Catalytic Activity of Amorphous Alumina Prepared in Aqueous Media

II. Nature of Active Sites in the Isomerization of Butene-1

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Selective poisoning of active sites in isomerization of butene-1 on amorphous alumina activated in vacuum between 260° and 800°C has been attempted. For acid sites, the poison used was ammonia, and acetic acid for basic sites. Oxidizing (electron accepting) sites are correspondingly poisoned by phenothiazine and reducing (electron donating) sites by tetracyanoethylene. Any one of these poisons is very effective in decreasing the isomerizing activity of alumina. It is concluded, therefore, that catalytic activity is simultaneously due to acid sites with oxidizing character and to basic sites with reducing character.

INTRODUCTION

The first studies of the surface chemistry of catalytic aluminas (1–4) led to the hypothesis of a creation of surface defects through dehydroxylation of aluminas, in order to explain the catalytic activity of these oxides in hydrogenation and exchange reactions. The acid character of certain surface sites of aluminas was demonstrated more recently (5–7) and was supposed essential in reactions with hydrocarbons (7, 8). However, the presence of only acid sites cannot explain the adsorption and isomerization of butene-1. Also Peri (7) postulated a formation through dehydration of aluminas of pairs of sites, acido-basic, formed by oxygen and aluminium ions in a particular environment. These double, isomerizing sites, active simultaneously in the adsorption of hydrocarbons, are neutralized both by acids and by bases (9). The neutralization of active sites by acids or bases of various forces (10, 11) gives an insight into the strength of acid or basic sites required to perform a given reaction.

On the other hand, water vapour is a poison for reactions on aluminas like isomerization, hydrogenation, exchange, and cracking (1–4, 12). Dehydration of alcohols, which also requires acid sites and elmininates water, should not involve the same type of sites as the previous reactions because of the poisoning effect of water for these former reactions. But even if only one type of hydrocarbon reaction is considered, like the isomerization of butenes, the neutralization of acid sites leads to the conclusion (13) that two types of isomerizing sites are actually active in this reaction.

An increased amount of work was therefore carried out in order to determine the spectrum of sites of each type (14–16). It was then discovered through these experiments that for a given type of sites a selective poisoning can inhibit some reactions whereas other reactions are not perturbed. However, the complexity of alumina surfaces is yet higher if their reducing and oxidizing power is taken into account (17, 18). These oxidizing and reducing sites seem to be active in some exchange reactions (19, 20) and isomerizations (21). But as ammonia and hydrochloric acid neutralize, respectively, oxidizing and reducing sites it appears that oxidizing sites are simultaneously acid and that reducing sites are simultaneously basic (22).

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In our previous work concerning the physicochemical (23, 24) and catalytic (25) properties of amorphous alumina we demonstrated that the activity at 260°C in the isomerization of butene-1 on amorphous alumina, previously heated in vacuum at temperatures from 260° to 800°C, may be correlated with the amount of ammonia which can be irreversibly adsorbed at 180°C but which is desorbed at 260°C. In other words acid sites active in the isomerization of butene-1 present a restricted energy spectrum or a restricted acid strength. But ammonia is also able to neutralize some basic reducing sites of amorphous alumina (26). These reducing sites are involved in the formation of charge transfer complexes with tetracyanoethylene (TCNE) (23, 25). Moreover, amorphous alumina also exhibits acid oxidizing sites as shown by the formation of charge transfer complexes with phenothiazine (PhTh) (l.c.). Only a fraction of basic sites exhibits the reducing character and a fraction of acid sites the oxidizing character. It was therefore concluded in the first paper of this series (25) that isomerization of butene-1 requires the presence of acid sites of oxidizing character and simultaneously the presence of basic sites of reducing character. In the present paper we attempted to poison selectively these different types of sites (acidic, basic, reducing, oxidizing) which are liable to be involved in the isomerization of butene-1 and we followed the catalytic activity and the selectivity in this reaction of amorphous alumina neutralized in these various ways.

EXPERIMENTAL

Amorphous alumina was prepared in an aqueous medium, as described in a previous paper (27). Its surface area of 104 m²/g remains almost constant within the whole range of the activation temperature in vacuum (260°–800°C). The poisons for acid and basic sites are, respectively, ammonia (Merck, purity 99.8%) and acetic acid (Prolabo, dehydrated on acetic anhydride). The poisons for oxidizing and reducing sites are, respectively, phenothiazine (Touzart and Matignon) and tetracyano-ethylene (Eastman) of C.P. grade. Butene-1 (Air Liquide, purity 99%) is isomerized into cis and trans butene-2 in a dynamic differential reactor, already described (25). Amorphous alumina (100 mg) is activated in vacuum (10^{-6} Torr), between 260° and 800°C, directly in the reactor. The catalyst is then cooled to a selected temperature and the poison, in the gas phase, introduced. After 30 min of exposure the catalyst is evacuated for 4 hr at a temperature equal to or higher than the temperature of the isomerization of butene-1 (260°C). The reacting feed, composed by a mixture of butene-1 (10%) and hydrogen, is passed over the catalyst at a rate of 6 l hr^{-1}. The initial activity in isomerization is measured 2 min after the introduction of the feed (25) by gas chromatography, and the activity is followed during 60 min of reaction.

RESULTS AND DISCUSSION

I. Poisoning by Ammonia

In principle, ammonia can neutralize Lewis acid sites through a coordination bond (28, 29). Ammonia (100 Torr) was introduced for 30 min exposure to amorphous alumina at 260°C and the sample was subsequently evacuated for 4 hr at 260°C or at some higher temperature, as stated below. It has been pointed out (25) that nonpoisoned alumina, activated between 260° and 800°C, exhibits at 260°C an initial conversion (after 2 min) of butene-1 much higher (of the order of 2 to 10%, depending on the temperature of activation) than the conversion after 30 min of reaction (of the order of 0.5 to 1%). This behaviour was explained by inhibition of active sites by the preferential adsorption of cis-butene-2, since no traces of polymer on the catalyst were detected by uv or visible spectroscopy, or by gas chromatography.

After poisoning by ammonia at 260°C and evacuation for 4 hr at this temperature, a catalyst activated at any temperature between 400° and 800°C exhibits a reduced initial (after 2 min) activity (see below). However, the conversion increases during

the first 30 min to a maximum and then decreases to an equilibrium value after 60 min of reaction. These preliminary experiments may be explained by the poisoning effect of ammonia which reduces the initial activity. However, during the experiments ammonia was flushed off by the reacting feed which produces an increase of the catalytic activity. After a maximum registered after 30 min of reaction the inhibiting effect of cis-butene-2 is responsible for a decrease of the catalytic activity to a stationary value. Finally, after 60 min of reaction, the behaviour of the poisoned catalyst is comparable to that of unpoisoned catalyst.

It was shown previously (25) that the isomerizing activity (conversion % after 2 min) of amorphous alumina depends on the activation temperature of the catalyst in vacuum. Two maxima of activity were recorded for the activation temperatures of 470°C and of 650°C. They were explained by a modification of the nature of the active sites and in particular of the reducing centers created either at 470°C or at 650°C (26). Those formed at 470°C would be surface hydroxyls, whereas those formed at 650°C would be adjacent O^{2-} ions (6). Simultaneously, the determination of the reducing and oxidizing power (23), through the formation of charge transfer complexes, $TCNE^-$ and $PhTh^+$, respectively, also showed almost the same maxima with respect to the temperature of the activation of amorphous alumina. It was therefore concluded that not only the nature of reducing centers but also of oxidizing centers is not the same for the two maxima. Those formed at 470°C would be Lewis acid sites whereas those formed at 650°C would be adjacent Al^{3+} ions (6, 23). For these reasons, in the work which follows, the poisoning experiments are performed on samples of amorphous alumina activated at 470°C (catalyst A) and on those activated at 650°C (catalyst B) because different properties may be expected for these two catalysts.

In order to estimate the strength of the acid sites developed by activation on catalysts A and B, ammonia was adsorbed at 100 Torr and 260°C for 30 min and was then evacuated during 4 hr at increasing temperatures. The isomerization test was finally performed on such poisoned catalysts. Table 1 summarizes these results.

For the catalyst A ammonia is progressively desorbed at increasing temperatures, because the catalytic activity increases with the temperature of ammonia desorption and the conversion recorded after desorption of ammonia at 460°C is almost the same as that observed for unpoisoned catalyst.

TABLE 1

INITIAL CATALYTIC ACTIVITY AT 260°C OF AMORPHOUS ALUMINAS[a] AFTER POISONING BY AMMONIA AND ITS SUBSEQUENT DESORPTION AT INCREASING TEMPERATURES

Catalyst A + NH₃				
Temperature of evacuation of NH₃ (4 hr)(°C)	260	350	420	460
Initial conversion (%)	1.37	1.77	3.6	6.1
Initial conversion of unpoisoned catalyst (%)		6.65		

Catalyst B + NH₃				
Temperature of evacuation of NH₃ (4 hr)(°C)	260	350	450	550	620
Initial conversion (%)	1.12	1.55	1.9	0.8	0.68
Initial conversion of unpoisoned catalyst (%)			10.55		

[a] Activated in vacuum at 470°C (catalyst A) or at 650°C (catalyst B).

Most of the active sites are therefore acid centers of a moderate strength. On the contrary, for catalyst B, even an evacuation of ammonia at 620°C does not liberate sites for the isomerization of butene-1. A small maximum of activity is recorded after evacuation of ammonia at 450°C (Table 1) but in no case is the conversion for an unpoisoned catalyst recovered. The interpretation of this result must be worked out in a different reaction of ammonia with catalyst B than a simple neutralization of acid sites.

In an infrared study of the adsorption of ammonia on γ-alumina Peri (7) showed that most of the ammonia is adsorbed as NH_3. However, for samples dehydrated above 600°C, a formation of NH_2^- species on sites active in the isomerization of butene-1 was demonstrated. Also decomposition of ammonia on this catalyst was found by mass spectroscopy and the following reactions with the catalyst were proposed:

$$NH_3 + O^{2-} \rightarrow NH_2^- + OH^-$$
$$NH_3 + O^{2-} \rightarrow NH^{2-} + H_2O$$
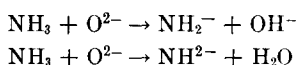
In the case of amorphous alumina the formation of species NH_2^- and NH^{2-}, strongly adsorbed (26), would explain a lack in the recovery of the catalytic activity, even after evacuation at 620°C. This would also signify that basic or reducing sites (like O^{2-}) are required for the reaction, since their poisoning by ammonia leads to a negligible activity on catalyst B.

If ammonia reacts with reducing sites (like O^{2-}), these modifications of the reducing power, produced by ammonia, should be detected by ESR through the formation of charge transfer complexes. For this purpose, catalysts A and B, poisoned by ammonia at 260°C, were evacuated at increasing temperatures and then were immersed, in vacuum at room temperature, in a solution of tetracyanoethylene in benzene. The ESR spectrum of TCNE$^-$ ion was finally registered (26). The results of Figs. 1 and 2 show that for catalyst A and B, respectively, poisoned by ammonia (curves b and b') and evacuated at 260°C for only 1 hr, the concentration of reducing sites is decreased, because the intensity of the TCNE$^-$ signal is decreased by comparison with unpoisoned catalysts (curves a and a').

However, for catalyst A the reducing power is partially recovered after evacuation of ammonia for 1 hr at 450°C (Fig. 1c) and is almost completely recovered after evacuation for 4 hr at 450°C, whereas for catalyst B, even an evacuation at 530°C (Fig. 2c') does not significantly increase the concentration of reducing centers.

Summing up, poisoning of amorphous alumina by ammonia gives evidence of the following facts. The isomerization of bu-
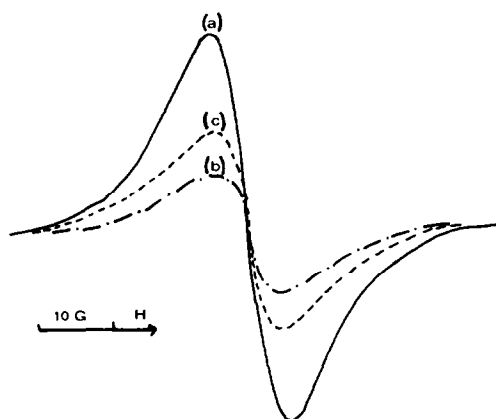

FIG. 1. The effect of ammonia adsorption on the reducing centers of amorphous alumina activated in vacuum at 465°C. (a) Sample activated in vacuum at 465°C (A); (b) A + NH_3 (100 Torr, 260°C, 30 min) + evacuation at 260°C for 1 hr; and (c) b + evacuation at 450°C for 1 hr.
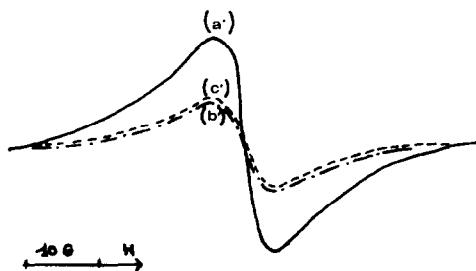

FIG. 2. The effect of ammonia adsorption on the reducing centers of amorphous alumina activated in vacuum at 630°C. (a') Sample activated in vacuum at 630°C (B); (b') B + NH_3 (100 Torr, 260°C, 30 min) + evacuation at 260°C for 1 hr; and (c') b' + evacuation at 530°C for 1 hr.

tene-1 at 260°C proceeds on acid sites of a moderate strength, which can retain ammonia up to approximately 400°C. But ammonia may also be adsorbed on reducing sites which seem to be necessary to account for the isomerizing activity of amorphous alumina (25). These sites, of a peculiarly high strength towards ammonia, are formed by activation of alumina at 650°C (catalyst B). The catalytic activity of the initial unpoisoned catalyst B cannot then be recovered, even after evacuation at 620°C (Table 1). These results confirm the hypothesis, made previously (25), concerning the variation of the nature of the active sites in the isomerization of butene-1 with the temperature of activation of amorphous alumina (at 470°C, catalyst A or at 650°C, catalyst B).

If the poisoning of amorphous alumina by ammonia is not entirely selective (acid sites and reducing or basic sites involved) it may be anticipated that both acid sites and reducing or basic sites are involved in the reaction. It must also be noted that for all experiments of poisoning given in Table 1 the selectivity (the ratio cis/trans butene-2) is practically identical to that for the unpoisoned catalyst (0.60).

II. Poisoning by Tetracyanoethylene

Two maxima have been recorded by ESR in the concentration of TCNE⁻ versus the temperature of activation of amorphous alumina. They were correlated with the maxima for catalytic activity (at 470°C and 650°C) (25).

Adsorption of TCNE may block the reducing sites, but in addition the rather large molecular size of the poison may contribute physically to the shielding of active sites. Also it is important to check that the total number of irreversibly retained TCNE molecules, under the catalytic test conditions, corresponds to the number of TCNE⁻ radical ions recorded by ESR (23). For this purpose, a TCNE adsorption experiment was performed on a McBain balance. After exposure of catalyst A to the vapour of TCNE at 150°C for 30 min, about 2×10^{19} TCNE molecules were retained by 1 g of the catalyst. After evacuation of the

catalyst at 260°C (catalytic test temperature) until equilibrium, the number of irreversibly held TCNE molecules was found equal to 1×10^{19}. On the other hand, the number of TCNE⁻ ions formed on the catalyst surface after contact at room temperature with the solution of TCNE in benzene (23, 25) is of the same order (0.4 $\times 10^{19}$ ions per g of catalyst). These results show a good agreement, taking into account the differences between adsorption of TCNE followed by ESR and gravimetric techniques.

Finally, the number of TCNE molecules (molecular area of the order of 45 Å²) irreversibly retained at 260°C corresponds to about one TCNE molecule per 1000 Å² of the catalyst surface. Therefore, under the catalytic conditions, all the reducing sites are blocked by TCNE⁻ ions with a surface coverage by TCNE of only 5%. The possibility of physical shielding of active sites by TCNE may be then discarded.

The results in the butene-1 isomerization at 260°C on poisoned catalysts A and B by exposure to the vapour of TCNE at 150°C for 30 min and then evacuation at increasing temperatures are summarized in Table 2.

The results of Table 2 show that TCNE, which is an electron acceptor forming a charge-transfer complex (23, 26) is an active poison in the isomerization of butene-1. But progressive desorption of TCNE at increasing temperatures and for various lengths of time (Table 2) regenerates the catalytic activity of both catalysts A and B. Therefore, the reducing sites of amorphous alumina, activated at 470°C or at 650°C, are required for the isomerizing activity of this oxide.

For low evacuation temperatures of TCNE (up to 450°C) the observed reduction of catalytic activity is due to the poisoning of reducing sites by TCNE. For higher temperatures of evacuation, chemical transformations of TCNE molecules adsorbed on alumina cannot be discarded. Nevertheless, the surface properties of the sample do not seem to change since the initial activity (of the unpoisoned catalyst) is practically recovered (Table 2).

TABLE 2

INITIAL CATALYTIC ACTIVITY AT 260°C OF
AMORPHOUS ALUMINAS[a] AFTER POISONING BY
TCNE AND ITS SUBSEQUENT DESORPTION
AT INCREASING TEMPERATURES

Catalyst A + TCNE		
Temperature of evacuation of TCNE (1 hr)(°C)	260	450
Initial conversion (%)	1.25	3.3
Initial conversion of unpoisoned catalyst (%)	6.65	

Catalyst B + TCNE				
Temperature of evacuation of TCNE (1 hr)(°C)	260	600	600[b]	650
Initial conversion (%)	1.17	3.9	6.2	9.3
Initial conversion of unpoisoned catalyst (%)		10.55		

[a] Activated in vacuum at 470°C (catalyst A) or at 650°C (catalyst B).

[b] Evacuation during 6 hr.

Again, the selectivity for all the poisoning experiments of Table 2 is practically identical with that for the unpoisoned catalyst (0.60).

III. Poisoning by Phenothiazine

Phenothiazine (PhTh) gives a cationic charge transfer complex of the type Ph Th[+]. Two maxima were recorded by ESR in the concentration of PhTh[+] versus the temperature of activation of amorphous alumina. They were correlated with the maxima in the catalytic activity (at 470° and 650°C) (25).

In order to compare the number of irreversibly retained molecules of PhTh by amorphous alumina at 260°C (catalytic test temperature) with those of PhTh[+] radical ions adsorbed from benzene solution at room temperature and recorded by ESR (23), the adsorption of PhTh was carried out on catalyst A. The sample, in a McBain balance, was exposed to the Ph Th vapour (molecular area of the order of 50 Å[2]) at 110°C for 30 min and was then evacuated at 260°C until equilibrium was observed. The amount of PhTh irreversibly held by the catalyst at 260°C was within the limits of the sensitivity of the balance, i.e., about 10[18] molecules of PhTh were retained per g of catalyst. The number of PhTh[+] ions detected by ESR was of the same order (2.3 × 10^{17} ions per g of catalyst (23, 25)). Hence about one molecule of PhTh is adsorbed on 10,000 Å[2] of alumina surface representing a coverage of 0.5%. The blocking of oxidizing sites by extracting electrons from the molecules of PhTh is again not related to the physical shielding of the alumina surface by PhTh molecules.

Table 3 summarizes the results of the isomerization activity of butene-1 on amorphous alumina at 260°C, after poisoning by the exposure of catalysts A and B to the vapour of PhTh at 110°C for 30 min and subsequent evacuation of increasing temperatures.

These results show that PhTh, which is an electron donor forming a charge transfer complex, is an effective poison in the isomerization of butene-1, since it reduces by 30% the initial activity of catalyst A and by 70% that of catalyst B, if they are evacuated at 260°C for 4 hr. Again, progressive desorption of PhTh at increasing temperatures (for 4 hr) (Table 3) regenerates the catalytic activity of both catalysts A and B. Heating of PhTh at high temperatures (up to 640°C) adsorbed on amorphous alumina may again result in a chemical transformation of the PhTh molecule. Nevertheless, the surface properties of the catalyst do not significantly change, since its catalytic activity is progressively recovered with increasing desorption temperatures (Table 3).

A significant difference is found between (i) PhTh-poisoned catalysts and (ii) the unpoisoned catalyst or the catalyst poisoned by TCNE or ammonia. Indeed, for this second group of catalysts the catalytic activity decreases with the time of reaction (Fig. 3a) and reaches a stationary value after roughly 40 min (25), whereas the isomerizing activity of both catalysts, A and B, poisoned by PhTh does not show

TABLE 3

INITIAL AND STATIONARY STATE CATALYTIC
ACTIVITIES AT 260°C OF AMORPHOUS ALUMINAS[a]
AFTER POISONING BY PhTh AND ITS
SUBSEQUENT DESORPTION AT
INCREASING TEMPERATURES

Catalyst A + PhTh			
Temperature of evacuation of PhTh (4 hr)(°C)	260	370	450
Initial conversion (%)	4.52	5.03	5.53
Initial conversion of unpoisoned catalyst (%)		6.65	
Conversion at stationary state (%)	3.32	3.92	4.41

Catalyst B + PhTh				
Temperature of evacuation of PhTh (4 hr)(°C)	260	400	615	640
Initial conversion (%)	3.16	3.20	6.70	7.38
Initial conversion of unpoisoned catalyst (%)		10.55		
Conversion at stationary state (%)	3.03	2.99	3.32	3.44

[a] Activated in vacuum at 470°C (catalyst A) or at 650°C (catalyst B).

the abrupt decrease from the beginning of the reaction (catalyst A, evacuated at 260°C, Fig. 3b). It is almost constant during a 40 min test of the activity of the catalysts of Table 3. It is, in particular, higher than the activity of unpoisoned catalyst after 40 min (Fig. 3a and Table 3). Moreover, the selectivity of the poisoned catalysts of Table 3 is of the order of 1 instead of 0.65 for the catalysts of the second group. These results tend to show that the sites which are eliminated during the initial decrease of the catalytic activity of the unpoisoned catalyst (Fig. 3a) (25) are of an electron acceptor (oxidizing) character, because their poisoning by PhTh suppresses this initial decrease of the catalytic activity (Fig. 3b). This interpretation is of the same type as that given for the isomerizing activity of silica–alumina catalysts in the case of cis-butene-2 (30). In that case the initial strong decrease of the
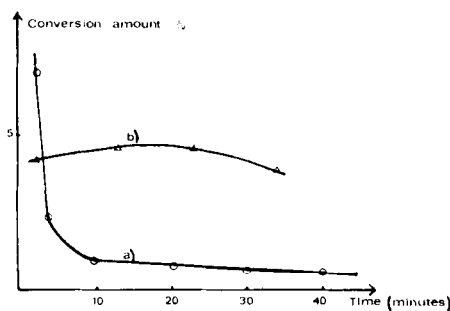

FIG. 3. The influence of poisoning by phenothiazine on the ageing behaviour of amorphous alumina (A) toward the isomerization of butene-1. (a) Unpoisoned catalyst (A), activated at 470°C and (b) A + phenothiazine (110°C) + evacuation at 260°C for 4 hr.

activity was correlated with the presence of Lewis acid sites exhibiting an oxidizing character and showing simultaneously an isomerizing and polymerizing activity. Formation of polymers on these sites was considered responsible for the decrease of the activity. But in the case of amorphous alumina the polymerizing activity was not indicated by uv or visible absorption and gas chromatography (25) and the decrease of the activity was attributed to a preferential adsorption of cis-butene-2. If the oxidizing sites adsorbing this olefin are poisoned by PhTh it is not surprising that the selectivity (the cis/trans ratio) is increased from 0.65 to 1. This high value of the catalytic activity in the stationary state of PhTh poisoned catalysts, compared to the activity of unpoisoned catalysts, or ammonia- or TCNE-poisoned catalysts, may also be explained as follows. It is considered that a new type of active site is formed, derived from the association of an oxidizing site, with PhTh (23). Some authors (31, 32) in fact believe that isomerization of olefins does not occur directly on Lewis acid sites of oxidizing character, but involves ionic species formed by interaction between the olefin and these sites, to produce an active site.

IV. Poisoning by Acetic Acid

Finally, an attempt to poison the basic sites of amorphous alumina was achieved

TABLE 4

IRREVERSIBLE ADSORPTION AT 180°C OR 260°C OF ACETIC ACID ON A BARE SURFACE OF THE CATALYST A OR ON A SURFACE CONTAINING IRREVERSIBLY ADSORBED AMMONIA

	Catalyst A + AcOH		Catalyst A + NH₃		(Catalyst A + NH₃) + AcOH	
Adsorption temperature (°C)	180	260	180	260	180	260
Number of molecules of adsorbate irreversibly retained per g of the catalyst ($\times 10^{20}$)	3.5 ± 0.1	2.6 ± 0.1	1.2 ± 0.2	0.6 ± 0.2	3.4 ± 0.1	2.4 ± 0.1

by exposing the catalysts A and B to the vapour of acetic acid (AcOH) at 260°C for 30 min. It must be first shown that under conditions of catalytic activity (260°C) acetic acid does not significantly occupy also Lewis acid sites, through a formation of surface formate structures (33). For this purpose acetic acid irreversible adsorption experiments were performed on a McBain balance on the catalyst A, either bare or after preadsorption of ammonia (Table 4).

The results of Table 4 unambiguously show that acetic acid adsorbed at 180° or at 260°C does not significantly occupy the active sites involved in the adsorption of ammonia (at 180° or at 260°C), i.e., mainly Lewis acid sites. Indeed, the number of AcOH molecules irreversibly retained by the catalyst is identical, within experimental error, for the bare surface and for the surface containing irreversibly adsorbed ammonia (Table 4). Furthermore, these results imply that acetic acid does not undergo a chemical transformation with adsorbed ammonia on the surface of the catalyst.

The results concerning the isomerization of butene-1 at 260°C on amorphous alumina poisoned by acetic acid are reported in Table 5. After exposure of catalysts A or B to the vapour of acetic acid at 260°C, the samples were evacuated at increasing temperatures for 4 hr and the catalytic activity was tested.

These results definitely show that acetic acid very sharply decreases the isomerizing activity of amorphous alumina. The basic sites are therefore required for the isomerizing activity of this catalyst. In the same

way as for unpoisoned catalyst or the catalysts poisoned by ammonia and TCNE the equilibrium value of the activity is very low.

CONCLUSIONS

A method of selective poisoning of sites of acidic, basic, oxidative, or reducing nature is particularly interesting when a suspicion arises concerning the rather complex nature of active sites in the isomerization of butene-1 on amorphous alumina (25). A dualistic character of alumina, i.e., acidic and basic, may be expected by considering the amphoteric properties of this oxide. However, in addition, the presence of electron donating (reducing) and electron ac-

TABLE 5

INITIAL CATALYTIC ACTIVITY AT 260°C OF AMORPHOUS ALUMINA[a] AFTER POISONING BY ACETIC ACID AND ITS DESORPTION AT INCREASING TEMPERATURES

Catalyst A + AcOH		
Temperature of evacuation of AcOH (4 hr)(°C)	260	350
Initial conversion (%)	0	0.95
Initial conversion of unpoisoned catalyst (%)	6.65	

Catalyst B + AcOH		
Temperature of evacuation of AcOH (4 hr)(°C)	260	400
Initial conversion (%)	0.48	2.25
Initial conversion of unpoisoned catalyst (%)	10.55	

[a] Activated in vacuum at 470°C (catalyst A) or at 650°C (catalyst B).

cepting (oxidizing) centers was demonstrated on amorphous alumina (23).

Since a different behaviour of amorphous alumina is encountered if this oxide is dehydrated (activated) in vacuum at 470°C or at 650°C (23–26) the previous sites may be of a different nature according to the temperature of the activation of the catalyst.

For the catalyst activated at 470°C, showing a maximum of activity in the isomerization of butene-1, acid sites were ascribed to Lewis centers whereas basic sites were considered to be surface hydroxyls (23). For the catalysts activated at 650°C, also showing a (second) maximum of activity (25), acid sites were assumed to be adjacent Al^{3+} ions whereas basic sites were ascribed to adjacent O^{2-} ions (23). The reducing character was attributed to a fraction of basic sites and the oxidizing one to a fraction of acid sites (23). The technique of a selective poisoning of such a complicated surface of amorphous alumina may therefore be able to cast some light on the nature of sites required for the isomerizing activity.

The poisoning by ammonia shows that acid sites are necessary for the catalytic activity. But ammonia is liable to poison some reducing sites which also may be required for the catalytic activity. On the other hand acetic acid which neutralizes basic sites is also a very effective poison of the isomerization. This reaction would therefore necessitate acid and basic sites together.

But if poisons of electron donating or accepting centers are used, like tetracyanoethylene or phenothiazine respectively, again the catalytic activity is reduced for both poisons. The final conclusion is therefore that acid sites of simultaneously oxidative nature and basic sites of simultaneously reducing nature are both required. The behaviour of amorphous alumina in catalyzing the shift of the double bond from butene-1 to butenes-2 may be explained if it is assumed that the mechanism of this reaction involves the neighborhood of an electron accepting center (oxidative, i.e., acid) in the vicinity of the π bond between carbons 1 and 2 and the presence of an electron donating (reducing, i.e., basic) center in the vicinity of the σ bond between carbons 2 and 3. The shift of the double bond is therefore of a concerted type. The cis/trans ratio which is unusually small (0.65) compared to that found on crystalline aluminas (34, 35) where a carbanion mechanism has been proposed in connection with a mainly basic character of these solids, may here result from the electron and hydrogen shift mechanism as in a homogeneous reaction.

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