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The Isomerization of *cis*-2-Butene over Silica–Alumina Catalysts

I. Study of the Deactivation of Active Surface Sites

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Two independent exponential laws are involved simultaneously to describe the deactivation which occurs in the isomerization of butenes on silica–alumina. This permits the calculation of two complementary initial rates for the reaction on a fresh catalyst. The action of poisoning reagents on such rates demonstrates which types of surface sites (Lewis or Brønsted acid–base sites, oxidizing or reducing centers) are acting as primary catalytic centers. Furthermore the experimental conditions (pressure and temperature) for which one of them is more active are determined.

INTRODUCTION

A great deal of research has been done on the isomerization of butenes. The reaction may be carried out under a variety of conditions, e.g., in gas or solution (*1, 2*) or in the presence of many different catalysts. In the restricted sphere of oxide catalysts, several mechanisms have been proposed (*3–9*), which imply different kinds of active sites. For instance, in certain conditions, these are protonic centers in the solid surface (*7*). In fact the catalytically active sites are not always the surface centers of the solid. They may be formed by the adsorption on surface sites of a reactant which assumes the nature of a catalytic site. The surface centers look like "primary" active sites. Thus on silica–alumina, Clark (*6*), Ozaki *et al.* (*7*), and Hall (*8*) believe that the active site is a polymeric complex adsorbed on a Lewis acid site. This active residue is formed on the surface during the first few minutes during which the reactant is contacted with the catalyst. At the same time the activity of the solid is decreased by a poisoning effect. It was shown that this deactivation phenomenon depends on several factors (temperature, pressure, origin of the sample).

In reinvestigating butene isomerization on silica–alumina, the first part of our work has concerned the deactivation phenomena. This has provided interesting information not only on the active centers, namely the polymeric complexes formed on the primary sites, but also on the nature of the primary sites.

NOMENCLATURE

$A_{(i)}$—activity in % conversion per g of catalyst
$a_{(i)}$—activity on a fresh catalyst in mole liter^{-1} g^{-1}
$v_{(i)}$—initial rate on a fresh catalyst in mole sec^{-1} g^{-1}
$c_{(i)}$—lifetime of active site in min^{-1}
(i)—T, 1, 2, L or B (see text for definitions)
W—weight of catalyst
F—flow of gaseous mixture.

EXPERIMENTAL

Techniques

Catalytic activity measurements. The microcatalytic technique was employed to check the catalytic activity. The catalyst (20–75 mg) was heat-treated in the microreactor at 400°C for 16 hr in flowing hydrogen (4 liter hr^{-1}) before the test. The catalyst was white after such a treatment. The temperature was decreased until it reached the desired value (between 100 and 28°). A stream of *cis*-2-butene–hydrogen mixture was passed through the catalyst under conditions of low conversion (less than 10% of the equilibrium conversion). The partial pressure of the reactant was maintained between 30 and 200 Torr. The products were analyzed by gas chromatography with a dimethylsulfolane on chromosorb column (6 m) maintained at 30°. The analysis started two minutes after the beginning of the run and it was continued for a long time, up to 5 hr.

UV studies. Irreversibly adsorbed species were investigated by uv spectroscopy. Butene was adsorbed for 36 hr at 200 Torr on catalysts previously heat-treated for 2 hr at 200° under vacuum, 1 hr at 400° under oxygen (200 Torr), 0.5 hr at 400° under vacuum, 2 hr at 400° under oxygen (200 Torr) and 15 hr at 400° under vacuum. The butene was then progressively desorbed at 25, 85, 150 and 200°. The spectra were recorded at room temperature with an OPTICA CF4 spectrophotometer.

Materials. An industrial silica–alumina catalyst has been employed (Ketjen—14% Al_2O_3). After outgassing for 15 hr at 400° its surface area determined by the BET method with N_2 was 580 m^2 g^{-1}.

In some experiments the catalyst was treated with various reagents before introducing the *cis*-2-butene. The compounds NH_3, phenothiazine, anthracene, thianthrene, and trinitrobenzene were introduced in the microreactor just before measuring the activity. The time and the temperature of the adsorption are given in Table 1.

TABLE 1
INFLUENCE OF THE NEUTRALIZATION OF ACTIVE SITES ON THE INITIAL RATES

Catalysts	$v_1(= v_L)$ (mole sec^{-1} g^{-1}) (1-butene + *trans*-2-butene) × 10^6	$v_2(= v_B)$ (mole sec^{-1} g^{-1}) (1-butene + *trans*-2-butene) × 10^6
Neutralization of oxidizing sites		
unpoisoned sample	12.8	0.85
treated with phenothiazine		
¼ hr at 110°C	2.20	0.85
4 hr at 110°C	0.00	0.15
treated with anthracene		
2 hr at 90°C	1.10	0.84
treated with thianthrene		
2 hr at 110°C	0.11	0.88
5 hr at 110°C	0.00	0.83
Neutralization of acid sites		
unpoisoned sample	12.8	0.85
treated with NH_3		
desorbed at 235°C	0.7	0.00
desorbed at 350°C	6.2	0.74
Neutralization of protonic sites		
unpoisoned sample	61.0	4.1
containing 0.28% Na	58.0	2.1
1.26% Na	3.0	0.24
4.6% Na	0.14	0.07
Neutralization of reducing sites		
unpoisoned sample	57.0	4.1
treated with trinitrobenzene		
¼ hr at 110°C	3.6	2.3

Catalysts containing various amounts of Na^+ ions (0.28, 1.26, 4.6%) were prepared by exchange with NaCl, CH_3COONa and Na_2CO_3 solutions.

RESULTS

Deactivation phenomena. The isomerization of *cis*-2-butene over silica–alumina leads to the formation of *trans*-2-butene and 1-butene. No other products can be detected. In regard to the deactivation phenomena, the experimental results are quite similar for the two products. Therefore the activity may be expressed in terms of the sum of the amounts of the two products obtained. The results given in % conversion are reported in Fig. 1.

Whatever the partial pressure of the *cis*-2-butene or the temperature of the reaction, all the experimental curves are of the same type, showing a rapid loss in activity during the first few minutes followed by a very slow decrease during several hours.

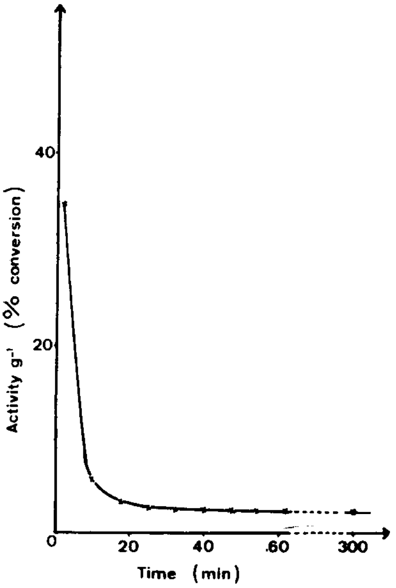

FIG. 1. Catalytic activity versus the time of the run.

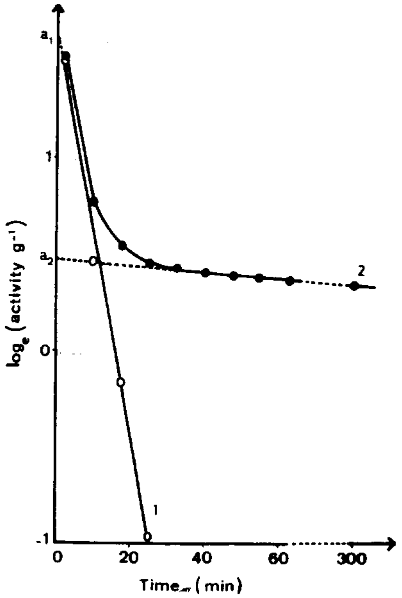

FIG. 2. Log$_e$ of the catalytic activity versus the time of the run.

Such curves may be described by very simple mathematical laws as shown in Fig. 2. Curve 2 gives the logarithm of the total activity A_T versus the time. The equation of its straight part is:

$$\log_e A_T = \log_e A_2 = \log_e a_2 - c_2 t. \quad (1)$$

For $t < \sim 20$ min, plotting $\log_e (A_T - A_2)$ vs t gives a straight line (curve 1 in Fig. 2). Its equation is:

$$\log_e (A_T - A_2) = \log_e A_1 = \log_e a_1 - c_1 t. \quad (2)$$

Therefore the activity A_T of the catalyst is the sum of two independent terms A_1 and A_2 which decrease very differently during the course of a run:

$$A_T = A_1 + A_2. \quad (3)$$

The preexponential factors a_1 and a_2 give the limiting values of the A_1 and A_2 activities for a catalyst without any deactivation. The total activity a_T for a fresh catalyst may then be written:

$$a_T = a_1 + a_2. \quad (4)$$

The initial rates v_T, v_1, v_2 per gram of fresh catalyst are obtained from the slope of the curves $a = f(W/F)$ at the origin. Different values of W/F can be obtained by varying either W or F. The last way is quicker, but unfortunately the residue deposited on the surface is very sensitive to the gas flow through the catalyst and a change of the F alters the active surface. Thus F must be kept constant and W/F changed only by changing W. Each point of the curves $a = f(W/F)$ has to be obtained from a different weight of catalyst. It has been verified carefully that this gives reproducible results as long as the weight of sample lies between 20 and 75 mg.

Each of the three curves a_T, a_1 and a_2 versus W/F gives an initial rate of reaction on a fresh catalyst v_T, v_1 and v_2. According to Eq. (4) the three values are linked together and:

$$v_T = v_1 + v_2. \qquad (5)$$

The total rate of formation of 1-butene and *trans*-2-butene is due to the participation of the two independent rates v_1 and v_2. The discrepancies between the two isomers will be discussed in the kinetic part of the work (*10*).

Thus the determination of mathematical laws for the deactivation phenomena leads to the evaluation of the $a_{(i)}$ activities and $v_{(i)}$ rates on a fresh catalyst. They characterize the surface sites of the solid, i.e., the primary active sites on which some polymeric complex may be further formed.

The fact that the catalytic activity may be decomposed into two independent terms implies that the isomerization of *cis*-2-butene simultaneously involves two different kinds of deactivation. As shown later, this can be ascribed to two types of active sites, sites (1) and sites (2). To verify such a hypothesis and to determine the nature of the active sites, systematic poisoning has been attempted.

Nature of the active sites. It is known that the chemical properties of the surface sites of silica–alumina catalyst are very diverse. Several types of reagents have been used in such conditions to interact irreversibly with oxidizing–reducing and acidic–basic centers. Thus thianthrene, anthracene and phenothiazine have been used to neutralize oxidizing centers, and NH_3 for Brønsted and Lewis acid sites. Na^+ ions have been exchanged with protons. Trinitrobenzene interacts with reducing centers.

Oxidizing Centers

The number of sites neutralized by the reducing reagents depends on their ionization potential and on the time and temperature of the adsorption. The total rate (1-butene + *trans*-2-butene) after poisoning with these reagents is shown in Table 1. For the three reagents there is an important decrease for v_1 while, except for one experiment, v_2 is constant. This particular lowering of v_2 may be explained by an interaction of phenothiazine with protons when substantial amounts of reagent are adsorbed (*11*). In every case it can be seen that the increase of the amount adsorbed with the time of adsorption leads to an important decrease of v_1.

These experiments show that the neutralization of oxidizing sites of the catalyst modifies only the v_1 rate of reaction and is not acting on the v_2 rate. Such results indicate that sites which isomerize *cis*-2-butene with v_1 initial rate are quite different from the sites which transform the butene with the v_2 rate. The v_1 rate is linked to oxidizing sites and v_2 is not.

Acid Sites

The oxidizing properties of silica–alumina catalysts are correlated with Lewis acidity (*12*). Consequently it is interesting to study the variation of the reaction rate by poisoning these acid sites. Very selective Lewis bases are lacking, so NH_3 has been employed. It has been adsorbed on the catalyst and evacuated either at 235 or at 350°. Table 1 shows that the decrease in catalytic activity follows the number of neutralized sites, the number being greater after desorption at 235 than at 350°. Note that both v_1 and v_2 are lowered. However, one of them is more sensitive to the NH_3 neutralization than the other. For desorption at 235°, v_1 and v_2 are decreased nearly in the same way (95% for the first, 100% for the other), while the desorption at 350° leads to a decrease of 50% for v_1 and only 12% for v_2. It may be concluded from this that a larger number of sites (1) is still poisoned at 350°. This implies that sites (1) have the highest acid strength.

NH_3 is known to react with both Lewis and Brønsted sites. In order to estimate the part played by the protonic acidity in butene isomerization, the catalytic activity of Na catalysts has been measured. Table 1 gives the v_1 and v_2 values for three sodium exchanged catalysts. The introduction of 0.28% of Na^+ ions in the acid silica–alumina decreases v_2 by nearly 50% while v_1 is not modified. An increase in Na^+ ions lowers both v_1 and v_2. Some Lewis acid sites, able to give protonic sites in aqueous solutions, may hence be neutralized by Na^+ ions *(12)*. Increasing the amount of Na^+ ions in the catalyst lowers the selectivity of the ion poisoning. Thus the results obtained with the 1.26 and 4.6% Na catalysts are doubtful with regard to the selective neutralization of Brønsted sites. Then it is more accurate to consider and to discuss only the results concerning the 0.28% Na catalyst.

Poisoning the Brønsted sites by Na^+ ions reduces v_2. Hence, the neutralization of Lewis and Brønsted sites by NH_3 adsorption lowers v_1 and v_2 rates. Then it may be concluded that v_2 is linked to Brønsted sites while v_1 is to be attributed to Lewis acid sites. This last assumption is supported by the additional results already given by the adsorption of reducing agents. It was shown that they lower only the v_1 rate. Lewis acid sites having oxidizing properties lead to butene isomerization with the v_1 rate.

In order to signify the attribution of a known rate to a particular site, v_1 will be referred to as v_L (L: Lewis sites) and v_2 as v_B (B: Brønsted sites). In the same way A_1 will be A_L and A_2 will become A_B.

Reducing Centers

The last type of site which can easily be studied by selective poisoning consists of reducing centers.

EPR measurements have shown *(11)* that trinitrobenzene (TNB) interacts with reducing centers of the catalyst. The isomerization behavior of such a catalyst is shown in Table 1. The v_L rate is reduced much more than v_B (95% and 40%, respectively) by the poisoning with TNB. This fact implies that a large number of the type L sites (95%) has reducing properties strong enough to be neutralized by TNB while type B centers consist of only 40% of such strong sites. It has already been shown by NH_3 poisoning at 350° that a great number of Lewis acid sites is still neutralized at 350° and that they are stronger than Brønsted sites. It may be concluded from these results that the type L isomerizing sites have both stronger acid and reducing properties than the type B ones.

Table 2 summarizes the results concerning the efficiency of a particular type of site on each of the rates v_L and v_B. The v_L rate implies only oxidizing Lewis sites and the v_B rate, Brønsted sites. However, the two initial rates v_L and v_B, are also dependent on the reducing sites.

Dependence of activity on experimental factors. According to the nature of the active sites, the dependence of the A activity versus the time of a run can be stated more precisely. Equation (3) becomes $A_T = A_L + A_B$ in the new frame of reference. A_L has a measurable value during the first minutes of a run (Fig. 2) and it depends on the oxidizing–reducing properties and on Lewis acidity. On the other hand the A_B activity which is the residual activity after cancelling the first one is due to Brønsted acid sites and reducing centers. Then oxidizing–reducing Lewis sites work at the beginning of the experiment. After a time close to 20 min, they become inactive and the isomerization only takes place on Brønsted sites associated with reducing centers.

TABLE 2

DEPENDENCE OF v_L AND v_B ON THE NATURE OF THE SURFACE SITES

Nature of the sites	$v_L(v_1)$	$v_B(v_2)$
Oxidizing sites	yes	no
Lewis acid sites	yes	no
Brønsted acid sites	no	yes
Reducing sites	yes	yes

The activity decay during a run follows the equation:

$$A_T = a_L \exp(-c_L t) + a_B \exp(-c_B t). \quad (6)$$

For different pressures of reactant and different temperatures of reaction the $a_{(i)}$ and $c_{(i)}$ coefficients have been determined (Tables 3 and 4).

Table 3 reports the a and c values for a constant temperature (85°) and a butene pressure increasing from 30 to 150 Torr. The c_L and c_B values vary in the same way with the pressure of butene but c_B is always very much smaller than c_L. The effect of the pressure is thus rather small on c_B and the A_B activity gives a $\log_e A_B$ curve which, whatever the pressure, is not much different from a parallel to the time axis. But the high value of c_L leads to a very sensitive effect of the pressure on the A_L activity. Hence it can be deduced from the results that A_L becomes negligible compared to A_B more rapidly for a high pressure of butene.

Table 4 gives the values of a_L, a_B and c_L, c_B at 28, 85, and 100°. As the activity was very sensitive to an increase of the temperature, it was necessary to choose a pressure of the reactant of 120 Torr for the run at 28° and to reduce it to only 30 Torr when the temperature was 100°. The comparison, for the same reactant pressure, of the a_L values for 28 and 85° on the one hand and for 85 and 100° on the other hand shows that the activity is the highest at 85° on the Lewis centers. Regarding the properties of the sites at 85°, the values of a and c confirm the qualitative explanation already given. The two types of sites act simultaneously.

TABLE 3

$a_{(i)}$ AND $c_{(i)}$ VALUES FOR DIFFERENT *cis*-2-BUTENE PRESSURES AT 85°

Pressure (Torr)	a_L mole liter^{-1} g^{-1}	c_L min^{-1}	a_B mole liter^{-1} g^{-1}	c_B min^{-1}
29	0.0087	0.16	0.0005	0.0016
30	0.0082	0.07	0.0005	0.0016
130	0.0366	0.23	0.0024	0.0041
135	0.0380	0.14	0.0025	0.0023
150	0.0405	0.14	0.0030	0.0023

TABLE 4

$a_{(i)}$ AND $c_{(i)}$ VALUES FOR DIFFERENT TEMPERATURES AND PRESSURES OF *cis*-2-BUTENE

Temperature (°C)	Pressure (Torr)	a_L mole liter^{-1} g^{-1}	c_L min^{-1}	a_B mole liter^{-1} g^{-1}	c_B min^{-1}
28	120	0.0035	0.27	0.0000	—
85	130	0.0366	0.23	0.0024	0.0041
85	30	0.0082	0.07	0.0005	0.0016
100	30	0.0011	$\gg 0.27$	0.0023	0.0018

Important discrepancies are noted for the lowest and the highest temperatures. At 28° the Brønsted sites are completely inactive ($a_B = 0$), and only Lewis sites isomerize the butene. This result is in good agreement with other studies made at very similar temperatures on silica–alumina catalysts (*8–13*). At the highest temperature a_B is high enough and c_B sufficiently low to give a high activity for the Brønsted sites during a very long time. For the same experimental conditions c_L is so high that Lewis sites have a very short life as active centers.

Thus, by changing either the temperature or the butene pressure, one may determine which kind of site is the main primary center for the catalytic isomerization during the complete time of a run. The a and c values which are so obtained very easily from experimental curves determine with a great accuracy the catalytic properties (value and lifetime) of a given type of site according to the conditions of an experiment. Such a determination could be very easily extended to other experimental parameters, e.g., the gas flow.

UV measurements. In this paper only the results on the variations of butene adsorption with temperature will be given. No discussion of the nature of the adsorbed species or of the correlation with the mechanism of the catalysis will be presented.

It has been shown that butene reacts with Lewis acid sites of silica–alumina catalysts and provides an ultraviolet spectrum in which the 300–330 mμ band is characteristic of the active adsorbed species, while a band near 380 mμ is attributed to the transformation of this surface complex (*14–15*).

The uv spectra obtained with the catalyst heat-treated at 400° are reported in Fig. 3. The butene has been desorbed at four temperatures: 25 (A), 85 (B), 150 (C), 200° (D). The band near 320 mμ is only slightly modified between 25 and 85°. Beyond 85° it shifts towards shorter wavelengths and decreases when the temperature is increased. The 385 mμ band grows as the adsorption temperature is raised up to 200°.

Hence, while one band (320 mμ) decreases the other (385 mμ) increases. According to the properties of the species they describe, such complementary development is very logical. The results for the 320 mμ band between 25 and 85° corroborate the greater catalytic activity for Lewis sites at 85°.

The variations with temperature of the two bands are in good agreement with results given in Table 4. Then it is well confirmed that the activity of Lewis acid sites is high at relatively low temperatures and then decreases. This reduction of the catalytic properties is related to a change in the active surface complex.

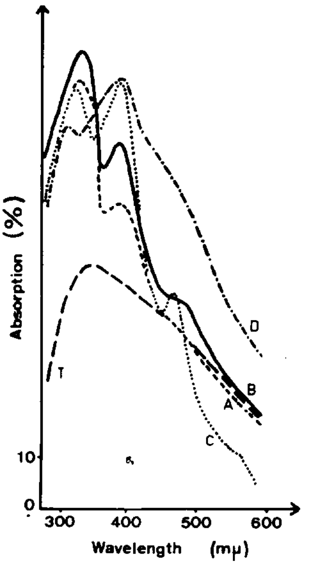

Fig. 3. Ultraviolet spectrum of *cis*-2-butene adsorbed on a silica–alumina catalyst. T: thermal treatment at 400°C and A: butene desorbed at 25°C; B: butene desorbed at 85°C; C: butene desorbed at 150°C; D: butene desorbed at 200°C.

Discussion

The isomerization of *cis*-2-butene on silica–alumina catalysts is associated with a loss of activity at the beginning of a run. This important decay prevents any estimation of the activity before this poisoning takes effect. Therefore the only approach to the true value is a mathematical treatment of the experimental results in order to find the laws they obey.

Such a method has led to the division of the measured activity into two independent terms A_L and A_B. One of them, A_L is linked to the oxidizing Lewis acid sites and the other one A_B to Brønsted acid sites while the reducing centers are active in the two cases.

Each of these activities is characterized by two coefficients $a_{(i)}$ and $c_{(i)}$. The first one, $a_{(i)}$, expresses the initial activity of a fresh catalyst while the second one, $c_{(i)}$, gives the ability of the sites to be deactivated in the course of a run. The dependence of the pressure of *cis*-2-butene and of the reaction temperature on $a_{(i)}$ and $c_{(i)}$ determines which kind of surface site is preferentially involved in the isomerization. Moreover it allows one to predict the best experimental conditions for which only one of the superficial centers will be active.

The knowledge of $a_{(i)}$ and $c_{(i)}$ allows one to characterize an unusual variation of the activity of L sites versus temperature (Table 4). Such an effect is corroborated by the uv study of the *cis*-2-butene adsorption, and it would not have been detected or even expected from a superficial interpretation of the curves in Fig. 1.

Thus, to sum up, the deactivation phenomena have been elucidated by studying different catalysts and the types of primary surface sites involved in the isomerization have been determined. A further paper will describe the mechanism of the isomerization on these sites, and it will show that the Lewis sites work according to the known scheme described (*6–8*) which involves a polymeric complex.

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