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Isomerization of Butene over Alumina[1]

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The isomerization of *n*-butenes over γ-alumina is reconsidered in order to elucidate the origin of its stereoselectivity and the nature of the surface sites involved. Evidence is presented for a base-catalyzed double bond migration when the surface is completely covered with hydroxyl groups and for a *cis–trans* isomerization probably involving Brønsted acid sites. When the alumina is heated above 600°C the interconversion between 1-butene and *trans*-2-butene does not occur. The results suggest a mechanism for the double bond shift similar to that proposed by Gerberich and Hall [*J. Catal.* 5, 99 (1966)].

INTRODUCTION

The catalytic interconversion of *n*-butenes has been studied for many years (*1*) using many different catalysts (*2–5*). The problems of interest are the stereoselectivity of the reactions (*6–8*) and the nature of the surface sites involved in the *cis–trans* and double bond isomerization (*7–9*). Concerning the isomerization one may in general discern between acid, base, and metal catalysts.

On acid catalysts a mechanism involving carbonium ion formation on Lewis or Brønsted acid sites is generally proposed (*10–13*). In some cases (*6*) a common secondary butyl carbonium ion has been postulated to account for the stereoselectivity and the relative reactivity of the *n*-butenes in the *cis–trans* and double bond isomerizations. However, for alumina it was concluded that different sites and different mechanisms operate in the double bond migration and the *cis–trans* isomerization, and there is no common intermediate.

On basic catalysts an anionic reaction involving an allylic carbanion has been proposed as a reaction intermediate (*2*); an allylic carbonium ion was proposed also for the acid-catalyzed reaction (*14*). In both cases direct interconversion between *cis*- and *trans*-2-butene is precluded; both compounds exclusively form 1-butene at low conversion levels. A detailed picture of the isomerization over zinc oxide (base catalyst) was given by Chang *et al.* (*15*). From infrared measurements it was concluded that the butenes are adsorbed as π-complexes which are converted into reactive π-allyl species.

For metal catalysts probably a radical mechanism controls the reaction. An alkyl radical is formed by addition of hydrogen; after alkyl reversal and hydrogen abstraction the isomerized olefin is obtained (*16*).

The different types of catalysts mentioned give rise to different stereoselectivities (*17*), which is most pronounced in the conversion of 1-butene.

In Table 1 the *cis*/*trans* ratios found with various catalysts are summarized. From Table 1 it becomes clear that alumina is an exceptional catalyst because it gives rise to stereoselectivities in the class of acid as well as base catalysts. In the past this anomaly was attributed to complex reaction mechanisms or to differences in the nature of the acid sites. However, the anomaly might equally well be explained by a combined acid- and base-

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[1] This work was carried out at the Interuniversity Reactor Institute at Delft.

TABLE 1
Cis/trans RATIOS FOUND IN THE ISOMERIZATION OF 1-BUTENE OVER VARIOUS CATALYSTS

			cis/trans			
Class	Catalyst	Reaction temp	Equilibrium	Ratio observed	% Conversion[a]	Ref.
Base	MgO	26	0.26	1.7–7	0	*(17)*
	MgO	0	0.22	4	0	*(17)*
	CaO	30	0.27	2–7	0	*(19)*
	TiO	150	0.46	3.3–6.1	0	*(18)*
	LiOH	440	0.8	2	4	*(2)*
	KOH	320	0.65	9	1.5	*(2)*
Metal	Ni	300	0.63	0.6	9.8	*(2)*
	Ag	375	0.7	0.7	0	*(2)*
	Pd/alumina	18	0.24	0.5	0	*(16)*
	Rh/alumina	166	0.48	0.6	0	*(16)*
	Pt/alumina	100	0.38	1	0	*(16)*
Acid	Silica/alumina	23–150	0.25–0.46	1–1.6	0	*(7)*
	H_3PO_4	150	0.46	1	2.2	*(2)*
	Silica/alumina	0	0.22	1.9	0.3	*(6)*
	Silica/alumina	0	0.22	1.0	1.2	*(6)*
	Zeolites	100–300	0.38–0.63	1–2	0	*(5)*
	H_2SO_4/hyflo	150	0.46	1.5	2	*(8)*
	Silicotungstic acid/silica	150	0.46	1.8	2	*(8)*
	Alumina	111	0.42	5	8	*(6)*
	Alumina	0	0.22	3.5	14	*(6)*
	Alumina	230	0.53	4.4	0	*(3)*
	Alumina	230	0.53	2.4	0	*(3)*
	Alumina	23–300	0.25–0.63	1.3–6	0	*(7)*
	Alumina	100	0.38	3	0	*(20)*

[a] 0% conversion means initial.

catalyzed mechanism. A prerequisite for a base-catalyzed isomerization is the presence of basic sites on the alumina surface. In the literature it has been suggested that alumina indeed possesses basic properties (*21–24*). In particular Ghorbel *et al.* (*24*) made a thorough study of the sites present on so-called amorphous alumina and its isomerization activity. They showed that their alumina possesses both oxidizing and reducing properties, which are related to acid sites and basic sites, respectively. Unfortunately, these types of sites all varied in nearly the same way with the pretreatment temperature of the alumina, as did the activity for the double bond isomerization. For this reason a correlation between a particular type of site and the catalytic activity could not be established.

The present study deals with *n*-butene isomerization over differently pretreated aluminas in order to evaluate the contribution of a base-catalyzed reaction.

EXPERIMENTAL METHODS

Catalysts

Aluminum isopropoxide was prepared by the reaction of pure aluminum with isopropyl alcohol in the presence of small quantities of mercury chloride (0.2% w/w) and carbon tetrachloride (0.5% w/w). The isopropoxide was distilled and the molten product was hydrolyzed with distilled water at 60°C. In order to convert small quantities of bayerite that might have been formed during the hydrolysis, into boehmite, the suspension was aged at room temperature for 1 wk (*25*). It was then washed thoroughly with water and filtered; the aluminum hydroxide was dried at 150°C. Finally, catalyst samples were obtained by heating the dried material for 24 hr in air at temperatures between 300 and 1000°C. On the basis of X-ray diffraction patterns and consideration of the work of Lippens (*25*), we concluded that the resulting alumina after heat treatment between 300 and 900°C was γ-Al_2O_3.

In the course of the experiments it appeared that this type of alumina gave rise to rather unusual stereoselectivities in the *n*-butene isomerization, especially the catalysts heated below 450°C. Therefore, a commercial alumina obtained from Ketjen N. V. Amsterdam, was also used. This catalyst was stored at the ambient and heated before use to the desired temperature.

The specific surface area was measured following the BET method using nitrogen or radioactive krypton as adsorbates (*26*). The porosity of the samples was derived from the differences in density using toluene and mercury as inhibition liquids in a pycnometric density determination (*27*). The water content of the samples was derived from the weight difference before and after heating during 24 hr at 1100°C.

Determination of the Isomerization Activity

The catalysts were transferred into a U-tube immediately after heating to prevent re-adsorption of water. The U-tube was closed and cooled to room temperature. After filling the U-tube with butene the U-tube was heated at 100°C during a certain time. The tube was then connected to a gas chromatograph and the reaction mixture was analyzed. In these experiments the reaction time at 100°C and the pressure of the butene in the U-tube were varied.

Determination of the Adsorption Isotherm

Adsorption isotherms of butene on alumina were determined with a gravimetric technique. Isotherms were determined at temperatures between 75 and 120°C for catalysts heated at 400°C. In order to prevent a substantial isomerization of the butenes the determinations were carried out quickly. In separate runs it was checked whether the isotherms thus obtained really resembled equilibrium situations.

RESULTS

Catalyst Characteristics

Activation analysis of the isopropoxide catalyst samples showed that chlorine (200 ppm), magnesium (100 ppm), iron (50 ppm), and sodium (50 ppm) were the main impurities. Minor quantities of copper (5 ppm), manganese (15 ppm), mercury (3 ppm), zinc (2 ppm), and gallium (2.5 ppm) were present. Because alumina catalysts are not very sensitive towards impurities (an influence is noticeable only above a level of 1000 ppm), there is probably no influence of impurities on its catalytic behavior in this case.

The specific surface area, the average pore diameter and the water content of the samples are given in Table 2. The specific surface area decreases with increasing temperature of the heat treatment in the same way as the gelatinous boehmite sample of Lippens (*25*). The average pore diameter derived from the ratio in pore volume and specific surface area is only slightly dependent on the heat treatment. The diameters are comparable to the values quoted by Lippens for gelatinous boehmite. In general a decrease in pore diameter from 120 to 90 Å will not seriously influence the conversion of small molecules like the *n*-butenes.

The water content of the samples de-

TABLE 2
SPECIFIC SURFACE AREA, AVERAGE PORE DIAMETER AND WATER CONTENT OF ALUMINA SAMPLES HEATED AT DIFFERENT TEMPERATURES

Heating temp (°C)	Specific surface area (m^2/g)	Av pore diam (Å)	Water content	
			mg/g Al_2O_3	mg/100 m^2
400	260	90	61	23
500	215	100	27	12
600	186	110	11	6
650	190	100	10	5
700	165	120	8.5	5
800	124	120	5	4

creases continuously with increasing calcination temperature. As the surface area decreases simultaneously the surface coverage with water is only seriously affected in the temperature range of 400 to 600°C. This change is not due to a structural change in the alumina, for all samples showed the γ-alumina structure. Comparison of the degrees of surface coverage with water with those given by De Boer *et al.* (*28*) reveals that on an alumina sample, pretreated at 400°C, approximately one layer of chemisorbed water is present. Below this temperature probably more than one layer is adsorbed. At higher temperatures (600°C) the surface coverage is reduced to 25% of a monolayer. As a result there is a strong change in the surface structure of alumina on going from 400 to 600°C pretreatment temperature. It might be possible that only part of the water is present as surface water, but the commercial catalyst which was heated beforehand at 700°C and then stored under ambient conditions showed similar surface coverages with water. In this case one is rather sure that the re-adsorption of water occurs at the surface only.

Reproducibility of the Activity Determinations

The reproducibility of the activity determinations was checked by repeatedly measuring the conversion of 1-butene over 200 mg alumina heated at 650°C. The results of these determinations together with the average, standard deviation and equilibrium composition at the reaction temperature are given in Table 3. The standard deviations of the conversion, product formation and product ratio varied between 10 and 20% of the values measured. Therefore, it was thought necessary to measure at least six times the conversion under one set of identical conditions in order to get reliable average results.

Activity Determinations

In Fig. 1 the influence of the pressure of 1-butene in the U-tube on the reaction rate and the product ratio is shown for catalysts heated at 410 and 650°C. (Charge II alumina was used in these experiments, see below). The conversion in these experiments is constant and smaller than 35% of the value necessary to reach equilibrium. It appears that the rate depends linearly on the pressure, indicating a first-order reaction. The product ratio is constant as might be expected from a constant conversion. Calculations (*29*) confirmed that diffusion control was not important in this case.

Butene conversion as a function of pretreatment of the catalyst (Charge I) is shown in Fig. 2. The rates of conversion of 1-butene and *cis*-2-butene are comparable whereas that of *trans*-2-butene is considerably smaller. From the standard deviations shown the sub-maximum in the 1-butene conversion over an alumina heated at

TABLE 3

CONVERSION OF 1-BUTENE ON DIFFERENT CHARGES OF ALUMINA HEATED AT 650°C (REACTION TEMP, 100°C; REACTION TIME, 15 min)

Charge no.	% Conversion	% *cis*-2-Butene	% *trans*-2-Butene	*cis*/*trans* ratio
1	33.0	11.4	21.6	0.53
2	30.3	9.6	20.7	0.46
3	23.3	7.3	16.0	0.46
4	29.2	9.8	19.4	0.50
5	38.1	13.0	25.1	0.52
6	35.3	11.9	23.4	0.51
7	36.0	13.4	22.6	0.60
Av	32.3	10.9	21.2	0.51
SD	5.1	2.4	3.0	0.05
Equilibrium	92.6	24.7	67.9	0.36

500°C and of a minimum for a sample heated at 600°C are not significant. Therefore, the conversion of 1-butene was measured again on a different charge (Charge II) of alumina prepared in the same way. The surface area of this alumina was assumed to be equal to the area of the alumina used before. The results of these measurements are indicated by the broken line in Fig. 2. The conversion rate is higher now, possibly due to an overestimation of the surface area; however, a maximum and a minimum are found again for the samples heated at 500 and 600°C, respectively. A similar behavior of the double bond shift activity as a function of pretreatment temperature has been found by Ghorbel *et al.* (*24*).

An impression of the selectivity of the isomerization over catalysts heated at different temperatures may be obtained from Fig. 3. This figure shows that the stereoselective isomerization over catalysts heated at or below 450°C differs considerably from the selectivity found for catalysts

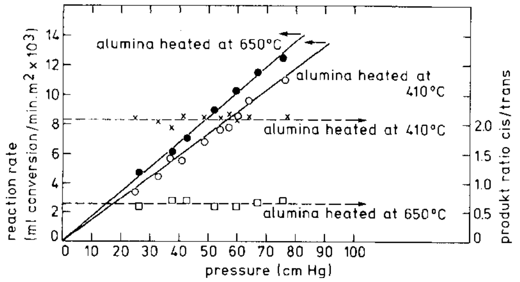


FIG. 1. Reaction rate and product ratio of 1-butene conversion versus pressure. Alumina heated at 410 and 650°C; reaction time, 15 min; reaction temp, 100°C.

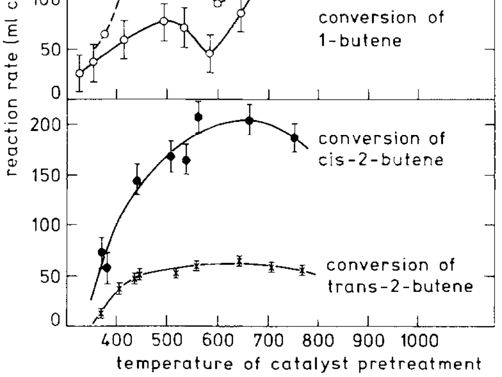


FIG. 2. Reactivity of *n*-butenes as a function of the pretreatment temperature of the catalyst. (– –) Results obtained with a different charge of alumina, see text. The standard deviations of the measurements are indicated by the 95% probability ranges. Reaction time, 15 min; reaction temp, 100°C.

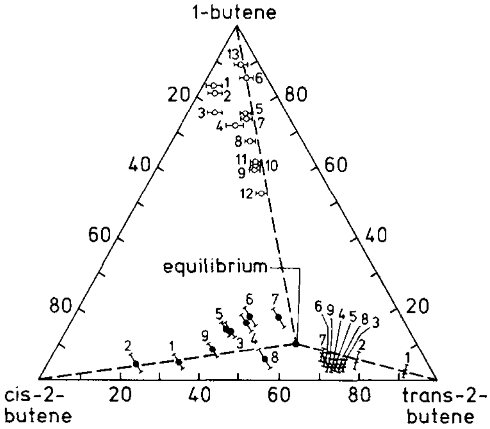


FIG. 3. Product ratios obtained with catalysts heated at various temperature. Reaction time, 15 min; reaction temp, 100°C. The point numbers correspond to pretreatment temperature (°C) as given below:

No.	1-Butene	*cis*-2-Butene	*trans*-2-Butene
1	310	370	370
2	335	390	410
3	410	450	450
4	480	510	460
5	520	535	535
6	580	560	560
7	650	650	650
8	655	750	710
9	725		780
10	790		
11	900		
12	910		
13	1000		

heated above 600°C. In between these two temperatures intermediate selectivities are found. A remarkable difference between 1-butene and 2-butene is that below a pretreatment temperature of 450°C the 2-butenes give approximately the equilibrium product ratio whereas 1-butene results in a product ratio that strongly differs from the equilibrium value. The selectivity of the *cis*-2-butene conversion shows an irregular behavior. However, one should take into consideration that due to the relative large standard deviations the product ratio at low conversion levels is rather inaccurate.

In Fig. 4 the composition of the reaction mixture as a function of contact time is given starting from 1-butene for catalysts heated at 410 and 650°C and starting from *trans*-2-butene for a catalyst heated at 650°C. There exists a considerable difference in the way the equilibrium is reached starting from 1-butene over these two catalysts.

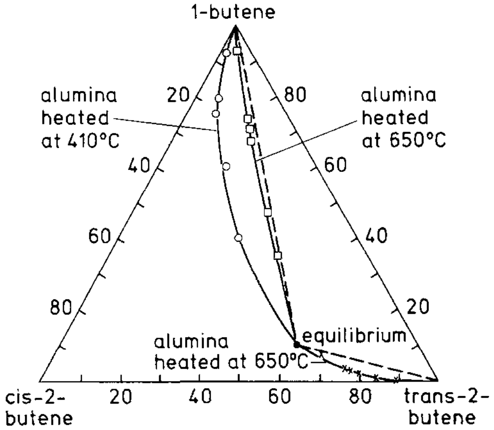


FIG. 4. Product ratio as a function of contact time starting from 1-butene for catalysts heated at 410 and 650°C and with *trans*-2-butene as the initial product for a catalyst heated at 650°C. Reaction temp, 100°C; contact time, between 25 and 60 min.

Adsorption Isotherms

In the pressure range of 0–50 Torr the isotherms appeared to be linear and most of the adsorbed butene could be removed by evacuation. Only a very small fraction of the surface (0.01%) adsorbed butene irreversibly. Adsorption isotherms of the three *n*-butenes, measured at the same temperature, showed that *cis*-2-butene is slightly more adsorbed than 1-butene but the quantity of adsorbed *trans*-2-butene is much less. At 75°C the quantity of adsorbed *trans*-2-butene is approximately half that of *cis*-2-butene at the same pressure. From isotherms measured at different temperatures the changes in free energy upon adsorption were evaluated as 2.7, 2.7 and 2.2 kcal/mol for 1-butene, *cis*-2-butene and *trans*-2-butene, respectively.

DISCUSSION

The results obtained with catalysts heated above 600°C showed that 1-butene behaves entirely differently from the 2-butenes. As a function of pretreatment this holds for the stereoselectivity (Fig. 3) as well as for the reactivity (Fig. 2). This indicates that double bond shift and *cis–trans* isomerization are processes taking place on different active sites without a common intermediate. On the basis of tracer experiments Hightower and Hall (*7*) came to the same conclusion and the experiments of Brouwer (*8*) demonstrated the same differentiation between 1- and 2-butene. Another conclusion that may be drawn from Fig. 4 is that the conversion of *trans*-2-butene into 1-butene seems to be precluded. At low contact times the *cis*/1-butene product ratio is very high (≈ 100). Therefore, in fact one might describe the isomerization over this type of catalyst by the reaction scheme:

$$\text{1-butene} \leftrightarrows \textit{cis}\text{-2-butene} \leftrightarrows \textit{trans}\text{-2-butene.}$$

This reaction scheme accounts for the absence of the *trans*-2-butene conversion into 1-butene and because of the reversibility also for the 1-butene into *trans*-2-butene conversion. A difficulty with this scheme is that one would expect a high initial *cis*/*trans* ratio starting from 1-butene, whereas a low selectivity is observed. An explanation for this might be found in a relatively fast *cis–trans* isomerization taking place over this type of catalyst. From the relative reactivities in Fig. 2 it is possible to calculate whether the isomerization can be described by this scheme. By means of the concentration–time functions for a three component system among which first-order, parallel and reversible reactions proceed, as given by Hightower and Hall (*7*), one may calculate the composition of the reaction mixture as a function of the contact time. This calculation should closely resemble the experimental result given in Fig. 4.

The relative rate constants of the interconversion of 1-butene and *trans*-2-butene are taken as zero. The rate constant of the 1-butene to *cis*-2-butene conversion is taken as unity and as a result of the equilibrium conditions the rate constant of the reverse reaction is 0.35. According to Fig. 2 *cis*-2-butene reacts three times as fast as 1-butene, but the conversion of *cis*-2-butene in this case is rather large (catalyst heated at 650°C) and the reverse reactions might have played a part. As a result the actual conversion rate of *cis*-2-butene is probably higher. If the lowest estimate of 3 for the ratio in reaction rates is used in the concentration time functions together with the equilibrium conditions curves very similar to those given in Fig. 4 are obtained, but at low contact times deviations appear. A better agreement between calculation and experiment is obtained when the ratio in conversion rates of 1-butene and *cis*-2-butene is taken as 5. This agreement is not an absolute proof for the reaction scheme given above but it serves to show that this scheme is allowed.

If this reaction scheme truly represents the isomerization over alumina, treated at high temperatures, then a reaction mechanism must be found which is in accordance with this scheme, in particular with the absence of the 1-butene and *trans*-2-butene interconversion. Hitherto only the reaction mechanism proposed by Gerberich and Hall (*6*) accounts for this effect. The intermediate in this mechanism is shown in Fig. 5. The terminal carbon atoms are adsorbed on two adjacent Lewis acid sites or exposed aluminum ions. The distance between the two terminal carbons is 2.74 Å, whereas the distance between the two exposed aluminum ions is 2.64 Å. Of course this only holds for the *gauche* structure of 1-butene and for *cis*-2-butene. *Trans*-2-Butene and the *trans* structure of 1-butene cannot be adsorbed in this way. Oxygen ions in an outer layer can then act as a medium for the transfer of a proton from an allylic carbon to the terminal olefinic carbon. The intermediate structure was sustained by Peri's conception of the alumina surface (*30*) and the finding of Peri

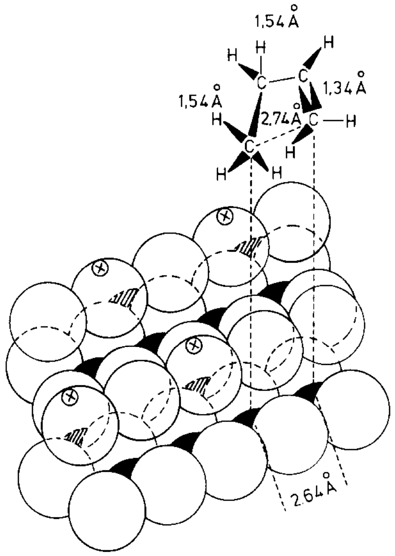
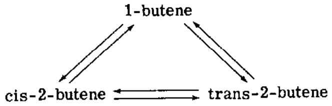


FIG. 5. Adsorption intermediate of 1-butene adsorbed onto two adjacent Lewis acid sites. Large circle: oxygen ion; dark segment: exposed aluminum ion; and small circle with cross: proton.

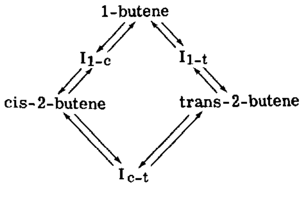
that strongly adsorbed butene on a highly dehydroxylated surface resembles the *cis*-2-butene structure in the infrared spectrum of the adsorbed species (*31*). Moreover, the proposed active sites in ion-exchanged zeolites, exposed cations, has been used as an argument (*32*). From the work presented here the absence of the 1-butene-*trans*-2-butene interconversion and the increase of the double bond shift activity with increasing dehydroxylation of the surface are in favor of the mechanism proposed by Gerberich and Hall. A similar model has been proposed by Bielikoff (*33*) to account for the deactivation of alumina during the isomerization of 1-butene.

The nature of the sites active in the *cis–trans* isomerization is still obscure. Obviously this reaction differs from the double bond shift. The slight decrease in reactivity with increasing dehydration temperature above 600°C (Fig. 2) might indicate that hydroxyls still present on the surface are responsible for this reaction. The acidity of the surface also seems to play a part in this reaction, as poisoning with bases (*20*) or addition of sodium (*33*) especially decreases the *cis–trans* isomerization.

For the catalysts pretreated below 450°C the product ratio at very small conversions is always between 0.1 and 10 indicating that interconversion between the three *n*-butenes is possible (Fig. 3). These ratios suggest for this type of catalyst the following scheme:

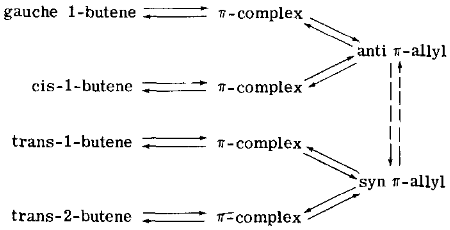


This scheme would suggest that there is one intermediate in the conversion of the butenes. However, from Fig. 2 it follows that also for aluminas pretreated at low temperature the *cis–trans* and the double bond isomerization are different reactions, and the poisoning experiments mentioned before (*20*) indicated a similar effect. Therefore, the reaction scheme is not correct. Another effect that has to be accommodated by the scheme is the high initial *cis*/*trans* ratio obtained in the isomerization of 1-butene (Fig. 3). Somewhere in the free energy diagram of the isomerization an energy difference must exist between the transition states of the 1-butene to *cis* and 1-butene to *trans* reaction. In our case an initial *cis*/*trans* ratio of five is comparable to an activation energy difference of 1.7 kcal/mol if the frequency factors are taken as equal. Therefore, it is more realistic to describe the double bond shift by two distinct intermediates. These intermediates are not interconvertible as follows from the difference in *cis–trans* and double bond isomerization. With these two conclusions the following reaction scheme may be considered, where I_{1-c}, I_{1-t}, and I_{c-t} represents the intermediate in the various reactions:



The absence of an interconversion between I_{1-c} and I_{1-t} implies that a carbonium ion mechanism is improbable. In an olefinic carbonium ion a positive charge causes a loosening of the double bond resulting in free rotation of the molecule (except for a carbonium ion adsorbed on two sites, where a rigid structure is formed). Therefore, a base-catalyzed double bond shift is more in accordance with the proposed reaction scheme.

A detailed mechanism of the base-catalyzed double bond shift was given by Chang *et al.* (*15*). They argued that butenes are adsorbed on ZnO as π-complexes which are converted into the *anti* and *syn* π-allyls as shown below:



A point of discussion in this mechanism is the interconversibility of the *syn* and *anti* π-allyl (*35*). Chang *et al.* (*15*) showed that the π-complexes of the *trans* structures are less stable than those resulting from the *cis* or *gauche* structure. It was found also that 1-butene preferentially forms the *anti* π-allyl. Both conclusions are in accordance with the results obtained with alumina pretreated at low temperature. The adsorption isotherms indicate that the *trans* π-complex is less stable and the relative high *cis*/*trans* ratio is in agreement with the preferential formation of the *anti* π-allyl from 1-butene.

A prerequisite for a base-catalyzed reaction is the presence of basic sites on the surface of alumina. There are several indications that basic sites do occur on alumina (*21–24*). Moreover, the high surface coverage with water or hydroxyl groups on alumina pretreated at low temperature will interfere with an acid-catalyzed reaction. If acid groups are present on alumina thus pretreated, they will be of a weak Brønsted acid nature (*24*), probably too weak to form carbonium ions. The adsorption of the butenes on alumina is too weak also to expel water from the surface. As a result there are no exposed aluminum ions which can act as Lewis acid sites.

One could argue that the results obtained with alumina pretreated at low temperature have been affected by the way in which the catalyst was prepared. However, comparable results were obtained with the Ketjen catalysts which were calcined beforehand at 700°C and after re-adsorption of water heated at different temperatures. Again, these catalysts show a high surface coverage with water when heated at 400°C as well as a strong decrease in the surface coverage at temperatures between 400 and 600°C. Therefore, the results must be explained in terms of hydroxylated surfaces rather than in terms of catalyst biography.

CONCLUSIONS

Additional evidence is presented that the double bond shift and *cis–trans* isomerization of the *n*-butenes over alumina are two different reactions proceeding via different intermediates on different active sites. On completely hydroxylated alumina the double bond shift is probably a base-catalyzed reaction. The results are in accordance with the model of a base-catalyzed reaction proposed by Chang *et al.* (*15*).

When the alumina is heated above 600°C a different selectivity of the isomerization is observed and a mechanism similar to that proposed by Gerberich and Hall (*6*) can account for the results obtained.

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