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Properties of Chlorinated Aluminas

V. cis-2-Butene Isomerization over Alumina and Chlorinated Aluminas

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Kinetics of *cis*-2-butene isomerization were studied on pure and chlorinated aluminas. The surface reaction is rate controlling and produces *trans*-2-butene and 1-butene by two parallel reactions. The variations of catalytic activity with chlorine content support the existence of different types of sites; at least three kinds of active sites are proposed: oxygen ions having electron donor properties, weakly basic sites, and strong Lewis centers.

INTRODUCTION

In previous works (*1–4*) the mechanism of the chlorination of alumina by carbon tetrachloride and the redox properties of the resulting solids were studied. The type of reaction of CCl_4 with alumina varies according to the nature of surface and reaction conditions. On a sample preheated above 300°C, CCl_4 exchanges 4 chlorine atoms against two surface oxygen atoms (*1*). The EPR study of the redox character of a chlorinated sample shows the existence of strong oxidizing sites; their number when measured by perylene$^+$ concentration (*4*) is proportional to the amount of chlorine; these sites could be identified as bicoordinated aluminum atoms which have a partial positive charge. The decrease of electron donor properties of the solid with increasing chlorine content can be correlated with elimination of O^{2-} ions from the surface (*3*).

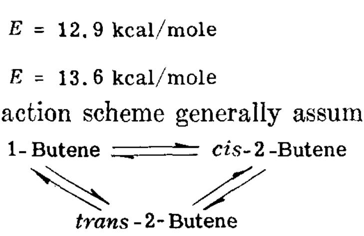
The calorimetric study of the chlorination reaction shows that at room temperature the ions with basic character and few other oxygen atoms have a great reactivity. On a solid treated at 200°C under vacuum, the chlorination proceeds through the exchange of OH groups by chlorine atoms. The chlorinated alumina so obtained has a weakly oxidizing power; it may have some Brönsted acidity.

In the present work, catalytic properties of these solids were tested in the isomerization of *cis*-2-butene to *trans*-2-butene and 1-butene. This simple reaction needs only double-bond migration or a change in configuration. Despite numerous studies devoted to this subject (*5–17*) the mechanism of the reaction is not clear. The reaction selectivities are not governed by purely thermodynamic factors but by kinetic parameters which depend chiefly on the nature of the catalysts and the geometry of the olefins (*12*). The reaction may be catalyzed by acids (*19*), bases (*20*), semiconductors (*21*), and insulator solid oxides (*17*). The kinetic study of this reaction is complicated by fouling of the catalyst with time; it has been performed by pulse, steady-state flow, and tracer techniques (*12, 17*). The various authors generally agree that the reaction is first order for the reactant; the activation energy is about 13 kcal/mole for both reactions (*18*).

$$\textit{cis}\text{-2-Butene} \longrightarrow \text{1-Butene} \qquad E = 12.9\ \text{kcal/mole}$$

$$\textit{cis}\text{-2-Butene} \longrightarrow \textit{trans}\text{-2-Butene} \qquad E = 13.6\ \text{kcal/mole}$$

The reaction scheme generally assumed is



On silica–alumina the experimental results lead to suppose the existence of a 2-butyl carbonium ion which would be the common intermediate for all reactions; on alumina no simple model can be formulated; at least two types of sites are active (*17, 16*); a carbon–hydrogen bond cleavage is involved in the rate-determining step for all reactions on alumina (*17*). According to the literature the selectivity of the reaction (1-butene/*trans*-2-butene) is low on alumina and very high on fluorinated alumina (*12*); this has not yet received any attention in the interpretation. It has been reported (*9*) that activating alumina by fluorine or chlorine increases the aging of the catalyst.

I. EXPERIMENTAL METHODS

(*a*) *Apparatus and Materials*

The methods of preparation of alumina have been described elsewhere (*1*). The kinetic study was performed with a differential microreactor; reactants and products were analyzed by gas-phase chromatography with a flame ionization detector Aerograph 600; a column of dimethylsulfolane on chromosorb (6 m) was used at 25°C, or for some experiments at 0°C.

(*b*) *Procedure*

To avoid any contact of the catalyst with air, chlorine was introduced *in situ.* A sample of 100 mg of alumina was heated in the reactor at 500°C, (except when indicated) for 15 hr in a stream of dry nitrogen. A partial pressure of 5 torr CCl_4 was then established on the solid at a temperature of 200°C; the time of the treatment was calculated from previous results (*2*). After this chlorination, the reactor was purged with nitrogen to remove the remaining carbon tetrachloride and reaction products. Then, the catalytic reaction was performed, at a specific flow rate and partial pressure of the reactant. The first analysis was done after a period of 90 sec; the peak heights of *trans*-2-butene and 1-butene represent the catalytic activity. First the rate decreased (Fig. 1), then became constant after 300 min. The kinetic studies were performed with the stabilized catalyst. The chlorine content of the solid was measured at the end of the reaction according to the procedure described else-

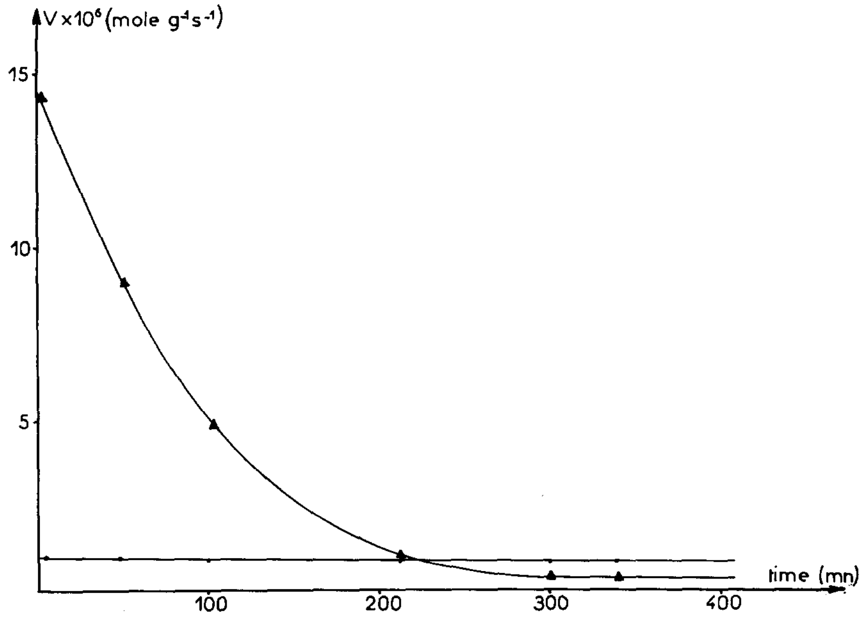


FIG. 1. Time dependance of isomerization rate at 200°C on alumina: ▲, rate of formation of *trans*-2-butene; ●, rate of formation of *n*-1-butene.

where (*1*). The rate can be obtained from experimental results by the relationship:

$$V = \frac{D}{22400} \cdot \frac{P}{760} \cdot \frac{1}{m},$$

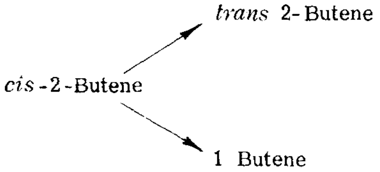
where V is the rate in moles/sec g; D = total flow rate; P = partial pressure of products; and m amount of catalyst (g).

II. KINETICS OF THE REACTION

The *cis*-2-butene isomerization on alumina and chlorinated aluminas yields chiefly *trans*-2-butene and 1-butene. Traces of isobutene, butane, and butadiene were identified; we did not take them into account in this paper. The kinetic study was conducted to determine the rate constant and true activation energy, but also the influence of chlorination on the kinetic factors of the reaction.

(*a*) *Influence of the Contact Time*

A set of results is given in Fig. 2. Above 10% conversion, the rate is not proportional to contact time. This may be explained by diffusion or by interconversion reactions. To avoid this, we have chosen a rather high flow rate (9 liter/hr) which allowed us to measure the straight forward reactions:



(*b*) *Influence of the Partial Pressure of* cis*-2-butene*

An experimental curve is given in Fig. 3 for two catalysts. The plots of these data using the linear form of the Langmuir isotherm give a straight line (Fig. 4). The isomerization proceeding through a Langmuir-Hinshelwood scheme, the surface reaction must be rate controlling; (that is that the rate is not desorption controlled).

$$v = k\theta = k\frac{aP}{1 + aP}.$$

A set of results is given in Table 1; as shown, chlorination does not change the rate of 1-butene production.

(*c*) *Determination of Kinetic Factors*

The linear form of the rate equation $\{v = k - [(1/a)(v/p)]\}$ allows the calculation of the rate constant k from the intercept at $v/p = 0$ and the adsorption coefficient a from the slope. The true activation energy can be obtained from experiments at different temperatures. The a is an equilibrium constant so we have:

$$\Delta G = -RT \log a = \Delta H - T \cdot \Delta S,$$

ΔG, ΔH, and ΔS corresponding to the transfer of one mole of *cis*-2-butene from the gas phase to the adsorbed layer. From this we get:

$$d \log a / d\left(\frac{1}{T}\right) = -\Delta H/R,$$

and

$$\Delta S = \frac{\Delta H - RT \log a}{T}.$$

We have chosen as standard state $p^0 = 1$ atm for the gas phase, and $\theta = 1/2$ for the adsorbed layer (θ represents the coverage) (*23*).

The values so obtained are given in Table 1. The translational entropy of gaseous *cis*-2-butene at 760 torr pressure was calculated according to:

$${}_{g}S^{0}{}_{tr} = R(\tfrac{3}{2}LnM + \tfrac{5}{2}LnT) - 2.3.$$

The rotational entropy was obtained from the equation (*22*):

$${}_{g}S^{0}{}_{rot} = R\left[Ln\frac{1}{\pi\Sigma}\frac{8\pi^{3}(I_{A} \cdot I_{B} \cdot I_{C})^{1/3}}{h^{2}} \cdot kT^{3/2} + \frac{3}{2}\right],$$

where Σ represents the symmetry number, here $\Sigma = 2$. The I_A, I_B, I_C are the moments of inertia relatively to 3 perpendicular axes.

(*d*) *Conclusions*

The kinetic study shows that the isomerization of *cis*-2-butene proceeds through a Langmuir mechanism on both alumina and chlorinated alumina. Chlorination does not alter the kinetic parameters for 1-butene production; in contrast the factors relative to *trans*-2-butene formation are noticeably changed. It seems likely that

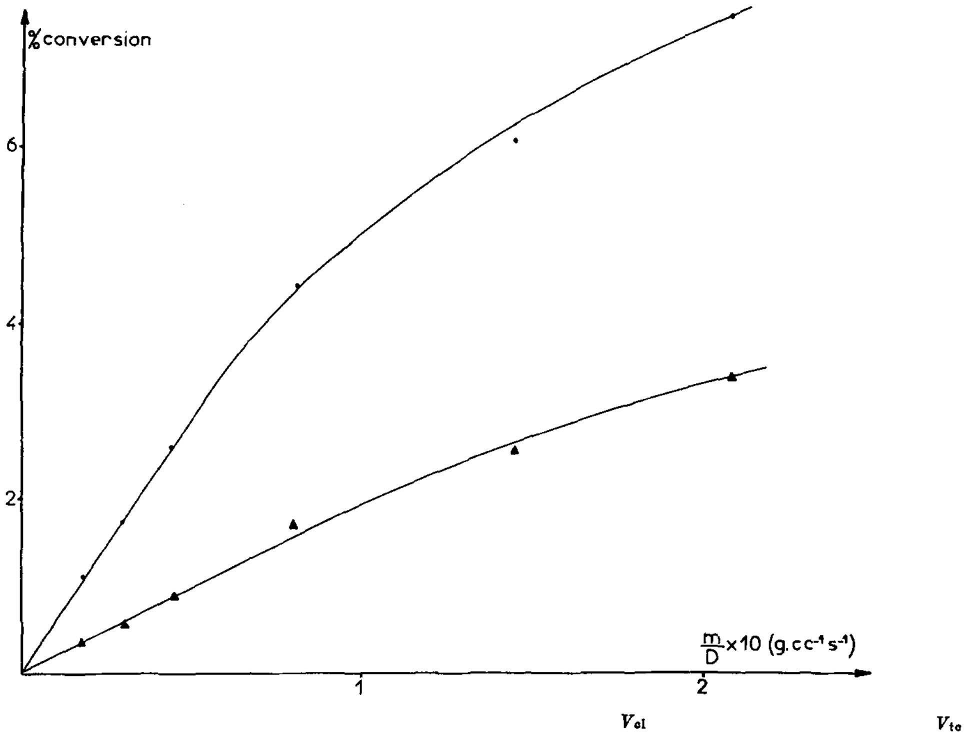


FIG. 2. Influence of contact time on the conversion: ●, *cis*-2-butene → *n*-1-butene; ▲, *cis*-2-butene → *trans*-2-butene.

the two parallel reactions do not occur on the same sites on alumina and chlorinated alumina; *cis*-2-butene mobility on the sites producing *trans*-2-butene is lowered on chlorinated alumina, as is shown by the entropy variations. On alumina the reactant keeps some translational freedom, but after chlorination of the solid the calculated entropy variation corresponds to the loss of some rotational freedom.

III. STUDY OF THE CATALYSTS

(*a*) *Influence of Chlorine Content on the Initial Activity*

The aging of the catalyst observed in the butene isomerization over insulator

TABLE 1

KINETIC PARAMETERS OF THE TWO REACTIONS ON ALUMINA AND CHLORINATED ALUMINA

Reaction:	*cis*-Butene-2 → *n*-Butene-1						*cis*-Butene-2 → *trans*-Butene-2					
Catalyst:	Alumina			Chlorinated alumina (30 mg of Cl/g)			Alumina			Chlorinated alumina (30 mg of Cl/g)		
Temp. (°C):	160	180	200	160	180	200	180	200	220	180	200	220
$k \times 10^7$ mole/sec g	2.3	11	34	2.3	9	32	5	21	64	0.8	3.4	14.7
E_a (kcal/mole)		28.5			27			29			25.6	
$a \times 10^3$ (torr^{-1})	18.7	5.75	3.61	19.6	8	3.87	10	3	1.85	19.6	5.66	2.28
ΔH (kcal/mole)		17			17			18.5			24	
ΔS (u.e.)		−34.6			−33.9			−36.9			−47.4	
$+_gS_{tr}^0$ (u.e.)					40.2							
$+_gS_{rot}^0$ (u.e.)					19.9							

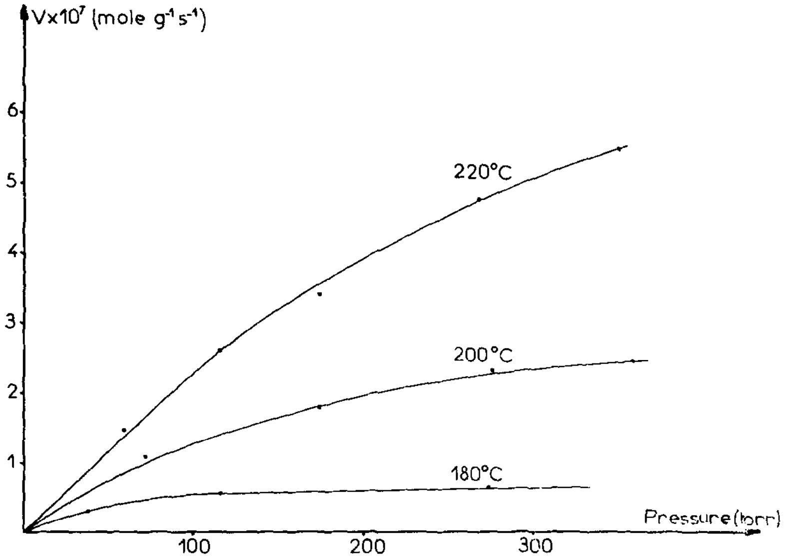


FIG. 3. Influence of partial pressure of *cis*-2-butene on the rate of isomerization in *trans*-2-butene on chlorinated alumina (30 mg/g of Cl$^-$).

oxides is generally presented as the poisoning of sites by carbonaceous residues or by π complexes formation. Due to fouling, the initial activity is the only proper characteristic of the solid, so it has been chosen to study the catalysts.

The work was performed with solids preheated at 500°C, which contained various amounts of chlorine. The *cis*-2-butene partial pressure was 100 torr and the isomerization temperature, 200°C; under these conditions the order relative to *cis*-2-butene is 1. The results are represented in Fig. 5a: the variations of the initial activity plotted versus chlorine content are very different for the two products. Up to 10 mg of Cl/g the production of *trans*-2-butene decreases while that of 1-butene increases. Above this content, *trans*-2-butene production increases linearly with the amount of chlorine; to the contrary 1-butene formation remains constant above

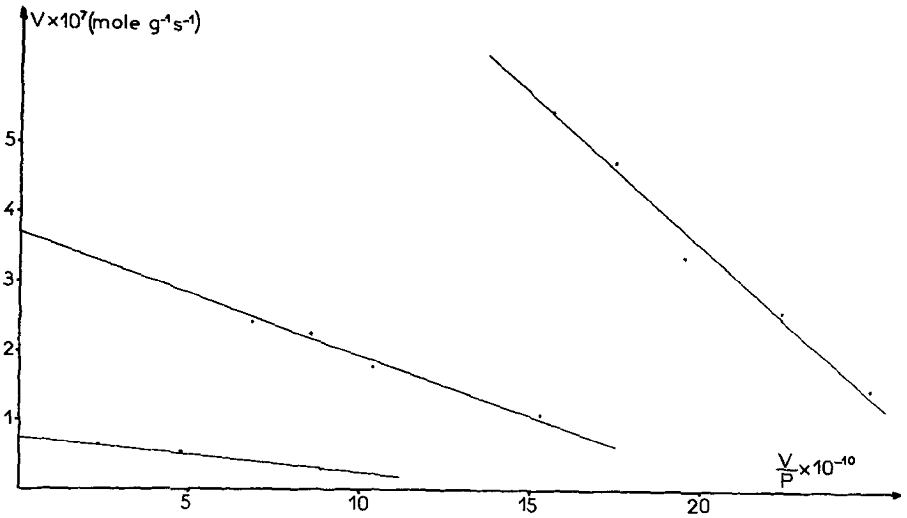


FIG. 4. Determination of "*k*" and "*a*" at three temperatures, after results mentioned on Fig. 3.

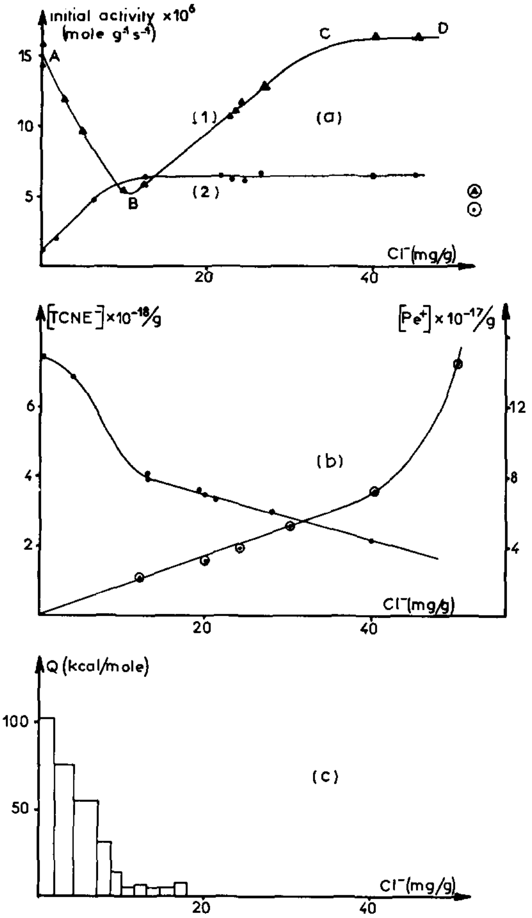


FIG. 5. Influence of chlorine content: (a) on initial activity: ▲, rate of formation of *trans*-2-butene (⊛, $AlCl_3/Al_2O_3$) (V_{ct}) ●, rate of formation of 1-butene (V_{cl}) (⊙, $AlCl_3/Al_2O_3$) (b) on redox properties of chlorinated alumina: ●, $TCNE^-$; perylene$^+$ (c) on the heat produced by the reaction of chlorination at room temperature.

10 mg of Cl/g. For the *trans*-2-butene production represented by curve 1, the experimental results seem to suggest two simultaneous phenomena: (i) elimination of the active sites of the initial alumina (part AB of the curve). (ii) formation of new centers, the number of which is proportional to the amount of chlorine (part BC).

The last part (CD) is related to the presence of adsorbed CCl_4. For the 1-butene production, represented by curve 2, the disappearance of the sites active for *cis-trans* isomerization coincides with the formation of new centers for the production of 1-butene.

(b) *Influence of the Temperature of Pretreatment before Chlorination on the Initial Activity*

The pretreatment before chlorination greatly affects the mechanism of the chlorine fixation and the nature of the solid. The influence of this preheating temperature on isomerization was investigated. The experimental results are presented in Fig. 6. With preheating temperatures between 200 to 300°C, *trans*-2-butene production increases greatly while 1-butene is only slightly affected. In this temperature range, the chlorination reaction proceeds through an exchange of OH groups by chlorine atoms. Above 300°C the chlorine fixation consists of substitution of some oxygen ions by two chlorine atoms. The catalytic activity remains unchanged. This suggests that the active sites are not modified by the thermal pretreatment of alumina. From 700 to 800°C the catalytic activity falls slightly and this may be caused by sintering of the alumina.

(c) *Poisoning of the Catalysts*

A simple method to investigate the nature of active sites is to poison them selectively; for example, with respect to 1-butene isomerization on alumina, Medema and Houtman (*13*) found two types of active sites using triethylamine as poison.

(1) **Oxidizing sites.** In a previous calorimetric study (*3*) we found that γ-alumina possesses some labile oxygen, which can be reduced by CO at 200°C. The catalytic activity of the so reduced solid was unchanged.

(2) **Reducing centers.** An EPR study of the solid (*4*) shows the existence of oxygen ions having an electron donor character; these ions can react with CCl_4 at room temperature. We tried to poison these centers by tetracyanoethylene which is known to form a charge transfer complex on these sites. In that case we found for the poisoned solid, that the *trans*-2-butene conversion was decreased by a factor 4 while 1-butene formation was unchanged. Catalyst lifetime was greatly altered, the activity disappearing after 10 min. This ex-

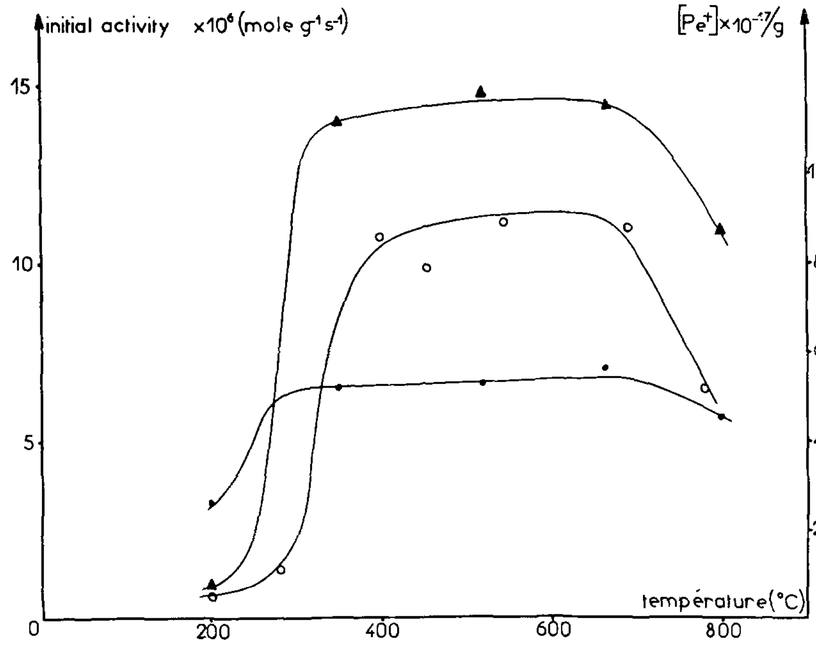


FIG. 6. Influence of preheating temperature before chlorination on the initial activity and on the oxidizing properties of the solid: ▲, rate of formation of *trans*-2-butene (V_{ct}); ●, rate of formation of 1-butene (V_{c1}); ○, relative concentration in perylene⁺ (the chlorine content of all the solids is approximately the same, 30 mg/g of Cl^-).

periment establishes the catalytic role of the reducing centers of the solid.

DISCUSSION

From these experimental results some conclusions can be drawn with respect to the kinetics of the reaction and the nature of active sites. The surface reaction is rate controlling since a Langmuir equation is followed. Several observations support the hypothesis of two different sites producing either 1-butene or *trans*-2-butene: (a) The change in selectivity with time on alumina, (Fig. 2) previously found by Brouwer (*15*), shows a different behavior for 1-butene and *trans*-2-butene formation rates; *trans*-2-butene sites are progressively poisoned while 1-butene centers remain nearly unaltered. (b) Chlorination greatly affects selectivity. (c) Kinetic factors of *trans*-2-butene formation (activation energy, the entropy and enthalpy of adsorption) are changed by the chlorination while those corresponding to 1-butene are not greatly modified; this suggests the presence of two different types of adsorption for *cis*-2-butene. All these experimental results led us to think that at least two types of sites exist on the surface.

A. Nature of the sites producing trans-*2-butene*

The minimum observed in *trans*-2-butene formation rate with respect to the chlorine content (Fig. 5a) leads us to propose the existence of two types of sites: one type initially present on alumina and a second one created by chlorination. The elimination of some oxygen ions from the alumina surface corresponds to a decrease in the *trans*-2-butene formation rate. These ions possess strong electron donor properties as shows the decrease in $TCNE^-$ concentration against chlorine content (Fig. 5b). The calorimetric data on the chlorination prove that these ions are the only ones which react with CCl_4 at room temperature (Fig. 5c). So we can conclude that *trans*-2-butene producing sites can be identified to these particular oxygen ions. Their poisoning by TCNE is not a sufficient proof to correlate their activity with their reducing character. It can be accepted, as suggested, by Hall (*17*) that a geometrical factor favors *trans*-2-butene production. The *trans*-2-butene configuration allows adsorption on O^{2-} ions according to the scheme represented on Fig. 7. It can be supposed that under the influence of the electric field of the O^{2-} ion, the π electrons of the double bond can be delocalized to obtain the formation of the intermediate complex represented in Fig. 7. Though purely speculative, this model accounts for the observed selectivity of alumina. This mechanism is supported by some other results (*13*) which supposes that *cis*-2-butene is adsorbed on the surface more closely than *trans*-2-butene. As a function of chlorine content above 10 mg/g, the number of sites producing *trans*-2-butene increases like the concentration in perylene$^+$ ions. The initial activity and the concentration in perylene$^+$ ions vary approximately in the same way as a function of the temperature of pretreatment. So we are led to suppose that the oxidizing sites created by the chlorination are active for *trans*-2-butene production. The great decrease of entropy associated to the chemisorption of *cis*-2-butene on these sites can be attributed to adsorption on a strong site which limits the mobility of the adsorbed molecule. In conclusion, from our results the existence of two types of sites for *trans*-2-butene isomerization is postulated: on one hand, surface oxygen ions possessing some donor character; on the other, Lewis sites which are created by chlorination.

B. Nature of Sites Active for 1-Butene Formation

(a) On Initial Alumina

Haag and Pines (*20*), Foster and Cvetanovic (*14*) published that basic solids can isomerize *cis*-2-butene selectively to 1-butene, the activity encountered on pure alumina may be attributed to such basic centers. However the lack of change with time of the activity which is not poisoned by TCNE and the mobility of the adsorbed molecule show that these sites are weak. The activity of aged chlorinated aluminas is the same as for pure alumina, so it appears that these centers are not destroyed by chlorination.

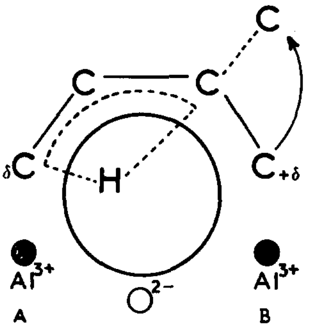


FIG. 7. Surface complex for *cis*-2-butene *trans*-2-butene interconversion over alumina [after the model proposed by Hall (*18*)].

(b) On Chlorinated Alumina

Besides the above mentioned sites, these aluminas have particularly oxidizing Lewis sites. The initial increase of catalytic activity which is parallel to the increase in acidity shows that Lewis acid sites are active for 1-butene production. The scheme proposed by Hall, that we have previously used, allowed us to find an interpretation of the results: we attributed the selectivity on pure alumina to a geometric factor that some surface oxygen ions might possess. Chlorination causes the elimination of these oxygen atoms and the appearance of Lewis sites; on acidic centers, the isomerization proceeds through a carbonium ion mechanism, with a decrease in selectivity, as was observed on silica–alumina (*17*). Some experimental results relative to aluminum chloride deposited on alumina support these conclusions: this catalyst, for which a carbonium ion mechanism is postulated, gives an activity lower than chlorinated alumina and a selectivity of 1. This selectivity is effectively observed for a chlorine content of 10 mg/g, i.e., when all the basic oxygen atoms of the surface have been taken off. Between 0 and 10 mg/g, the total conversion is approximatively constant and this shows that the elimination of one oxygen selectively active for *trans*-butene production yields one Lewis site which has nearly the same activity but a poorer selectivity. For chlorine contents above 10 mg/g, 1-butene production remains constant while *trans*-butene increases with acidity. The sites created here present again a particular selectivity for *cis–trans* isomerization. Two explanations can be invoked: either a favorable configuration of the site, by analogy with the arguments precedently proposed; or a different nature of the Lewis site which is created by the reaction of oxygen ions tightly bound to the surface.

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