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Catalytic Activity of Amorphous Alumina Prepared in Aqueous Media

I. Catalytic Activity in Isomerization of Butene-1

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The activity and the selectivity (*cis/trans* ratio of butene-2) for the isomerization of butene-1 have been investigated on amorphous alumina activated in vacuo between 260 and 800°C. The selectivity remains constant over the whole temperature range of activation, which seems to show that the reaction mechanism does not change for this series of catalysts. However, the isomerizing activity, which changes with the temperature of the activation, is correlated with the parallel change of the oxidizing and reducing properties of alumina.

INTRODUCTION

The nature of active centers on the surface of aluminas is still not well defined, though it is assumed that, in general, these oxides have an acidic character. However, no satisfactory correlations have been found between acidity and catalytic activity of these solids in reactions of cracking, isomerization, alkylation, dehydration, etc. This may be explained by the fact that a particular reaction requires active sites presenting a well defined energy spectrum (*1*), or also by a dualistic character, e.g., acidic and basic, of these sites (*2*, *3*). For a better understanding of the catalytic activity of aluminas, the study of the basic character of their surfaces cannot be neglected at the expense of generally well studied acidic properties.

Aluminas also exhibit oxidizing and reducing properties which have been considered responsible for some exchange (*4*, *5*), isomerization (*6*), and charge transfer reactions. These properties are evident from the formation of colored, paramagnetic complexes when an electron donor or acceptor is adsorbed on alumina (*7*, *8*). A typical example of such complexity of the solid surface is given by amorphous alumina, prepared in aqueous media (*9*), activated in vacuo between 400° and 800°C. This activation generates also surface lattice vacancies, of anionic type below 730°C and of cationic type between 730 and 800°C, responsible for the *n* or *p* type of conductivity of alumina (*10*). The catalytic activity in the oxidation of CO at 450°C could be correlated with these vacancies (*11*). Such a correlation, at least for anionic vacancies, appeared incorrect if the formation of paramagnetic charge transfer complexes was considered (*12*), or when the isomerization of butene-1 at 260°C was studied, as is shown in this work.

The ESR study of charge transfer complexes formed on alumina with tetracyanoethylene (TCNE → $TCNE^-$) and with phenothiazin (PhTh → $PhTh^+$) has demonstrated the existence of different types of electron donor and electron acceptor centers, created at different temperatures of the activation of alumina in vacuum (*12*). Below 550°C, the oxidizing centers, i.e., electron acceptors, were identified with Lewis acid sites, whereas the reducing centers, i.e., electron donors, were identified with basic OH surface groups. Above 550°C, electron donors and acceptors would be polarity defects, as proposed by Peri (*13*), of the type adjacent O^{2-} ions or Al^{3+} ions, respectively. Finally, for a temperature of activation higher than 750°C, the electron acceptor centers would be aluminum vacancies created by the distillation of aluminum in vacuo at this temperature (*10*).

The adsorption of bases such as ammonia and pyridine at moderate temperature (*14*) by amorphous alumina, activated in vacuo between 350 and 800°C, shows that surface OH groups retain these bases by a hydrogen bond. Evidently, acid sites are also involved in this adsorption, but a fraction of these sites is also able to oxidize the pyridine to give a charge transfer complex. This type of complex is particularly well observed with PhTh by ESR technique (*12*). Conversely, a fraction of basic sites exhibits reducing character (electron donor) in the formation of the charge transfer complex with TCNE (*15*). Therefore, despite the fact that amorphous alumina develops an acidity quite comparable to that of gamma alumina (*16*), prepared according to a method described by MacIver (17), the complexity of its surface towards adsorption of bases is demonstrated by various types of sites involved, viz. acid sites, OH groups, acid sites of oxidizing character and also basic sites of reducing character (*14, 15*).

In this paper, a correlation is attempted between (a) the catalytic activity of amorphous alumina in the isomerization of butene-1 and (b) the nature of sites developed by activating treatment in vacuo between 260 and 800°C. The isomerization of olefins and, in particular, the migration of the double bond is often selected as a simple test of catalytic activity of oxides or metals. In the case of butene-1, two products only are formed, namely, *cis*- and *trans*-butene-2. The mechanism of this reaction seems to depend on the nature of the catalyst: (i) radical type for metals (*cis/trans* ratio < 1) (*18*), (ii) carbonium ion intermediates (*cis/trans* ratio $= 1$) on acid catalysts (*19*), and (iii) carbanion intermediates (*cis/trans* ratio > 1) on basic catalysts (*20*). In the case of aluminas, carbonium ion intermediates involve the participation of aluminum sites, which act as electron acceptors (*19, 21, 22*). The selectivity of alumina in the butene-1 isomerization was found equal to 2 (*22*) or even 4.4 (*20*), which tends to prove rather a basic character of sites involved in alumina. A well defined correlation between basic sites (O^{2-} ions), donating electrons, and the isomerization of butene-1, was found on MgO (*23*). But the basic character of MgO is well established, whereas for alumina rather a dualistic character (acidic and basic) may be expected.

EXPERIMENTAL METHODS

Catalysts and reactants. Amorphous alumina, used in this work, is prepared in aqueous media according to a method described previously (*9, 11*). The solid resulting from the final heating in air at 400°C for 20 hr is amorphous and contains less than 0.01% by weight of Cl^- and 0.25 moles of H_2O per mole of Al_2O_3. Its surface area is of the order of 104 m^2/g and remains almost constant during the activation treatment in vacuo from 260 to 800°C (*9*).

Butene-1 (99%), hydrogen (99.995%) and oxygen (99.95%) were C. P. grade and were furnished by Société Air Liquide. Helium C. P. grade was furnished by Canadian Helium Ltd.

Activation procedure and reactor. The activation of amorphous alumina consists of a thermal treatment under vacuum (10^{-6} Torr) for 15 hr at temperatures from 260 to 800°C. The upper temperature limit was set in order to keep alumina in the amorphous state, because above 800°C eta phase is formed, and its properties can hardly be compared with those of the starting amorphous material.

The isomerization of butene-1 is performed in a dynamic differential microreactor, under a total pressure of 1 atm. The scheme of the reactor circuit is shown in Fig. 1. The catalyst is activated in situ.

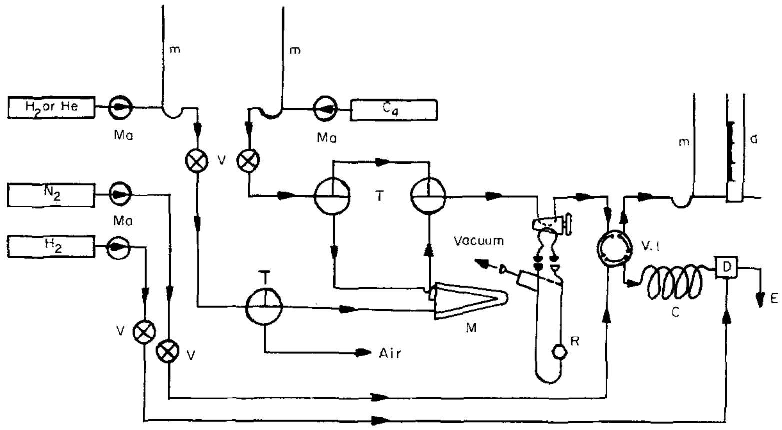

FIG. 1. The scheme of the reactor circuit: m, mercury manometer; Ma, pressure reducer; V, flow regulating valve; VI, injection valve; T, 3-way stopcock; C, column; D, detector; R, reactor; M, gas mixer; d, flowmeter.

The gas chromatographic analyser is of the type Aerograph 1200 with a flame ionization detector. The reaction products are separated in a column (length, 12 m; internal diameter, 3.125 mm) filled with dimethylsulfolane (D.M.S.) deposited (20%) on chromosorb W (60–80 mesh). The column is maintained at 0°C and it allows a good separation of C_4 olefins and paraffins but does not separate butene-1 and isobutylene. However, it has been checked that this skeletal isomerization does not occur for the temperatures of the reaction not exceeding 400°C, when a column filled with silver nitrate–diethylene glycol ($AgNO_3$ – D.E.G.) deposited (15%) on chromosorb P.W. (60–80 mesh) and maintained at 25°C was used. This column separates entirely the two skeletal isomers. Linearity between detector recordings and butene pressures, for the D.M.S. column, was observed for hydrocarbon pressures not exceeding 76 Torr.

Reaction procedures. One-hundred milligrams of amorphous alumina are deposited on sintered quartz in the microreactor and activated in vacuo (10^{-6} Torr) during 15 hr between 260 and 800°C. The temperature of the reactor is then readjusted to 260°C, which is standard reaction temperature. After each catalytic test, a new sample is used. The reagent, butene-1, is diluted (10%) in hydrogen or helium (total pressure 1 atm) and a flow rate of 6 liters/hr is used during the test. The analysis of reacting gases starts 2-min after the introduction of the reagent and is performed during 60 min. In these conditions, the only reaction products are *cis*- and *trans*-butene-2. In some cases, traces of butane were detected, but in no case were isobutylene or cracking and polymerization products present.

RESULTS AND DISCUSSION

Deactivation of the Catalyst

When the reaction mixture (butene-1 and hydrogen or helium) is introduced onto the catalyst, the amount of conversion decreases very rapidly during the first 15 min. The isomerizing activity is then slowly stabilized and reaches a constant level which is negligible compared with the initial activity, determined 2 min after the introduction of the reaction mixture.

Amorphous alumina which has not been activated in vacuo is completely inactive. A catalytic activity is recorded for samples activated at or above 350°C. All catalysts activated between 400 and 800°C exhibit the same deactivation behavior. During the recession of the catalytic activity, the selectivity (*cis/trans* ratio) remains almost constant and equal to 0.60. This value is close to the thermodynamic equilibrium value (0.48) at 260°C (*24*).

Figure 2 shows a typical result for the conversion and selectivity of a sample activated at 470°C. Because the deactivation is very fast during the first 10 min, three runs, each with a new sample, were made to establish this curve. The reproducibility of the measurements was about 10%.

Various authors have observed a similar aging of alumina catalysts during isomerization of butene-1 in a dynamic reactor. Bielikoff (*25*) found that the activity of the catalyst decreased gradually, but the selectivity remained constant and equal to 0.7. Brouwer (*19*) observed a sharp decrease of the amount of butene-1 formed from *cis*-butene-2 on a γ-alumina. The decrease in the formation of *trans*-butene-2 was slower but continuous throughout the whole run.

Rooney and Pink (*26*) assume that Lewis sites are responsible for the deposit of polymer or "coke" which deactivates alumina for isomerization. However, McIver *et al.* (*27*) reject the poisoning of active centers caused by a deposit of carbonaceous residue or even by traces of water, occasionally present in reagents. This conclusion is also confirmed in our work, since the deactivating behavior of Fig. 2 is not modified using hydrogen containing 10 ppm of water, or less than 1 ppm of water. On the other hand, when helium is used instead of hydrogen, the samples activated at 500 or 600°C become covered during reaction at 260°C by a black residue. However, a mere evacuation at the temperature of activation restores the initial activity despite the persistence of the black residue on the sample of alumina. Summing up, neither traces of water, nor black residue which would result from secondary reactions, are responsible for the sharp deactivation at the beginning of the reaction of the type of Fig. 2.

Hydrogen does not seem to play any role in the reaction (except for the lack of change of the color of alumina), because when helium is used instead, the same initial activity and the same type of deactivation (Fig. 2) are observed.

The problem of the black residue was also considered by Germain (*28*), who envisaged that during the reaction of hydrocarbons on alumina the decrease in catalytic activity is due simply to the formation of highly condensed hydrocarbons, of a general formula CH_n ($n < 1$). This residue, according to this author, is reduced by hydrogen, forming volatile hydrocar-

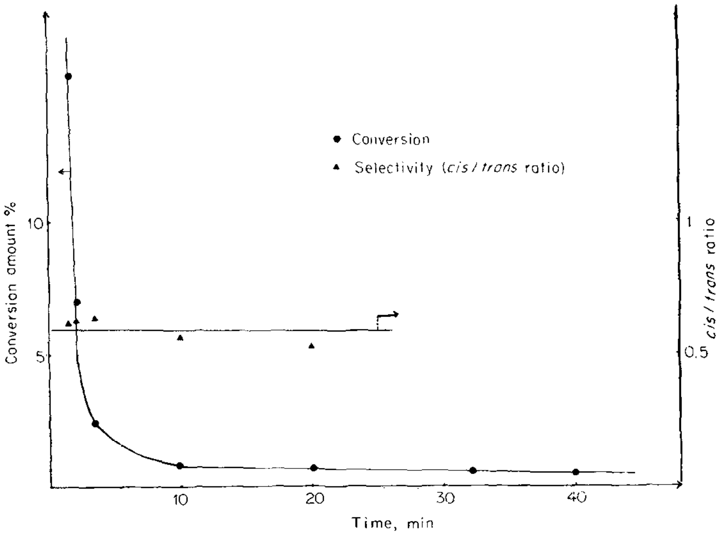

FIG. 2. The variation with time of the activity and the selectivity of amorphous alumina, activated at 470°C.

bons. Therefore, in the presence of hydrogen, the initial aging or decrease of the activity should be avoided. It was, however, observed in this work that, if the presence of hydrogen actually prevents the formation of the black residue on alumina, it does not change the deactivation law of Fig. 2. The active centers on the surface of alumina are therefore not poisoned by the black residue but by some other nondesorbable species, since a catalyst, which has been used in a test at 260°C, recovers its initial activity after evacuation at temperatures higher than 350°C.

On the contrary, Bielikoff (*25*) explains the initial deactivation of eta alumina during the isomerization of butene-1 and also the small ratio *cis/trans* of butene-2, by a preferential chemisorption of *cis*-butene-2, strongly linked by two terminal methyl carbons (separated by 2.64 Å for the plane 100), as shown in Fig. 3. The same considerations concerning the preferential adsorption of *cis*-butene-2 are also developed by Lunsford (*23*) for the interaction of butene-1 and *cis*- and *trans*-butene-2 with magnesia. Similarly, on γ-alumina, Peri (*29*) found by ir spectroscopy that, during the isomerization of butene-1, the adsorbed phase has a structure resembling that of liquid *cis*-butene-2.

It is supposed in this work that the initial rapid deactivation of amorphous alumina (Fig. 2) is due to the preferential and strong adsorption of *cis*-butene-2. The low *cis/trans* ratio (0.60), which may be thermodynamically controlled (but not kinetically), also supports this conclusion. The fast deactivation of the catalyst during the first 10 min of the reaction prevents the determination of a quantitative law of aging of Fig. 2 which would yield the initial reaction rate. On the other hand, the quantitative analysis of isomers at the stationary state is imprecise, due to the small conversion registered (0.5%). In order to avoid these difficulties, we defined an activity, close to the initial activity, by the amount and the rate of conversion of butene-1 into butene-2, observed 2 min after the admission of reagents into the reactor.

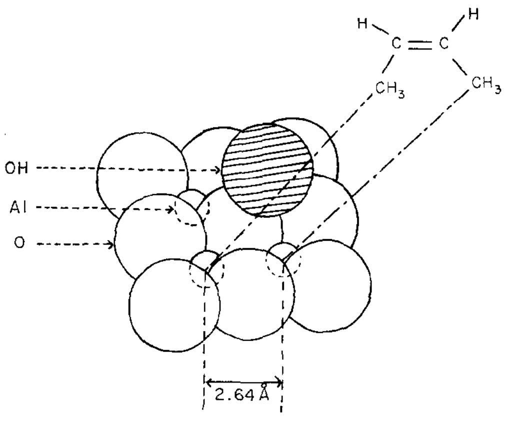

FIG. 3. Adsorption of *cis*-butene-2 on dehydrated eta alumina (face 100).

Influence of the Activation Temperature of Alumina on the Activity of Selectivity

The curves of Fig. 4 represent the variation of activity (conversion of butene-1 into isomers after 2 min) with the temperature of the activation of amorphous alumina in vacuo. The activity almost negligible at 260°C, shows two maxima, at 470 and 650°C, and two minima, at 520 and 750°C.

Table 1 and Fig. 4 summarize the changes of the activity, the selectivity, and the activity at the stationary state as a function of the activation temperature of alumina. It is important to mention that the selectivity (*cis/trans* ratio) is practically constant (0.65) for all catalysts and close to the equilibrium value (0.48). A few analyses for the selectivity at the stationary state also gave values close to 0.60. The activity at the stationary state remains also almost constant, taking into account the errors encountered in the determination of small conversion amounts.

These results show that the activity in isomerization of butene-1 depends on the activation temperature of amorphous alumina (Fig. 4) mostly in the same way as its oxidizing and reducing properties (*12*). These properties show maxima and minima when the activation temperature is considered. The constancy of the *cis/trans*

TABLE 1

Activity, Selectivity and Rates of Reaction at 260°C for 100 mg of Alumina

Activation temperature (°C)	260	410	470	500	600	650	705	750	800
Rate *trans* (10^7 moles^{-1} g^{-1} sec^{-1})	0	9.72	27.5	12.2	28.9	43.9	7.9	3.06	27.5
Cis/trans ratio		0.64	0.64	0.65	0.62	0.64	0.65	0.87	0.69
Conversion at stationary state (%)	0	—	0.41	0.35	0.55	0.54	0.37	0.9	0.57

ratio of butene-2 (except for the sample activated at 750°C) (Table 1) seems to indicate that the mechanism of the reaction remains the same for all samples activated between 400 and 800°C.

Various authors also observed that the catalytic activity of aluminas depends to a large extent on the state of dehydration of the surface (*19, 25, 27, 30*). Some of the workers observed maxima and minima of activity for certain dehydration temperatures (*25, 30*), whilst others (*27*) found that the activity was increasing rather uniformly with the activation temperature between 300 and 800°C.

An increase of the catalytic activity for increasing temperatures of activation may result either from an increase of the number of sites of the same efficiency, or from the increase of the efficiency of preexisting sites. Hindin and Weller (*31*) observed that the activity of γ-alumina increased more rapidly than the amount of dehydration of the surface and concluded in favor of an increasing efficiency of active sites with the temperature of activation.

The effect of dehydration on the activity and the selectivity of γ-alumina in the isomerization of butene-1 was, in particular, studied by Medema and Houtman (*30*). They distinguished two types of sites (A and B) and explain the variation of

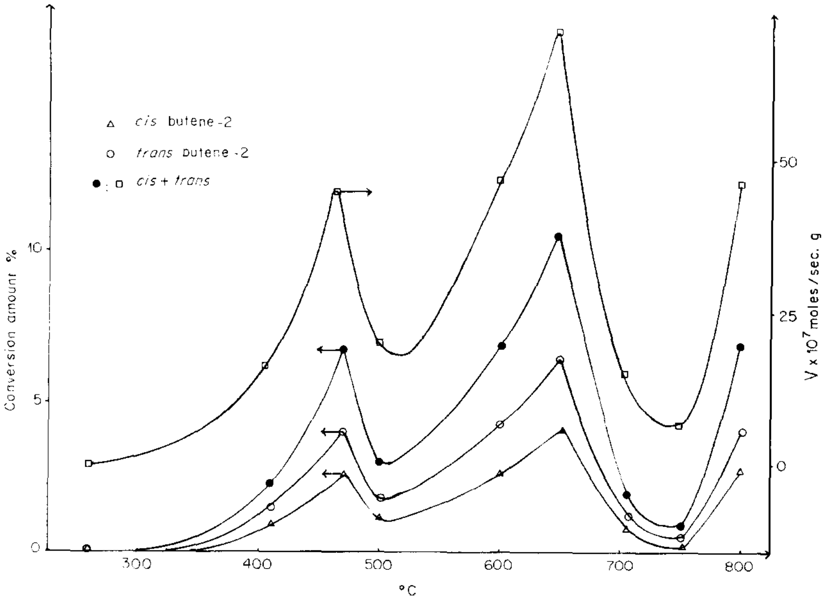

FIG. 4. The variation with the activation temperature of the initial activity (left ordinate; conversion amount; right ordinate; rate of isomerization) of amorphous alumina in the isomerization of butene-1.

the activity by a change in the overall number of sites during dehydration of the sample and the variation of the selectivity by the modification of the ratio, A/B. However, the influence of the state of dehydration of the alumina surface on the catalytic activity may differ for different varieties of alumina, the nature of the catalyst being an independent variable in this type of reaction (*19*). These considerations tend to show that the thermal activation treatment has the effect of a rather monotonic decrease of the state of hydration of alumina surface, but it may also modify in a nonmonotonic way some other surface properties.

In the case of amorphous alumina studied here, the minima in the catalytic activity (Fig. 4) observed for the activation temperatures of 520 and 750°C suggest a modification of the nature of active sites since a mere continuous dehydration (*12*) with the temperature would also give a steadily increasing curve of activity. A comparable modification of the nature of sites has already been postulated in order to explain the development of oxidizing and reducing character of amorphous alumina activated in the same temperature range (*12*).

The variation of properties of amorphous alumina with the activation temperature are summarized in Fig. 5, where curves 1 and 2 represent respectively the reducing (electron donating) and oxidizing (electron accepting) power as determined from the charge transfer complexes formation ($TCNE^-$ and $PhTh^+$). Curve 3 gives the isomerizing activity and curve 4 represents the acidity of alumina as determined by irreversible adsorption of ammonia at 180°C. Obviously, the best correlation between the two maxima (at 470° and 650°C) and the minimum (at 520°C) fits for curves 3 (catalytic activity) and 1 (reducing or electron donating power). The first maximum of curve 3 (but not the second) is also well correlated with the oxidizing (electron accepting) power of curve 2. However, above 750°C, where the catalytic activity increases again, the reducing power continues to decrease (curve

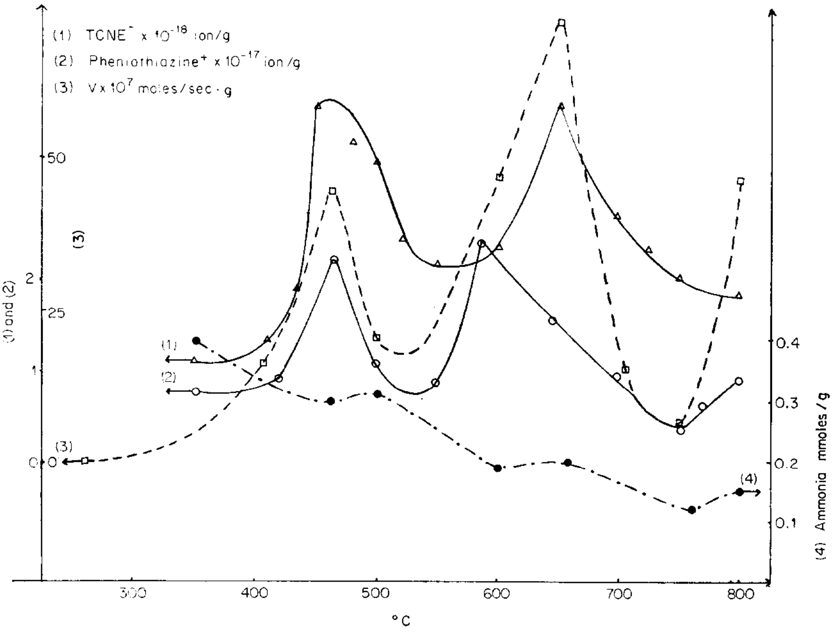

FIG. 5. The variation of various properties of amorphous alumina as a function of the activation temperature: (1) formation of $TCNE^-$, (2) formation of $PhTh^+$, (3) initial rate of reaction, (4) irreversible adsorption of ammonia at 180°C.

1) while the oxidizing power (curve 2) shows now a trend similar to the isomerizing activity. Clearly, oxidizing and reducing properties of amorphous alumina (4.0×10^{18} reducing sites per gram and 2.3×10^{17} oxidizing sites per gram after activation at 450°C) (*12*) are better correlated with the catalytic activity than is the acidity of alumina represented by ammonia adsorption (curve 4).

Ammonia adsorption at 180°C or even irreversible adsorption at 180 or 260°C plotted against the temperature of activation of amorphous alumina (*14*) shows a steadily decreasing trend with no maxima and minima. In the main, this probably reflects the acidity of alumina, though a small fraction (~10%) of ammonia is also able to react with reducing (electron donating) centers (*15*).

The results of Fig. 5 are not surprising because only very few examples of correlation between the acidity and the isomerizing activity have been obtained. It was even shown (*25*) that the maximum of isomerizing activity for butene-1 of γ-alumina almost coincided with a minimum of acidity, as determined by the adsorption of ammonia.

A second important point comes from the comparison of the reducing and oxidizing power with a certain fraction of the total acidity of amorphous alumina. It has been shown previously (*14*) that ammonia is held irreversibly at 180 or 260°C by activated amorphous alumina, the amount fixed at 260°C (Q_{260}) being smaller than that held at 180°C (Q_{180}). As already pointed out, both amounts decrease steadily with the temperature of activation. The difference $Q_{180} - Q_{260}$ represents a fraction of the total acidity of a rather weak strength, because it is unable to retain ammonia between 180 and 260°C. When this fraction (reproducibility, 5%) is plotted against the temperature of activation of amorphous alumina, a very similar plot (compare Figs. 5 and 6) to the oxidizing ($PhTh^+$) or reducing ($TCNE^-$) power is obtained for the first maximum, whereas the second maximum fits with reducing ($TCNE^-$) power. The final increase of the adsorption, above an activation temperature of 750°C, may be again compared to the increase of the oxidizing power ($PhTh^+$). It has therefore been concluded that, below the activation temperature of 550°C, Lewis acid sites may behave as

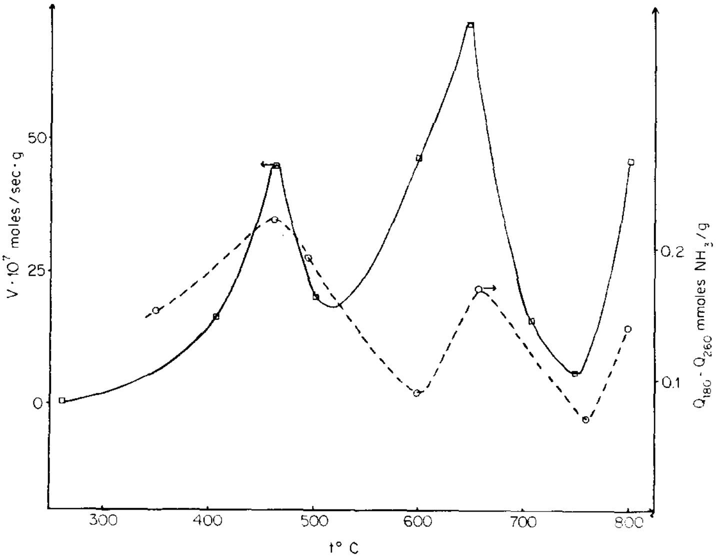

FIG. 6. The variation of the rate of reaction and of the quantity of ammonia $Q_{180} - Q_{260}$ (see text) as a function of the activation temperature of amorphous alumina.

oxidizing centers (electron acceptors), whereas basic OH surface groups may behave eventually as reducing centers (electron donors). Above 550°C basic O^{2-} sites are playing the role of reducing centers towards ammonia (*15*), and finally above 750°C aluminum vacancies, which are electron acceptors (*12*), behave as oxidizing centers. If the catalytic activity in the isomerization of butene-1 is compared with the difference $Q_{180} - Q_{260}$ as a function of the activation temperature of amorphous alumina, a very satisfactory correlation is found (Fig. 6). This result would indicate that catalytically active acid sites in the isomerization of butene-1 belong to the fraction of a rather weak strength ($Q_{180} - Q_{260}$) and are also able to act as electron acceptors (oxidizing power). Simultaneously, for temperatures of activation of alumina above 550°C, basic sites (reducing power) would be catalytically active in the isomerization. Finally, above 750°C acid sites (aluminum vacancies) (*12*) of oxidizing power would be again active in catalysis.

The isomerization activity could be correlated for the whole temperature range of activation (Fig. 6) with a rather weak acidity of the amorphous alumina, represented by the amount of ammonia desorbed between 180 and 260°C. However, this weakly adsorbed ammonia is also able to react with reducing sites of a basic type (*15*). It is therefore difficult to consider that this type of ammonia adsorption represents exclusively a weak acidity.

The catalytic activity may be still correlated (for the first peak of Fig. 5) with the oxidizing power of the catalyst represented by electron donation of PhTh to Lewis acid sites (*12*), but simultaneously (Fig. 5), the same correlation still holds with the reducing power of alumina represented by electron acceptance of TCNE from basic sites, probably OH groups (*12*). For the second peak of activity of Fig. 5, a better correlation is found with the reducing power coming from basic sites, probably O^{2-} pairs (*12*). The correlation between the catalytic activity and the oxidizing power ($PhTh^+$ formation), which would come from Al^{3+} pairs (*12*) is poorer. Finally, after the minimum of the isomerizing activity registered after the activation temperature of 750°C, the rise in the activity (Fig. 5) corresponds to the rise in the oxidizing power for which aluminum vacancies would be responsible (*12*), whereas the reducing power ($TCNE^-$ formation) continues to decrease.

This situation appears very peculiar because for the first activation temperature range (below 550°C) acidic (Lewis) and also basic (OH groups) of oxidizing and reducing power, respectively, would be a cause of catalytic activity, whereas for the second range of the activation temperature (between 550 and 750°C) mainly basic sites of reducing power would assume the catalytic behavior of alumina. Finally, for the third temperature range (above 750°C), again oxidizing power (aluminum vacancies) would fit the rise of the catalytic activity.

Now, for the whole temperature range of activation, the selectivity (*cis*/*trans* ratio of butene-2) remains the same, which tends to show that the mechanism of the reaction remains the same. It is, however, difficult to assume that the preferential strong adsorption of *cis*-butene-2, which is the cause of the inhibition of the reaction, and low *cis*/*trans* ratio would remain the same if acidic (oxidizing) sites or basic (reducing) sites are consecutively involved. The answer to this problem would be that acidic (oxidizing) and basic (reducing) sites are simultaneously involved for any temperature range. This hypothesis is not difficult to test by the selective poisoning technique. On one hand, TCNE is a selective poison of reducing sites, whereas PhTh is similarly poison for oxidizing sites. Because these sites are simultaneously of basic or acidic nature, acids like acetic acid and bases like ammonia would be also selective poisons. It has been precisely shown (*32*) that any one of these "selective" poisons is able to inhibit the isomerizing activity for the whole temperature range of activation. Therefore, catalytic activity is rather of a dualistic type, acidic (oxidizing) and basic (reducing) for the whole temperature range of activation of amorphous alumina.

It was mentioned before that anionic vacancies may be developed in amorphous alumina after activation in vacuo at temperatures higher than 450°C (*10*). These defects result from the loss of some surface oxygen ions and are responsible for the *n*-type conductivity of amorphous alumina. The activity in the oxidation of CO was successfully correlated with the presence of these sites (*11*). Though these sites are not electron donors towards TCNE (*12*), they eventually could play a role in the isomerization of butene-1. Experimental evidence was actually obtained concerning the inertness of anionic vacancies in the isomerization. Indeed, oxygen treatment (160 Torr) of amorphous alumina at 600°C, which fills the vacancies (*10*) previously developed by the vacuum treatment at 600°C, does not change the isomerization activity of the sample. The sites involved in this reaction are therefore of a different nature from those active in CO oxidation (*11*).

CONCLUSIONS

The present study tends to show that the catalytic activity of the amorphous alumina in the isomerization of butene-1 follows the variations of acidic and basic properties which simultaneously present oxidizing and reducing power. The minima in the catalytic activity observed for the activation temperature of the catalyst around 550 and 750°C suggest a change of the type of catalytic sites because at the same time other properties also change (Figs. 5 and 6). However, the mechanism of the reaction would remain the same for the whole temperature range of activation, as seems to be indicated by a constant selectivity (*cis/trans* butene-2 ratio) of the order of 0.65. This value of the selectivity is probably not linked with a carbonium ion mechanism (for acid catalysts) or a carbanion mechanism (for basic catalyst), but simply with the thermodynamic equilibrium, or with the strong adsorption of *cis*- butene-2, which also explains the deactivation of the catalyst during the first 15 min.

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