°C was exposed to sufficient amounts of oxygen to cover a monolayer at room temperature, and then was evacuated at room temperature for 30 min. (C) To the BaO that had been evacuated at 600 or 1100°C, about 10^{16} molecules O$_2$/cm^2 were added at room temperature and part of it was evacuated at room temperature for 30 min.

Specific surface area of CaO evacuated at 700°C was 51.9 m^2/g; the BaO samples evacuated at 600 and 1100°C had surface areas of about 0.1 and 0.2 m^2/g, respectively.

Reactants

cis-2-Butene was obtained from Takachiho Chemical Co. Perdeuterated *cis*-2-butene was prepared by a repeated exchange of butenes with D$_2$ over MgO and separated from the other butenes by a preparative gas chromatographic column. The isotopic purity of d_8 isotopic species was more than 95%. Butenes were purified by passage through 4A molecular sieves at −78°C after a vacuum distillation. Deuterium was purified by passage through 13X molecular sieves at −196°C and stored over a well-degassed mixture of 13X molecular sieves and MgO. Ethylene, propylene, and oxygen were passed through 13X molecular sieves at −78°C and stored over well-degassed MgO.

Reaction Procedure

In the exchange reaction of *cis*-2-butene with D$_2$, about 10 Torr (1 Torr = 133.3 N m^{-2}) of *cis*-2-butene was introduced into a recirculation system and frozen in a trap at −196°C. To the system, about 100 Torr of D$_2$ was introduced. After the reactants were thoroughly mixed by being recirculated, the reaction was started. The reactions were carried out primarily at 0°C for exchange reactions, and at room temperature for poisoning experiments. The volume of the reaction system was about 1200 ml. For the exchange reaction of ethylene and propylene with D$_2$, 10 Torr of a mixture containing ethylene and propylene (composition ratio 1:1.02) and 62.5 Torr of D$_2$ were reacted at room temperature. The exchange reaction of ethylene with D$_2$ in the absence of propylene was also carried out.

For the coisomerization, a microcatalytic pulse reactor was employed, and the reaction was carried out at room temperature. About 20 μ mol of *cis*-2-butene, which consisted of an equal amount of d_0 and d_8 isotopic species, was introduced into the helium stream ahead of the catalyst. Helium carrier gas was purified by passage through 13X molecular sieves kept at −196°C and flowed at various rates (15–120 ml min^{-1}) to obtain different conversion levels.

TABLE 1

Activities of CaO and BaO for *cis*-2-Butene–D₂
Exchange Reaction

Catalyst	Evacuation temperature (°C)	Reaction temperature (°C)	Activity k, min⁻¹·g⁻¹
CaO	500	0	3×10^{-3}
CaO	600	0	6×10^{-2}
CaO	700	0	2.6
CaO	800	0	2.0
CaO	1038	0	4×10^{-3}
CaO	700	18	6.3
CaO[a]	700	16	1.1
CaO[b]	700	19	1.6×10^{-2}
BaO	800	0	1.8
BaO	600	17	$2.5 \times 10^{-}$
BaO[a]	600	18	1.6×10^{-2}

[a] Exposed to O₂ followed by evacuation at room temperature.

[b] Exposed to 4×10^{13} molecule/cm² of O₂.

The produced butenes were gas chromatographically separated. A gas chromatographic column of 10-m containing propylene carbonate on Celite in 8-mm OD Cu tubing was operated at 0°C. The separated isomers were trapped at −196°C and subjected to a mass spectral analysis. Mass spectra were measured on a Hitachi mass spectrometer RUM-2 at low ionization voltage to minimize fragmentation, and parent peaks were measured for calculation.

RESULTS

Exchange of cis-2-Butene with D₂ over CaO and BaO; Dependency on the Pretreatment Temperature

The activity for the exchange reaction was expressed by the first order rate constant k obtained from equation (8)

$$k = \frac{\phi_\infty}{t} \left(1n \frac{\phi_\infty}{\phi_\infty - \phi} \right) \times \frac{1}{w},$$

where ϕ is the average number of D atoms per molecule and ϕ_∞ is the equilibrium value of ϕ at $t = \infty$, which was calculated

from the relative numbers of D atoms and H atoms in a reacting system without taking account of the isotope effect for equilibrium, and w is a weight of catalyst.

In some runs where a quite low activity was observed, e.g., the reactions over CaO evacuated at 500 or 1038°C, and over poisoned CaO, plots of $1n\phi_\infty/(\phi_\infty - \phi)$ vs t gave a slightly curved line. The rate constant k in these cases has an uncertainty of ±50%.

In Table 1 are listed the activities of CaO and BaO which were pretreated at different temperatures. Over the CaO pretreated at 500, 600, or 1038°C, almost no H atoms of butene were exchanged with D₂ at 0°C. Substantially only isomerization occurred. Over the CaO pretreated at 700 or 800°C, both the exchange reaction and the isomerization occurred at 0°C at comparable rates, but only the isomerization proceeded at −30°C. Over the BaO pretreated at 600°C, both reactions occurred, though the ratio of the exchange reaction to the isomerization was lower than
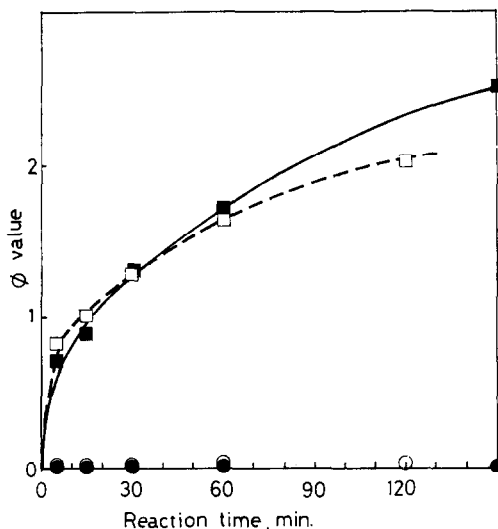

Fig. 1. The ϕ values of propylene and ethylene vs reaction time in the reaction of C₃H₆ + C₂H₄ + D₂ over CaO and BaO. □, Propylene; ○, ethylene over the 700° C evacuated CaO (0.0096 g) at 19.0°C. ■, Propylene; ●, ethylene over the 600°C evacuated BaO (0.1336 g) at 17.5°C.

TABLE 2

Selected Values of Isotopic Distribution for cis-2-Butene–D₂ Exchange Reaction

Catalyst (evacuation temp.) (weight)	Reaction temperature (°C)	Product	Percentage each product	Percentage each isotopic species									φ Value
				d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	
CaO (700°C)	18	1	3.0	65.9	22.3	8.0	2.5	0.9	0.3	0	0	0	0.509
(0.0034 g)		t	68.9	61.5	25.0	9.3	3.0	1.0	0.1	0	0	0	0.571
		c	28.1	67.3	21.4	7.9	2.5	0.7	0.2	0	0	0	0.485
CaO (700°C)[a]	16	1	3.2	78.4	17.9	3.3	0.4	0	0	0	0	0	0.257
(0.0034 g)		t	67.5	78.5	18.2	2.8	0.2	0	0	0	0	0	0.244
		c	29.3	79.6	17.2	3.0	0.2	0	0	0	0	0	0.238
CaO (700°C)[b]	19	1	3.1	80.9	16.7	2.1	0.3	0	0	0	0	0	0.218
(0.1150 g)		t	70.2	87.3	11.7	1.0	0	0	0	0	0	0	0.137
		c	26.7	80.2	17.4	2.1	0.2	0	0	0	0	0	0.222
BaO (600°C)	17	1	2.3	70.8	5.6	4.0	4.0	4.3	4.0	3.2	2.1	1.9	1.12
(0.1285 g)		t	21.4	31.1	11.9	10.2	10.2	10.3	9.7	8.2	5.7	2.8	2.63
		c	76.3	92.3	2.0	1.2	1.1	1.1	0.9	0.8	0.5	0.2	0.257
BaO (600°C)[c]	18	1	4.9	90.3	5.2	2.4	1.3	0.5	0.3	0	0	0	0.174
(0.5055 g)		t	28.9	67.6	17.3	8.2	4.1	2.0	0.6	0.3	0	0	0.588
		c	66.2	94.4	3.1	1.4	0.6	0.3	0.1	0	0	0	0.094

[a] Exposed to O₂ followed by evacuation at room temperature (poisoning method (B)).
[b] Exposed to 4 × 10¹³ molecule/cm² of O₂ (poisoning method (A)).
[c] Exposed to O₂ followed by evacuation at room temperature (poisoning method (C)).

that observed over the BaO pretreated at 800°C. If the maximum activity of BaO and CaO are compared on an unit surface area basis, BaO is much more active than CaO.

The Exchange Reactions of Ethylene and Propylene with D₂

In Fig. 1, the φ values are plotted against reaction time for the exchange reaction of a mixture of ethylene and propylene with D₂ over CaO and BaO pretreated at 700 and 600°C, respectively. Over both catalysts, the exchange rates for ethylene were much slower than those for propylene. The exchange rate for ethylene did not change much in the absence of propylene. The exchange rate for propylene was as fast as that for butene.

Poisoning Effect with O₂ on the Exchange Reaction and the Isomerization

Oxygen poisoned the isomerization and exchange reactions over both catalysts. By the poisoning method (A), the activity of CaO for the isomerization of cis-2-butene was reduced to about 3% of its original

activity: however, by the poisoning method (B), the activity was reduced to only 50% of its initial value. Over the BaO evacuated at 600°C, the activity for the isomerization also decreased to about 50% of its initial activity by the poisoning method (C).

Since the isomerization rates were so fast that the rate of circulation might influence the observed reaction rate, reliable data could only be obtained for an effectiveness of oxygen poisoning on the exchange reaction to that on the isomerization if slopes of φ values plotted against isomerization conversion are compared. In Fig. 2, the φ values of a mixture of three butenes are plotted against isomerization conversion of cis-2-butene over the unpoisoned CaO which had been evacuated at 700°C. The same plots are shown in Fig. 3 for BaO which had been evacuated at 600°C. Since the φ values were higher for the unpoisoned catalysts than for the poisoned catalysts when compared at similar conversion, it is apparent that the exchange reaction was poisoned with O₂ more intensively than the isomerization. Selected distributions of isotopic species in each isomer are listed in
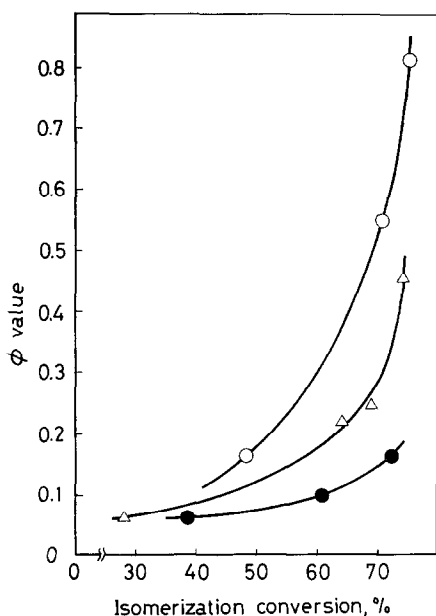
FIG. 2. The ϕ values of butenes vs isomerization conversion over CaO evacuated at 700°C. O, Unpoisoned CaO, reaction temperature 18°C. △, Poisoned with 6×10^{15} molecules/cm² of O_2 followed by evacuation at room temperature for 30 min. Reaction temperature 16°C. ●, CaO poisoned with 4×10^{13} molecules/cm² of O_2. Reaction temperature 19°C.

Table 2. The distributions were not binomial for either CaO or BaO; the fractions of highly deuterated isotopic species were larger than those expected from the ϕ values on the assumption of a binomial distribution. This tendency was prominent for BaO. The products were near thermodynamic equilibrium for CaO. The exchange is much slower than the isomerization over CaO.

The distributions of isotopic species in the coisomerization of cis-2-butene d_0/d_8 over poisoned and unpoisoned BaO which had been evacuated at 600 and 1100°C are given in Table 3. The distributions of isotopic species in trans-2-butene produced over the unpoisoned BaO showed triple peaks at d_0, d_4, and d_8. Although the peaks at d_4 are not distinct for 1-butene and cis-2-butene, these isotopic species could be divided into two parts as was done in the previous paper (7). One part consists of

a binomial distribution with a maximum at the d_4 isotopic species (the "binomial part"). The isotopic species were assumed to be at equilibrium regarding isotopic distribution in this part. Percentages of the "binomial part" in each butene are listed in the next to last column in Table 3. The other part (the "nonexchanged part") consists mainly of nonexchanged species, d_0 and d_8, with decreasing amounts of mono-, di-, and triexchanged isotopic species. This part could be calculated by the subtraction of the former part from the whole part on the assumption that all d_4-isotopic species belong to the "binomial part." The percentages of three butene isomers which belong to the "binomial part" are listed in the last column in Table 3. These values are calculated by the multiplication of the percentages of each product (fourth column) by the percentages of the "binomial part" in each product (next to the last column) and finally normalization to 100%
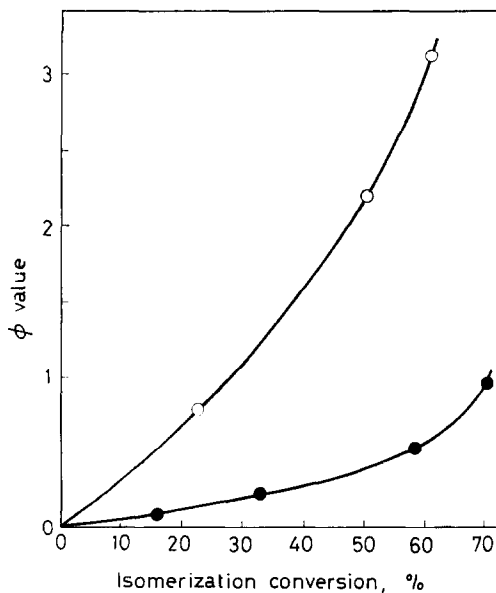

FIG. 3. The ϕ values of butenes vs isomerization conversion over BaO evacuated 600°C. O, Unpoisoned BaO. Reaction temperature 17°C. ●, BaO poisoned with 10^{16} molecules/cm² of O_2 followed by evacuation at room temperature for 30 min. Reaction temperature 18°C.

TABLE 3

Coisomerization of cis-2-Butene d_0/d_8 over BaO

Pulse no.	Flow rate (ml/s)	Product	Percentage each product	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	IE[a]	Percentage binomial part in each product	Percentage each isomer which belongs to binomial part
	BaO evacuated at 600°C (0.0513 g), unpoisoned; reaction temperature 18.5°C														
1	2.0	1	2.8	50.5	7.1	3.0	2.7	2.6	3.2	4.9	8.4	17.7	1.96	9.5	3
		t	11.0	23.9	12.1	9.9	10.4	10.8	9.8	7.8	6.0	9.4	2.25	50.3	71
		c	86.2	42.2	2.7	1.0	0.7	0.6	0.8	1.6	5.5	45.0	0.88	2.3	26
4	1.03	1	1.6	68.1	2.0	1.1	1.3	1.9	1.8	2.0	3.9	17.9	3.05	6.9	3
		t	6.3	22.6	7.6	8.5	11.3	12.4	10.7	7.4	5.2	14.4	1.57	45.2	81
		c	92.1	45.7	0.1	0.2	0.2	0.2	0.2	0.4	2.9	50.1	0.85	0.6	16
BaO evacuated at 600°C (0.1607 g), poisoned; reaction temperature 15.5°C															
3	0.503	1	2.6	71.7	0.8	0.6	0	0	0	0.6	2.6	23.7	2.72	0	0
		t	5.4	61.6	5.7	2.3	1.4	1.3	1.4	1.7	4.5	20.0	2.69	3.6	100
		c	92.0	48.1	0	0	0	0	0	0	2.5	49.4	0.93	0	0
BaO evacuated at 1100°C (0.0490 g), unpoisoned; reaction temperature 18.0°C															
3	0.65	1	2.2	56.8	12.1	1.1	1.5	1.4	1.6	2.2	4.8	18.4	2.76	5.3	3
		t	7.7	31.4	14.0	6.8	8.9	10.0	8.4	5.8	4.1	10.6	3.07	36.5	63
		c	90.1	42.2	2.7	0.4	0.4	0.5	0.5	1.2	3.9	48.2	0.85	1.7	34
BaO evacuated at 1100°C (0.1026 g), poisoned; reaction temperature 18.5°C															
1	0.51	1	5.3	28.7	7.8	3.6	2.0	1.9	3.4	6.8	14.5	31.3	0.74	7.1	4
		t	34.8	32.3	16.9	9.4	6.0	4.9	5.6	7.7	9.5	7.8	2.41	17.9	65
		c	59.9	26.7	7.0	3.2	1.6	1.4	2.0	4.8	12.7	40.5	0.63	5.0	31
2	0.97	1	4.3	55.2	7.4	0.6	0.3	0.3	0.6	1.8	7.1	26.7	1.77	1.1	3
		t	13.3	51.2	13.4	5.4	3.2	2.4	2.9	4.3	6.6	10.7	3.29	8.9	65
		c	82.4	43.5	2.7	0.5	0.4	0.3	0.4	1.1	6.5	44.6	0.89	0.7	32
4	2.00	1	2.7	69.3	4.6	0.5	0	0	0	0.8	3.7	21.0	2.92	0	0
		t	5.2	57.9	9.4	3.0	1.4	1.2	1.4	2.3	4.8	18.5	2.76	4.5	100
		c	92.1	44.8	0.9	0.1	0	0	0	0.4	3.6	50.1	0.85	0	0

Note: Columns d_0–d_8 fall under the spanning header "Percentage each isotopic species."

[a] The ratio of the "light molecule" to the "heavy molecule," calculated for the "nonexchange part."

for the total. These values are close to thermodynamic equilibrium values at 18°C, 3.0, 77.7, and 19.3% for 1-butene, *trans*-2-butene, and *cis*-2-butene, respectively (*9*). Oxygen poisoning resulted in a drastic decrease in the "binomial part." The "non-exchanged part" remained almost constant with oxygen poisoning.

DISCUSSION

The results suggest that two different types of sites exist on CaO and BaO. The appearance of these sites is dependent on the evacuation temperature. Evacuation of CaO at 500°C results in the generation of only one type of site (Site I) which is active for the isomerization but not for the exchange reaction of butene with D_2. Evacuation of CaO at a high temperature, e.g., 700°C, produces the other type of site (Site II) in addition to Site I. Site II is active for both the isomerization and the exchange reaction.

Two types of sites also appeared on BaO. Evacuation of BaO at 550°C results in the generation of only one type of site (Site I) and evacuation above 600°C results in the generation of the other type of site (Site II) in addition to Site I. The nomenclatures are the same as those on CaO because the nature of these sites are the same for both BaO and CaO in the sense that Site I is active only for the isomerization and Site II is active for both the isomerization and the exchange reaction.

A more intensive poisoning effect with oxygen on Site II than on Site I indicates that Site II is more accessible to oxygen. This suggests a participation of incompletely coordinated metal ions or oxygen-deficient sites in Site II. Incompletely coordinated metal ions have been reported to appear on the surfaces of some oxides such as Cr_2O_3 (*15*), ZnO (*16*), and Al_2O_3 (*17*) under rigorous degassing conditions. For Al_2O_3, oxygen-deficient sites have been produced by high temperature evacuation (*18, 19*) or by treatment with hydrogen

at elevated temperatures (*20*). The generation of Site II at a higher evacuation temperature seems to be consistent with the postulation that incompletely coordinated metal ions or oxygen-deficient sites are associated with Site II.

As for Site I, a relatively mild poisoning effect with oxygen suggests that a basic O^{2-} on the surface is a main component of Site I, which may be adjacent to completely coordinated metal ions. In a base catalyzed isomerization of butene, the reaction is considered to proceed via a π-allyl butyl carbanion intermediate whether the catalyst is homogeneous or heterogeneous (*10–14*). The intermediate in the isomerization of *cis*-2-butene over Site I is probably a π-allyl butyl carbanion. *cis*-2-Butene releases its allyl hydrogen to the surface O^{2-} as a proton to form a π-allyl carbanion, which may be stabilized by a metal ion adjacent to the O^{2-}. The proton transfers to the $C^{(3)}$ to produce 1-butene or returns to the terminal carbon after the rotation of the $C^{(2)}$–$C^{(1)}$ bond within the π-allyl carbanion to produce *trans*-2-butene.

For the exchange reaction of butene with D_2 which proceeds on Site II, an addition–abstraction mechanism and an abstraction–addition mechanism can be considered to account for the observed hydrogen transfer. In the addition–abstraction mechanism, a D atom (or ion) attacks butene first to form a C_4H_8D (half-hydrogenated state); an H atom is then abstracted from C_4H_8D to complete the exchange reaction. Any isomers of butenes can be produced depending on which H atom is abstracted from a C_4H_8D. If this were the case, the rates of the exchange reactions would not much differ for ethylene, propylene, and butene. This was not observed. On the other hand, in the abstraction–addition mechanism, butene adsorbs dissociatively first to form a C_4H_7 and then a D atom adds to the C_4H_7 to produce a C_4H_7D product molecule. In this case again, any isomers of butenes can be produced. Propylene and butene have

both allyl hydrogen atoms and olefinic hydrogen atoms but ethylene has only olefinic hydrogen atoms. An allyl hydrogen is more easily abstracted as a proton than a olefinic hydrogen. If the exchange reaction on Site II proceeds by an abstraction–addition mechanism and a hydrogen is abstracted as a proton, the exchange rate for ethylene would be much slower than those for propylene and butenes. This was the case observed. Because of a repulsion between positively charged species, an incompletely coordinated metal ion or an oxygen deficient site may not abstract a proton from butene or propylene. It is plausible that the O^{2-}, which should exist adjacent to the metal ions, abstract a proton. Therefore Site II is possibly a pair of an incompletely coordinated metal ion or an oxygen-deficient site and its adjacent O^{2-}.

No hydrogen scrambling among butene molecules on Site I indicates that a proton abstracted from butene does not migrate on the surface. As for a hydrogen, it still remains unknown whether or not a hydrogen molecule can dissociate on Site I. Even if a hydrogen molecule dissociates to H^+ and H^- on Site I, the exchange reaction may not occur if there is no migration. On the other hand, should the hydrogen molecule dissociate and the H^+ migrate from one of Site II's to the others, it would account for both the observed exchange reaction of butene with D_2 and the observed hydrogen scrambling among butene molecules.

One possible explanation for the difference between Site I and Site II may be as follows. The incompletely coordinated metal ion or oxygen-deficient site increases the electron density of the adjacent O^{2-}, and the O^{2-} attracts an H^+ on a neighboring O^{2-} and causes it to move over the surface. The O^{2-} of Site I may not be strong enough to pull the H^+ from the neighboring site. An alternative explanation is the difference in the distance between the sites. Each of the Site I may be isolated from others so that the migration of H^+ from one site to the other is slow. On the other hand, each of the Site II may be close to at least one of its own kind. A H^+ (or D^+) on one site produced from dissociative adsorption of butene or D_2 can easily migrate to the neighboring O^{2-} which is adjacent to an incompletely coordinated metal ion or an oxygen-deficient site on which a π-allyl carbanion adsorbs.

In the previous paper (7), similarities of BaO to Al_2O_3 were pointed out. Both of them have more than one type of active sites. One type of site is active only for the isomerization of butenes which involves an intramolecular H transfer. This type of site on Al_2O_3 corresponds to Hightower's I-sites (21) and Knözinger's type-A sites (22). The other type is active for the exchange of butenes with D_2. While these are independent of the "isomerization sites" for Al_2O_3 (23), they are also active for isomerization in the case of BaO. The exchange mechanisms over BaO and CaO differ from that over Al_2O_3. Olefinic hydrogen atoms are labile to exchange with D_2 over Al_2O_3 (24) while allyl hydrogen atoms are labile over BaO and CaO.

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