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Selective Isomerization of Butene to Iso-Butene

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Selective isomerization of butene to iso-butene has been studied with pure and variously modified alumina as catalysts. Results can be self-consistently explained by concluding that (i) the monomolecular mechanism operates and requires Lewis acid sites, the presence and quality of which can be modulated by heat treatment in hydrogen, by surface modification with halogens, and by application of certain catalytic poisons, and (ii) the bimolecular mechanism is related to the Brønsted acid sites and is stimulated, as expected, by increased pressure of *n*-butene. © 1994 Academic Press, Inc.

INTRODUCTION

There is considerable practical interest in the title reaction. Refineries forsee a coming overproduction of linear butenes, while isobutene would be a very desirable raw material to make methyl tertiary-butyl ether (MTBE).

The fundamental aspects of the reaction are equally attractive. It has been reported that, for example, *n*-butane can undergo an exchange of atoms on the positions of the C^1 and C^2 atoms, i.e., an isomerization in the C-label position, but it cannot be converted into isobutane. The authors conclude (1) that a delocalized carbenium ion of a cyclopropane-like structure is formed. Opening of the triangle, to yield butane with exchange C_1 and C_2, is actually formation of a *secondary* carbenium ion and is not prohibited. However, opening leading to isobutene means formation of a *primary* ion and thus has a high activation energy and a low probability. A similar conclusion should then be made for skeletal isomerization of butenes. If it is not a simple carbenium ion mechanism which is generally being proposed in the literature (2), what else could it be?

The spectrum of catalysts which have been reported as active in the isomerization of butenes to isobutene is very heterogenous: H_3PO_4 ($+H_2O$) on supports (2b), acidic zeolites (3), or zeolites with a suitably exchanged cation such as Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} (4), and tungsten oxide (5). A superficial conclusion would be that Brønsted acids, Lewis acids, and redox active oxides could all catalyze the reaction. The question is can an intermediate nevertheless exist, common to all these catalysts? It is not a priori sure that there should be one, but on the other hand it would be interesting if a common intermediate could be suggested.

Stimulated by the open questions presented above, we have initiated investigations along two lines:

(i) A search along the periods of the periodic table to identify systems with appreciable activity and the desired selectivity.

(ii) A systematic modification of the very versatile oxide, γ-alumina.

The results of (i) are presented in a subsequent paper; the results of (ii) are presented below.

EXPERIMENTAL

Experimental Description

The isomerization of *n*-butene is performed in a continuous plug-flow fixed-bed reactor at atmospheric pressure. The glass reactor is inserted into a cylindrical furnace equipped with a temperature programmer. A thermocuple well reaches the central portion of the catalyst. *n*-Butene (Hoek Loss 99.9%) is diluted to 5% in a carrier gas, nitrogen or hydrogen. Before entering the reactor, the flow of nitrogen could be supplemented by other components, by its being led through a saturator containing either water or an organic liquid a desired temperature. The individual flow rates are monitored by a thermal mass flow controller, and the overall flow rate is measured at the reactor exit.

The following parameters have been used in the standard test (all experiments, unless otherwise specified):

catalyst	1 g
carrier gas	N_2
n-butene	1 ml/min
total flow	20 ml/min
water	absence
temperature	350°C

The reactions with isobutene and *n*-octene, respectively, as the feed were also studied under the same experimental conditions as the standard test.

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The UV diffuse reflectance spectra were recorded on a Beckman Elmer 330 spectrometer equipped with a Perkin Elmer 3600 data station. The UV cell was connected to a reactor containing 2 g catalyst for a reaction. The UV cell could be removed from the reaction apparatus without exposure to air so that the UV spectroscopic measurements could be made *ex situ* at 25°C.

Data Evaluation

The exit gas was analyzed by a gas chromatograph (Hewlett–Packard) equipped with a column KCl/Al_2O_3: All hydrocarbons other than C_4H_8 isomers are reported below as "by-products". For the skeletal isomerization of *n*-butene in the standard test, the main by-products were propene, butanes, pentenes, and traces of C_6–C_8 alke(a)nes. Further, traces of methane, ethene, and ethyne are also observed, when the total amount of the by-products increases.

The composition of butenes is limited by thermodynamic equilibrium (2b). The relative concentration is defined as the weight of the particular hydrocarbon over that of all hydrocarbons together. For example,

$$C_{\text{isobutene}}\ \text{wt\%} = [C_{\text{isobutene}}/\Sigma C_i\ (i = 1\text{–}8)] \cdot 100. \quad [1]$$

The selectivity for double bond isomerication of *n*-butene to *trans*-2-butene and *cis*-2-butene or for skeletal isomerization to isobutene is put equal to the concentration defined by Eq. [1].

Catalyst Preparation

Alumina (boehmite) of a high purity from AKZO (Ketjen Catalyst) is calcined at 600°C in air for 6 h. It produces a pure γ-Al_2O_3 with a specific surface BET of 180 m^2/g and a pore volume of 0.52 ml/g. A further thermally treated γ-Al_2O_3, partially converted to α-Al_2O_3, is prepared by heating at 1200°C in air for 30 min. The other thermal treatments of alumina in N_2 or H_2 are directly carried out in the reaction apparatus, with a standard flow of 20 ml/min (Table 1).

The surface modification of pure γ-Al_2O_3 by halogen atoms (F, Cl, Br, and I) was also done *in situ*, in the reaction apparatus. Alumina (1 g) is placed in the reactor and heated to 350°C in nitrogen; the organic compound containing halogen was then introduced into nitrogen by bubbling through the organic compound liquid in a saturator, at room temperature. At 350°C the halogen atom of an organic molecule reacts with hydroxyl and oxygen vacancies on alumina surface (6) to become bound to aluminum cations. The reaction time for different compounds has been optimized to gain the best production of isobutene (Table 2a). The modified alumina is subsequently kept at 350°C in nitrogen flow for 15 min to remove the excess species adsorbed on alumina. By introduction of *n*-butene in nitrogen flow the reaction is initiated.

RESULTS AND DISCUSSION

Main Reactions

The overall picture of the formation of the main reaction products, as a function of temperature, with *n*-butene in the feed, is in general as shown by Figs. 1 and 2. Similar results can be found also in the literature (7, 8). The production of isobutene seems to be superimposed on the almost equilibrium distribution of linear butenes (compare Fig. 2 and Figs. 1a and 1b). When a series of catalysts is being compared, the temperature is kept constant at 350°C.

Fresh and Thermal Treated Pure γ-Al_2O_3

For reaction temperatures below 300°C, the pure alumina only shows selectivity to double bond isomerication (Fig. 1a). When the temperature increases from 300 to 500°C, the selectivity to isobutene increases to about 30%

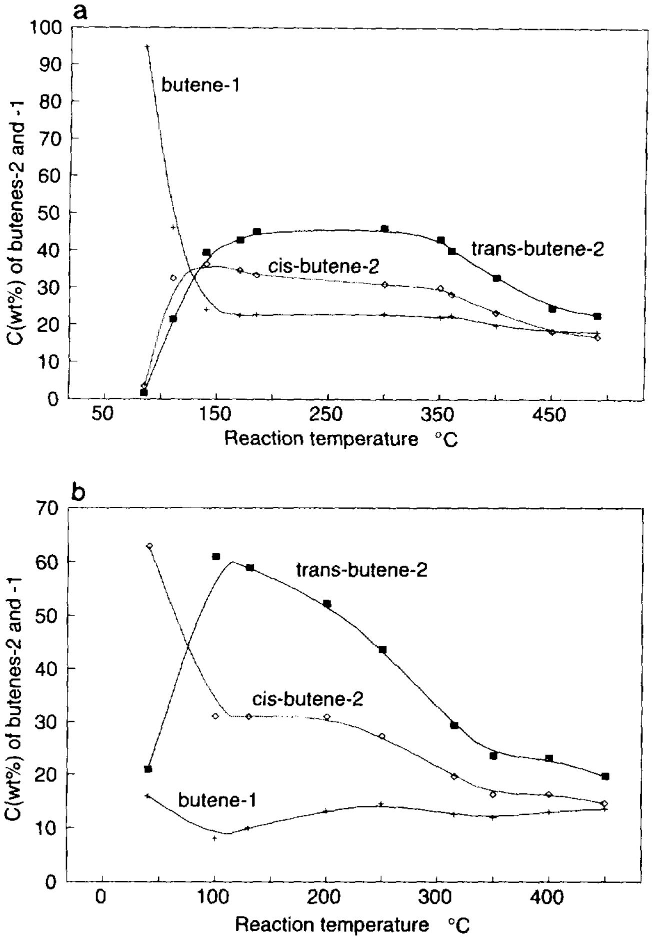

FIG. 1. (a) Double bond isomerization of butene-1 to butenes-2 over pure alumina. (b) Double bond isomerization of butene-1 to butenes-2 over butyl-Cl treated alumina in nitrogen carrier gas at 350°C for 1 h.

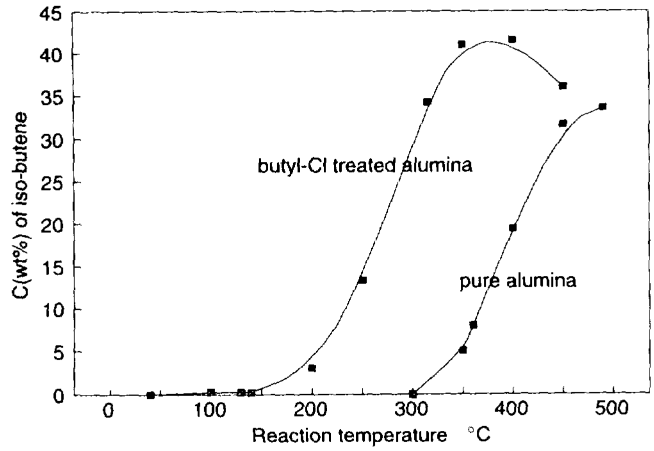

FIG. 2. Skeletal isomerization of butenes to isobutene for other products see Fig. 1 over alumina catalysts.

(Fig. 2). These results are consistent with the literature (7–9). Obviously, pure alumina is able to induce skeletal isomerization of butenes to isobutene above 300°C.

Let us now mention that Nortier *et al.* (7) compared one amorphous and four crystalline γ-aluminas prepared from different boehmites to study the effect of crystallinity and morphology on the surface properties of alumina. They claimed that selectivity for skeletal isomerization of butenes above 300°C is related to the number of strong Lewis acid sites and the less acidic amorphous alumina has the lowest selectivity to isobutene. Mac Iver *et al.* (9) also suggested that the skeletal isomerization of n-pentene at 390°C takes place on the Lewis acid sites of alumina. The more acidic η-alumina appeared to be better than the γ-alumina.

Obviously, the thermal treatment of alumina is of importance and therefore its effects have been investigated. In a standard test at 350°C (see Table 1), only 5% isobutene is found with untreated alumina. A thermal treatment at 450°C in nitrogen flow for 16 h, did not alter this figure. However, heating at 1200°C in air for 30 min, which changes the phase composition of the catalyst, leads to a sharp decrease of selectivity to isobutene (Fig. 3). This is in agreement with Mac Iver *et al.* (9), who have found that the activities in skeletal isomerization of *n*-pentene at 390°C over γ- and η-aluminas passed through a maximum at a drying temperature of 600–700°C. The authors correlated it to the total acidity determined by ammonia chemisorption. According to Lunsford *et al.* (10), the transition γ, η → α-alumina, induced by heating at 1200°C, leads not only to the removal of the OH groups, but also to the annihilation of the defects which function as Lewis sites. Heating of alumina at 450°C in hydrogen flow for 2 h increases the selectivity to isobutene to 14% (Fig. 3). Results of a quantitative determination of Lewis acidity (11) suggest that hydrogen treatment can increase this acidity. With reduced alumina, the concentration of *n*-butane in the products becomes important (9%), and the further increase in the heating temperature under the flow of hydrogen leads to a higher *n*-butane and a lower isobutene formation (Table 1). The observed intrinsic activity of alumina in the hydrogenation of olefins is well known (12, 13) and is here confirmed.

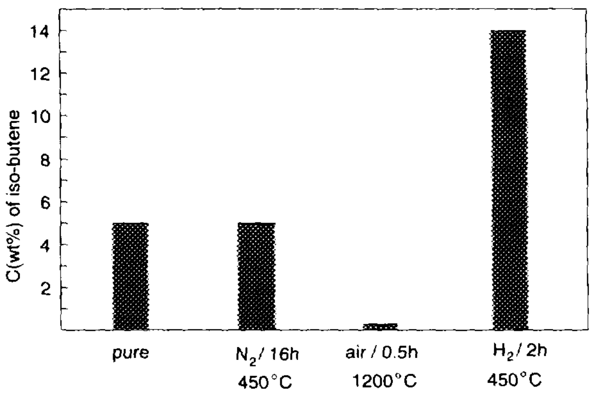

FIG. 3. Effect of thermal treatment on the isobutene production over alumina under standard test conditions at 350°C.

It is generally believed that γ-alumina exposes Lewis acid sites, the differently coordinated aluminium cations (14). The Brønsted acidity of surface hydroxyl groups is very weak; the ratio of Brønsted to Lewis acid sites is reported to be about 0.06 (15). The use of IR spectroscopy for the detection of Brønsted acid sites in alumina by adsorbed pyridine is difficult (16), since the Brønsted acid sites are reliably detected only by stronger bases than pyridine (17). In any case, we can conclude from the above-mentioned papers that the "heat" and "hydrogen" treatments cause changes in the number of Lewis sites. Of course, a parallel creation or annihilation of OH groups causes changes in the number of Brønsted sites.

Alumina Chemically Treated by Halogen Donors (F, Cl, Br, I)

Unlike the thermal treatment of alumina, the chlorination treatment makes pure alumina highly active for isomerization. At rather low temperatures, below 50°C (Fig.

TABLE 1

Products of 1-Butene Reacting over Thermally Treated Alumina at 1 h On-Stream at 350°C

Thermally treated alumina	C_4H_8				By-products	
	cis	*n*	iso	*trans*	C_3H_6	C_4H_{10}
No	43	22	5	30	0	0
$N_2$450°C/16 h	43	22	5	30	0	0
Air/1200°C/0.5 h	43	25	<0.3	32	0	0
H_2/450°C/2 h	35	17	14	24	1	9
H_2/450°C/16 h	5	3	0	4	0	88

1b), the chlorinated alumina shows a high double bond isomerization (63% *cis*- and 21% *trans*-2-butene) activity and also a high *cis*/*trans* ratio (about 3, determined kinetically, not thermodynamically). The skeletal isomerization starts at temperatures lower by 100°C than those at which skeletal isomerization occurs on the unmodified γ-Al_2O_3 (Fig. 2). The selectivity to isobutene at 350°C can reach 41%, close to the thermodynamic equilibrium limit (2b) of 43% (Table 2a). If the concentration of (i.e., the selectivity to) isobutene is expressed *formally* by an Arrhenius equation,

$$S = S_0 \exp(-E_a/RT) \qquad [2]$$

(for the data see Fig. 2), the conclusion is that the chlorination effect decreases the parameter E_a (from 25 to 9 kcal/mole) as well as the preexponential factor S_0 (from 2.4×10^7 to 5.9×10^2) (a compensation effect).

The standard test shows that the addition of other halogens such as F, Br, and I also increases the selectivity to isobutene and the effect is similar to the chlorination effect (Table 2a). The size of the effect is Cl = Br > I > F; this is shown by Fig. 4. Obviously, halogenation of alumina has a positive effect on skeletal isomerization. Let us mention that it has been argued that halogenation increases both the Lewis and Brønsted acidities (18). Let us make an attempt now to establish which of these sites is preferentially promoted by modification of alumina.

First we shall pay attention to the difference between the F- and Cl-modified alumina. It has been reported that upon fluorination of alumina by NH_4F, HF, and CF_3H (19–30), the acidity of Lewis sites is greatly strengthened and the less acidic hydroxyl groups are substituted by fluorine. When alumina is treated by chlorine-containing compounds at temperatures in the region of 300–400°C (6, 31–33), the acidic strength of the Lewis sites is greatly enhanced. Modification produces only a few Brønsted sites of strong acidity (31). For example, after HCl treatment of alumina at 500°C (34), the ratio of number of detected Brønsted to Lewis acid sites was found to be still low, about 0.3. One could thus speculate that in the alumina halogenated at 350°C by various halogen containing compounds (Table 2a), strong Lewis acid sites coexist with some Brønsted acid sites.

TABLE 2a

Products[a] of Early Reaction Stage (Less Than 1 h On-Stream) over Chemically Treated Alumina at 350°C

Chemically treated alumina at 350°C	C_4H_8				By-products		
	cis	*n*	iso	*trans*	C_3H_6	C_4H_{10}	C_5[b]
No	43	22	5	30	0	0	0
CF_3COOH/5 min	13	6	19	9	16	19	15
$CF_3CH_2COOCF_3$/10 min	21	12	22	16	8	10	9
C_4H_9–Cl/1 h	24	12	41	16	2	1	3
CH_2Cl_2/1 h	21	11	38	15	4	5	6
CCl_4/10 min	22	9	38	16	5	3	7
$(CH_3)_3$–Br/2 h	22	11	42	16	2	2	2
$(CH_3)_3$–I/2 h	27	14	38	19	<1	<1	0

[a] In the region C_3–C_5.

[b] Pentenes + pentanes.

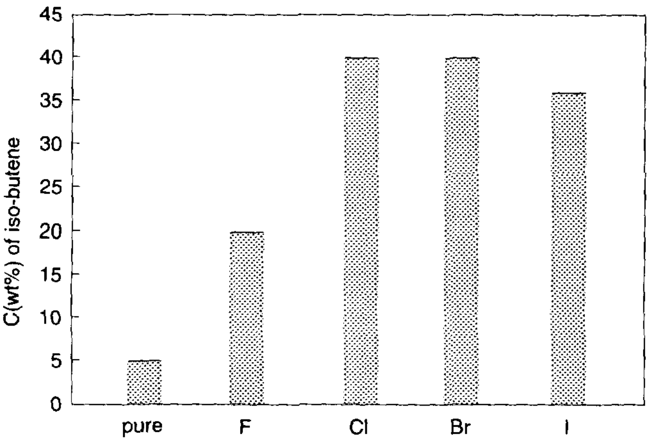

FIG. 4. Effect of halogenation on isobutene production over alumina at 350°C.

According to the literature, fluorine appears to be the strongest promoter of the Lewis and Brønsted acidities on the alumina surface, in compliance with the order of electronegativities: F > Cl > Br > I (35–36). However, the fluorinated alumina has the lowest selectivity to isobutene (Fig. 4) and shows the most abundant by-products (Table 2a). Alumina modified by Cl (31), Br, and I possesses fewer Brønsted sites of strong acidity than the fluorinated alumina, but in our experiment it shows a higher selectivity to isobutene than the F-modified alumina (see Fig. 4), with less by-products being formed (Table 2a).

Under standard test conditions, the activity of Cl-, Br-, and F- modified catalysts can be maintained for more than 48 h with less than a 10% decrease in the initial selectivity to isobutene (Table 2b). The skeletal isomerization selectivity of the I-modified catalyst decreases from 38 to 20% in 6 h and drops down to 7% in 48 h. This can be related to the too-easy loss of I from alumina at 350°C (a yellow–brown deposit is observed at the reactor outlet). This also indicates what could be responsible for a part of the activity decrease with the other halogenated alumina.

TABLE 2b

Stability for the Selectivity to iso-Butene

Water	F/Al_2O_3	Cl/Al_2O_3	Br/Al_2O_3	I/Al_2O_3
Absence	>20%/>48 h	40%/>150 h	40%/>90 h	>35%/<6 h
Presence	>20%/>30 h	<20%/20 min	<20%/20 min	<20%/20 min

Effect of Water

When saturated water pressure (20°C) is introduced into the flow of N_2 mixed with *n*-butene and the reaction is performed at 350°C, the selectivity of pure alumina to isobutene decreases from 5 to 2% overnight. With Cl-, Br-, and I-modified catalysts, water administered for 20 minutes causes the selectivity to drop down to less than 20% (Table 2b). Removal of water from the flow and heating of the catalyst in N_2 at 450°C for 2 h, cannot fully restore the initial selectivity. It is likely that a partial dehalogenation of the modified alumina occurs by steam at 350°C (37). However, the F-modified catalysts have good resistance against water for 15 h since no important skeletal selectivity decrease was observed here (Table 2b). It was reported that water above 300°C produces additional surface hydroxyl groups (38) on pure and fluorinated alumina and thus increases the number of Brønsted acid sites at the expense of Lewis sites (26).

Character of the Active Sites for Skeletal Isomerization

Poisoning of the Lewis acid sites. Rosset *et al.* [39] showed that H_2S is held on a limited number of sites in dehydrated γ-Al_2O_3 with a heat of adsorption up to 38 Kcal/mole. Lewis acid sites (differently coordinated surface aluminum cation) have been proposed (39) as the adsorption sites. Infrared studies (40) demonstrated that H_2S is associatively adsorbed on the Lewis acid sites at temperatures lower than 100°C, and then dissociates to form sulfide-type surface species. Lunsford *et al.* (10) showed that H_2S is a rather specific poison for the double bond shift reaction and it binds strongly to Lewis acid sites. Rosyneck *et al.* (41) showed that not only H_2S but also CH_3–SH is an effective poison at 25°C for sites on alumina that catalyse the double bond and *cis–trans* isomerization of butenes. According to John *et al.* (42, 45, 46) a complete poisoning of the activity by H_2S implies that the reaction involves π-allylic intermediates and Lewis acid sites. An absence of poisoning implies a reaction most probably running through a carbenium ion mechanism and on the Brønsted acid sites. With the help of this method, it has been concluded that the predominant mechanism of the alkene reactions depends on several variables (42–46) such as the molecular structure of olefins, pretreatment of the catalysts, etc. Having the information from the literature in mind, we used the poisoning as a diagnostic tool, supplying additional information on the character of the sites active in the skeletal isomerization.

Here, we used C_2H_5–SH (comparable with H_2S and H_3C–SH) as a poison to probe the mechanism. At low temperatures (below 100°C), 0.05 ml Et–SH injected into the feed is enough to fully suppress double bond isomerization, proving that this reaction on pure and halogenated alumina proceeds (for example, via a π-allylic intermediate) on the Lewis acid sites, just as postulated by Lunsford *et al.* (10) and Rosyneck *et al.* (39). At a higher temperature (350°C), Et–SH decomposes into H_2S and C_2H_4 (as seen by the GC analysis). Nevertheless, an injection of 0.2 ml Et–SH is able to strongly suppress skeletal isomerization, as shown in Fig. 5a. In fact, the activity was completely restored at a level as high as before the poisoning after desorption and decomposition of Et–SH under reaction conditions for 30 min. This could mean that the skeletal isomerization makes use of Lewis acid sites at some stage, just as the double bond isomerization does below 100°C.

Inspection of the literature concerning the intermediates which are related to the Lewis acid sites reveals that allylic intermediates seem to be ones most frequently mentioned and in relation to butene the realistic intermediates. This conclusion is made on the basis of the expectation that carbenium ions (with butene the primary carbenium ions) are not the likely intermediates.

UV spectra and poisoning by acetic acid of the acid–base pair sites. Two different intermediates have been proposed for the π-allylic mechanism with the Lewis acid sites to explain the double bond isomerization of

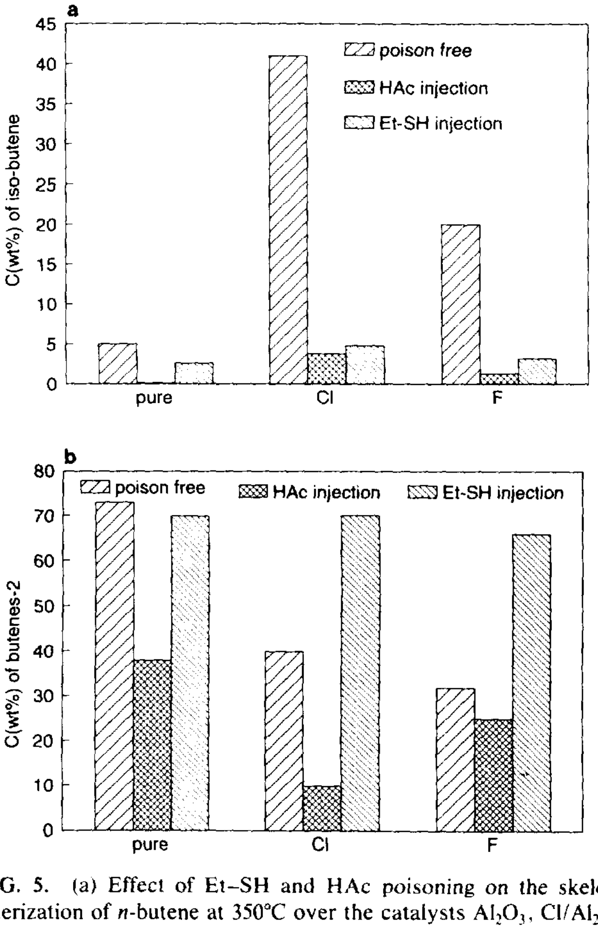

FIG. 5. (a) Effect of Et–SH and HAc poisoning on the skeletal isomerization of *n*-butene at 350°C over the catalysts Al_2O_3, Cl/Al_2O_3, and F/Al_2O_3. (b) Effect of Et–SH and of the HAc poisoning on the double bond isomerization of *n*-butene to *trans*- and *cis*-butenes-2 at 350°C over the catalysts Al_2O_3, Cl/Al_2O_3, and F/Al_2O_3.

olefins on alumina. One is the π-allylic *cation* (47, 48). In their UV spectroscopic study of *n*-butene adsorbed on silica–alumina (between 25 and 250°C), Leftin and coworkers (47, 48) ascribed the band at 310 nm to a butenyl cation and the band at 380 nm to "coke." This explanation is, however, not generally accepted. In another paper (49) Webb attributed the band seen at 330 nm to a polymeric carbenium cation and the band at 425 nm to "coke." In a study with 2,3-dimethylbut-l-ene reacting on alumina at 80°C, Knözinger and co-workers (50) suggest on the basis of UV, IR, and MS spectroscopic data that the UV absorption near 300 nm is due to "oxygen containing" compounds like 2-hexanone and that near 400 nm is due to condensation products of the latter one. Being aware of this information, we made a short UV spectroscopic study at 25°C of the catalysts shown in Table 2a after different times on stream. A band around 300 nm is always observed under all conditions. It was not influenced by contact with air and water, by storage of the catalysts for several months, etc. This is a behaviour different from that found by Leftin and Herman (48). The latter authors reported that contact with traces of air or water results in disappearance of the band at 310 nm and simultanous appearance of several other bands at 380, 465, and 560 nm. Such bands were observed by us at 420 and 580 nm with halogenated alumina catalysts, but regardless of the contact of the catalyst with air and water. On the other hand, the absorption intensity of these bands increases with increasing times on stream and leads to a visible successive darkening of the catalyst color: from white to light violet, the color of sand, and finally black. These are indications that if the π-allylic cation is correctly described by (47, 48) it has not been not seen by us (Fig. 6).

The other possible intermediate to be considered is the π-allylic *carbanion* originating from an olefin adsorbed on the Lewis acid and base pair site, formed by the so-called concerted mechanism. This mechanism was first postulated by Peri (51, 52) for the double bond isomerization of butenes on alumina. The conclusions are derived from results on NH$_3$-adsorption but there are also some additional arguments in favour of this idea. The band seen in IR spectra of rather firmly adsorbed butene-1, similar in character to *cis*-butene-2, indicates according to (51) that an abstraction of a proton from the adsorbate took place. Hightower and Hall (53, 54) and Gerberich and Hall (55) claimed that the mechanism of butene double bond isomerization over silica–alumina possibly involves carbenium ion formation (secondary butyl carbenium ion), but that on alumina the mechanism is completely different. The activity of alumina increases, namely, with the decreasing concentration of surface hydroxyls, but with silica–alumina the opposite is true (55) A so-called concerted mechanism, mentioned above, was therefore proposed by Gerberich and Hall (55) and also by Knözinger and co-workers (50, 56). The essence of this mechanism is as follows: the proton is split off from the olefin adsorbed on the Al^{3+} site and it is simultaneously attached to the basic oxygen site. In this way an allylic *anion* is formed on the Al^{3+} – site. Dent and Kokes (57) and Chang *et al.* [58] studied the mechanism of double bond isomerization of butene over ZnO and concluded that with ZnO the reaction proceeds through the above-mentioned π-allylic carbanion formation. The results of their IR studies (57) on ZnO are completely consistent with the kinetic (both for ZnO and Al$_2$O$_3$) data, and the reaction mechanism over alumina is thus believed to be the same or very similar on ZnO and Al$_2$O$_3$ (59, 60). Later, Gordymova and Davydov (61) concluded from a detailed IR study of propene adsorption on γ-Al$_2$O$_3$ and Na$^+$/Al$_2$O$_3$ at 25°C that it involves a heterolytic dissociation of propene into an allylic anion adsorbed on the Lewis acid site Al^{3+} and a proton reacting with an O^{2-} ion adjacent to the Al^{3+} with formation of a surface hydroxyl.

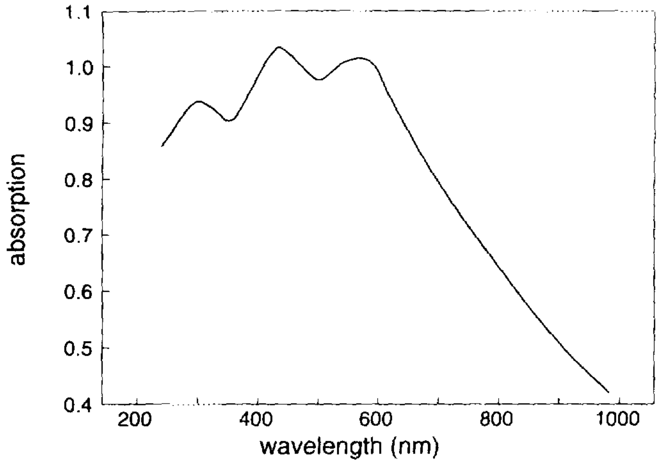

FIG. 6. UV spectrum of the sample of butylchloride-treated alumina at 350°C for 1 h and then *n*-butene reaction at 350°C for time-on-stream 2 h.

The cooperative action of acid/base pairs of sites is also believed to occur in reactions of dehydration (62) and dehydrochlorination over alumina (63–65) and therefore seems to be the main feature of aluminas. A potential poison for acid/base pairs of sites is a carboxylic acid. There is still some discussion on exactly how the acetic acid reacts with these active sites (66–70), but in any case, acetic acid is such a poison. It is more effective than Et–SH, for the skeletal as well as the double bond isomerization, over pure and halogenated alumina catalysts, as demonstrated here by Figs. 5a and 5b. This likely indicates that also the skeletal isomerization of *n*-butene requires the Lewis acid sites, possibly acting together with the neighboring basic sites. A possible intermediate could then be some intermediate like the π-allylic carbanion.

For the sake of completeness we have to mention that there are also some other potential intermediates of the skeletal isomerization to be considered. In principal, allylic radicals can also be formed, in addition to the anionic and cationic forms mentioned above. However, there have been no indications found that adsorbed radicals with unpaired electrons are formed upon chemisorption of higher olefins. Still another possibility is an "alkoxy intermediate" which is actually a covalent alternative for the more polar carbenium ion intermediate. An attempt has been made here to learn more about this possibility. An amount of Al tri-(*sec*)-butoxide corresponding to 50 wt% of Al tri-(*sec*)-butoxide on Al_2O_3, dissolved in cyclohexane (water free), was impregnated on γ-Al_2O_3, predried at 150°C (overnight). This sample was then dried at ambient temperature in vacuum for 48 h. Temperature programmed surface reaction, with a mass spectrometer as detector, revealed that above 150°C Al-tri-(*sec*)-butoxide decomposes into butene without any detectable isomerization.

Brønsted Acid Sites

Besides the above-described pathway hereafter called the unimolecular skeletal isomerization of butene, another possible pathway is the so called bimolecular one. It involves a dimerization of butenes into various octenes, a step which is followed by cracking to propene, pentenes, and butenes, including the formation of isobutene. The dimerizing and cracking steps are assumed to be carbenium ion catalyzed. The carbenium ion is assumed to be formed on the Brønsted acid sites.

The bimolecular mechanism was suggested, for example, in a study on the skeletal isomerization of *n*-butene over some zeolites modified by a cation exchange (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+}) (4). Dimerization was claimed on the basis of the fact that the isobutene, produced over the Ca-SAPO-11 and SAPO-11-extrudates, amounts up to 116% and 128%, respectively, of the equilibrium concentration. Weeks and Bolton (71) studied the mechanism of the reaction between *n*-butene and deammoniated ammonium-exchanged type Y zeolite, make use of highly enriched (4-^{13}C) *n*-butene. The authors (71) proposed that dimerization of *n*-butene, isomerization on dimers, and the hydrogen transfer mechanism, as well as the breakdown of polymeric molecules, may be responsible for the products found experimentally. The extent of hydrogenation was substantial (71) and the selectivity to isobutene (at 200°C) very low. The authors (71) stress in their paper that the cracked products are enriched in carbon-13 relative to the starting *n*-butene, so that there must be a transfer of ^{13}C amongst molecules.

However, the distribution of ^{13}C found experimentally was not compatible with a simple reaction: dimerization followed by random cracking. The data rather indicated that upon reaction strongly bound single carbon species are formed and transfered. An indication that some "bimolecular" mechanism can occur on our catalysts could be found in the Table 3a.

TABLE 3a

Products[a] of the Reactions of *n*-Butene, isoButene, and *n*-Octene over Various Catalysts Under Standard Experimental Condition

Reaction (350°C) of	C_4H_8				By-products			
	cis	*n*	iso	*trans*	$C_3^=$	C_4H_{10}	$C_5{}^b$	$C_8{}^b$
Catalyst: Alumina activated by C_4H_9–Cl/1 h								
5% *n*-$C_4^=$	24	12	41	16	2	1	3	<0.3
5% *n*-$C_4^=$ (450°C)	20	14	36	15	6	3	6	<0.3
100% *n*-$C_4^=$	18	11	27	12	7	7	14	4
5% iso-$C_4^=$	20	10	46	14	3	2	5	<0.5
1.5% *n*-$C_8^=$	9	4	21	6	11	1	19	29
1.5% *n*-$C_8^=$ (250°C)	1.5	0.5	6.5	1	2	0	3.5	85
Catalyst: Alumina activated by C_4H_9-Cl–1 h and then deactivated by H_2O								
5% *n*-$C_4^=$	31	16	28	22	1	0	2	0
5% iso-$C_4^=$	17	9	57	12	1	1	2	0
1.5% *n*-$C_8^=$	3.6	1.8	9.8	2.5	5	0	9	67
Catalyst: Alumina activated by CF_3COOH/5 min								
5% *n*-$C_4^=$	13	6	19	9	16	19	15	2
1.5% *n*-$C_8^=$	10	5	19	8	20	12	21	2

[a] Only gaseous molecules.

[b] Alkene + alkane.

In the reaction of *n*-butene over the catalysts studied under our standard conditions, the main by-products were propene, pentenes, butanes, and pentanes (Fig. 7 and Table 2a) and with F/Al_2O_3 the by-products are clearly more important than with the other catalysts. The unsaturated and saturated C_6–C_8 products were found to be in total less than 5% in the case of F/Al_2O_3, and they are insignificant in all other cases (see Table 3a). Such a large

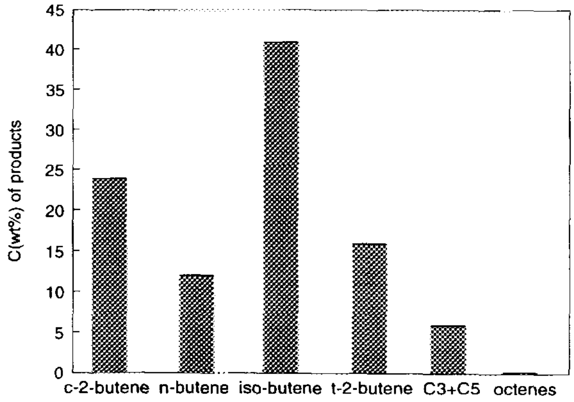

FIG. 7. Distribution of products for *n*-butene reaction over Cl/Al_2O_3 under standard test conditions at 350°C.

difference in production of by-products is probably related to the fact that according to the literature the catalyst F/Al_2O_3 should possess more Brønsted sites of strong acidity than all other catalysts. Furthermore, the increase of reaction temperature to 450°C, with Cl/Al_2O_3 as a catalyst, results in an increase of the content of by-products and also in a decrease in isobutene production (Table 3a and Fig. 2). In contrast to this, when *n*-butene pressure is substantially increased, a liquid polymer (smelling like gasoline) representing about 5% of the *n*-butene feed is also produced. The GC analysis (using manual injection) showed that this liquid is composed of alkenes and alkanes of a carbon number higher than 8. Obviously, dimerization or even polymerization can occur over the alumina activated by halogen. This is in agreement with earlier reports that the chlorinated alumina is good for polymerization of 4-methyl-pentene-1 (72), propene, butenes (73), and isobutene (31, 74–76) and also that the alumina activated by F is able to selectively *dimerize* isobutene (25) and α-olefins (77), as well as to *polymerize* olefins (78).

Further, the reaction of *n*-octene has been carried out over the catalyst Al_2O_3, Cl/Al_2O_3, and F/Al_2O_3 under the standard test conditions. In the case of pure alumina and at 350°C, about 95% of *n*-octene is already converted into more than 30 isomers of both octene and octane but without a significant formation of cracking products. In that direction, the conversion is low (only about 10%) even when the reaction temperature is increased to 450°C. After activation of alumina by F or Cl, the cracking of *n*-octene into C_3, C_4, and C_5, but not significantly into C_6 and C_7, becomes the predominant reaction (see Table 3a and Figs. 8 and 10).

The experimental results (see Table 3a) suggest that Brønsted acid-catalyzed reactions through carbenium ions, such as di- or polymerization of butenes followed by isomerization and cracking, can take place over the modified aluminas. These reactions produce many by-products, depending on both the acidity of the Brønsted sites and experimental conditions. A similar mechanism is proposed by Szabo *et al.* (2d) to explain the formation of by-products. However, we did not find product distributions like those reported by (2d).

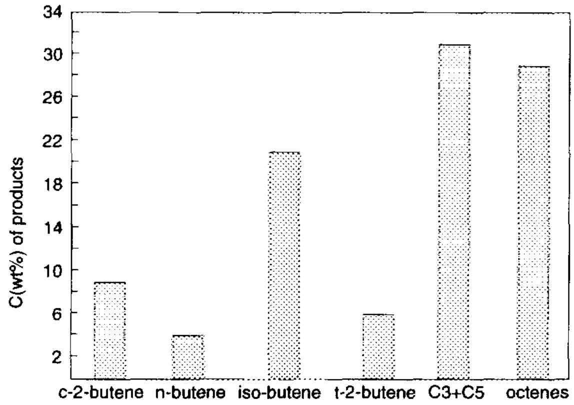

FIG. 8. Distribution of products for *n*-octene reaction over Cl/Al_2O_3 under standard test conditions at 350°C.

TABLE 3b

A Comparison of the Concentrations of isoButene Produced in Various Reactions with Equilibrium Concentration[a]

Catalyst	Feed	Reaction T	iso-$C_4^=$ (/$C_4^=$)	iso-$C_4^=$/equil.
Cl/Al_2O_3	5% *n*-$C_4^=$	350°T	41%	96%
	5% iso-$C_4^=$	350°C	46%	106%
	1.5% *n*-$C_8^=$	350°C	53%	122%
	1.5% *n*-$C_8^=$	250°C	68%	117%
Cl/Al_2O_3	5% *n*-$C_4^=$	350°C	28%	65%
deactivated	5% iso-$C_4^=$	350°C	57%	133%
by water	1.5% *n*-$C_8^=$	350°C	55%	128%
F/Al_2O_3	5% *n*-C_4	350°C	41%	95%
	1.5% *n*-$C_8^=$	350°C	45%	105%

[a] Only butenes considered.

An important observation concerning cracking of *n*-octene is that there is a considerable production of isobutene at 350°C (Figs. 8 and 10): about 20% of all cracking products. Moreover, the percentage of isobutene among butenes increases with the decrease of cracking temperature or with increasing deactivation of the catalyst. The value for *C* (wt%) of isobutene is always near to or over the equilibrium concentration (43% of butenes), as shown in Table 3b. The catalyst Cl/Al_2O_3 at 350°C is able to convert iso-butene into linear butenes but in less than the equilibrium concentrations, and therefore isobutene exceeds the equilibrium concentration (Table 3b). When the catalyst is poisoned by water the value for *C* (wt%) of isobutene in the reaction with *n*-butene in the feed drops from 41 to 28%, clearly under the equilibrium limit, but the value of *C* (wt%) of isobutene in the reactions with isobutene or *n*-octene in the feed is higher and thus even further exceeds the equilibrium concentration (Table 3b). These experimental results indicate that isobutene is not all produced directly and fully from the skeletal isomerization of linear butenes produced from octenes. At least partially, isobutene originates from the direct cracking of isomerized octenes. One could thus speculate that *n*-octene undergoes either a direct cracking reaction to propene, pentenes, and linear butenes of which a part isomerizes, or alternatively first the double bond in and skeletal isomerization of *n*-octene and then the cracking to other products (including iso-butene) takes place. The latter pathway looks more probable since skeletal isomerization of *n*-octene is easier than that of *n*-butene (5).

When looking at the product distributions in Table 3a, it is possible to make an important conclusion: besides

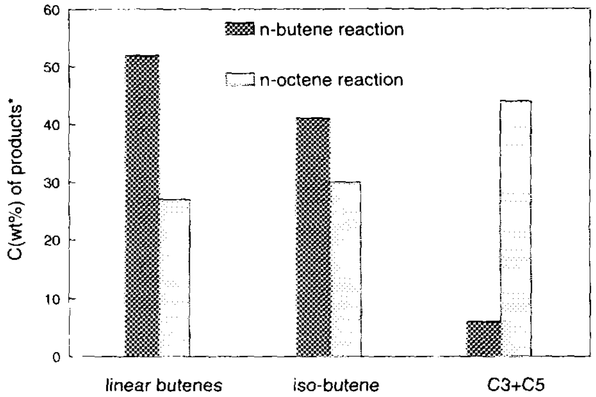

FIG. 9. A comparison of the product distribution within C_3–C_5 fractions for *n*-butene reaction and the *n*-octene reaction over Cl/Al_2O_3, under standard test conditions at 350°C.

the unimolecular mechanism, the skeletal isomerization of *n*-butene to iso-butene can proceed in parallel via the so called bimolecular mechanism: a dimerization of butenes, followed first by a skeletal isomerization over acidic sites (Lewis or Brønsted) and finally by cracking. The distributions of products in Table 3a for the reactions of *n*-butene on one hand and *n*-octene on the other hand over Cl/Al_2O_3 at 350°C are different (Fig. 9). Thus the bimolecular mechanism cannot be the unique mechanism either. Let us thus make a rough estimate of the contribution of this mechanism. If we assume that propene and pentenes are formed by a bimolecular reaction, then under indicated conditions about 96% of isobutene must be formed by unimolecular isomerization. This estimate is also supported by the Figs. 5a and 5b concerning poisoning experiments. Having made this conclusion concerning Cl/Al_2O_3 we have to add that F/Al_2O_3 is different (Fig. 10). One derives from Table 3a that here the bimolecular mechanism could even be the major mechanism, amounting to about 70%.

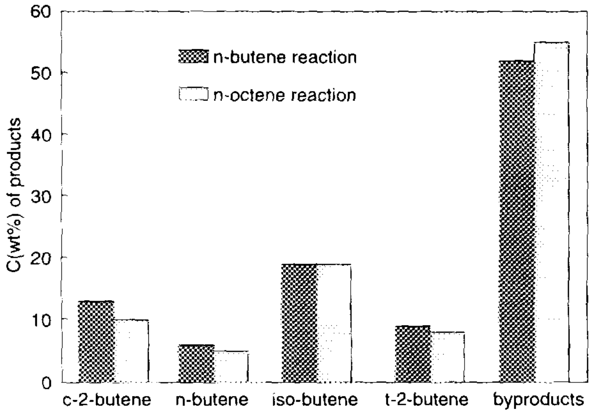

FIG. 10. A comparison of the distribution of all products for the *n*-butene reaction with that for the *n*-octene reaction over F/Al_2O_3 under standard test conditions at 350°C.

CONCLUSIONS

Pure alumina and alumina modified by organic compounds containing halogen as F, Cl, Br, and I have been investigated in the reaction of skeletal isomerization of *n*-butene. It appeared that *n*-butene skeletal isomerization is somehow related to the presence of the Lewis acid sites. The so-called unimolecular mechanism prevails under standard reaction conditions, and the mechanism involving secondary butylic carbenium ions (frequently proposed in the literature) is in our opinion unlikely. However, a carbenium-like mechanism may be possible in which *n*-butene is first polymerized into octenes which isomerize skeletally more easily than butenes, and which in their turn are again cracked down to isobutene, other butenes, propene, and pentenes. This is the so-called biomecular mechanism of isomerization.

It was found that at 350°C under standard experimental conditions the selectivity to isobutene varies as follows: Cl or Br/Al_2O_3 (40%) > I/Al_2O_3 (38%) > F/Al_2O_3 (20%) ≫ Al_2O_3 (5%). The content of by-products as C_3 and C_5 over F/Al_2O_3 is higher than over the other catalysts. With the catalysts Cl- or Br-modified Al_2O_3, the production of isobutene almost leads to the thermodynamic equilibrium concentration.

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