JOURNAL OF CATALYSIS 3, 502–511 (1964)

Catalytic Aluminas

II. Catalytic Properties of Eta and Gamma Alumina

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From the Gulf Research & Development Company, Pittsburgh, Pennsylvania

Received March 8, 1964

The catalytic activities and selectivities of two well-characterized samples of eta and gamma alumina for several acid-catalyzed reactions were measured, and, from the results obtained, it was concluded that the structure of the alumina is an important variable controlling its catalytic properties. In general, eta alumina was more active than gamma alumina for the double-bond and skeletal isomerization of 1-pentene, the cracking of 2,4-dimethylpentane, and the isomerization of *p*-xylene. Comparing the catalytic properties of these two aluminas with those of silica-alumina and silica-magnesia suggested that the strengths of the acid sites of eta alumina were stronger than those of gamma alumina.

INTRODUCTION

A previous paper (*1*) has described the differences in certain surface properties of two well-characterized samples of eta and gamma alumina and has demonstrated that the surface acidity of alumina, as measured by ammonia chemisorption, depends, at least in part, on the "form" or structure of the alumina. Thus, it was found that, while the total number of acid sites, that is, surface sites capable of chemisorbing ammonia, was about the same for both eta and gamma alumina, it appeared that the acid sites were, on the average, stronger on the eta alumina than on the gamma alumina. This fact suggested that these two aluminas would have different activities for acid-catalyzed reactions which, in turn, would indicate that the "structure" of the alumina is an important variable controlling catalyst activity and selectivity. The present paper deals with this latter point and reports on the comparative activities of eta and gamma alumina in the catalysis of several acid-catalyzed reactions.

EXPERIMENTAL

Materials. The source and purification of each of the gases used in the present work have been described in an earlier publication (*2*). Phillips Pure Grade 1-pentene, 2,4-dimethylpentane, and *p*-xylene were dried, before use, by contacting them with Linde 4A Molecular Sieves.

The preparation and properties of the samples of eta alumina, gamma alumina, silica-magnesia, and silica-alumina employed in the present research have been described in the preceding publication (*1*). A 60% phosphoric-acid-on-kieselguhr catalyst was obtained from Universal Oil Products Company and had a surface area of 5 m^2/g. The aluminum trifluoride catalyst was prepared by the method of Kaiser, Moore, and Odioso (*3*). It had a fluorine content of 67.8% and a surface area of 12 m^2/g.

Apparatus. Catalyst activities for pentene and xylene isomerization were determined using an all-glass, gas-flow reactor system described elsewhere (*2*). Reactant mixtures were obtained by saturating

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either an argon-helium carrier mixture with 1-pentene at —15°C or argon with *p*-xylene at 22°C and were passed first through a preheater and then through the reactor. The composition of the exuent gas was determined chromatographically. The cracking of 2,4-dimethylpentane was carried out in a fixed-bed, downflow reactor. The 2,4-dimethylpentane was introduced into the argon carrying gas by means of a constant speed syringe drive unit, and the reactant stream was then passed through a preheater and into the reactor. The liquid product was condensed in a series of traps at 0° and —78°C and analyzed chromatographically.

Procedure. In the majority of the 1-pentene isomerization activity measurements to be reported here, 0.5-g samples of 50- to 100-mesh catalysts were packed in the reactor and held in place with glass wool plugs. Each sample was dried in a stream of argon at 25°C for 16 hr before being pretreated in the argon stream at a selected temperature between 200° and 900°C for 22 hr. After this pretreatment, the pentene-argon-helium reactant mixture was passed over the catalyst for 1 hr at 150°C and a flow rate of 4.8×10^{-4} moles pentene/min at which time the conversion of 1-pentene was measured. The temperature was next raised to 390°C and after 1 hr at the same flow rate the conversion was again measured. Finally, the flow rate was lowered to 1.0×10^{-4} moles/min and the conversion after 40 min was determined. Occasionally, deviations from this standard sequence of operations were made for experimental purposes; these will be noted below at appropriate places in the text. In all cases, the only reaction products observed were *cis*- and *trans*-2-pentene at 150°C, and 2-methyl-1-butene, 2-methyl-2-butene, 3-methyl-1-butene *cis*-2-pentene, and *trans*-2-pentene at 390°C.

The *p*-xylene isomerization reaction was studied in a similar fashion using 1-g catalyst samples. These samples were diluted to a volume of 12 cc with quartz chips and then placed in the reactor between glass wool plugs. Pretreatment consisted of heating the catalyst in a stream of argon at 500° or 900°C for 16 hr. The reactant charge was then passed over the catalyst at a flow rate of 5×10^{-5} moles/min, and the exuent gas analyzed at periodic intervals. The only products obtained at 500°C and 1 atm pressure were the isomeric xylenes.

The cracking of 2,4-dimethylpentane was carried out, using 12 cc of catalyst, at 500°C, 1 atm total pressure, and a liquid hourly space velocity of 1, for a reaction period of 1 hr. The pretreatment was the same as described above for the *p*-xylene studies. Chromatographic and mass spectrometric analyses of the reaction products indicated that the principal (>95%) liquid product was the starting material, 2,4-dimethylpentane, and, therefore, the conversion was simply obtained from difference between the amount of liquid charged to the reactor and the amount recovered.

For all the above reactions, the activity of the catalyst was expressed as the per cent conversion divided by the total area of the catalyst in the reactor.

RESULTS

The reactions studied during the course of the investigation have all been regarded as acid catalyzed (*4*) and were selected so as to reflect a wide range of catalyst acidities. They included, in approximate order of acid strength requirement, the double-bond isomerization of 1-pentene, the skeletal isomerization of 1-pentene, the cracking of 2,4-dimethylpentane, and, finally, the isomerization of *p*-xylene. As will be shown presently, the activities of eta and gamma alumina for these reactions differed considerably, thereby indicating a corresponding difference in their surface acidities.

The double-bond isomerization of 1-pentene was studied over the two aluminas at 150°C as a function of the temperature at which the alumina had been dried, prior to use. In general, it was found that considerable care had to be exercised in order to obtain reproducible results. The flow rate of the inert gas (i.e., argon) which was passed over the catalyst during the dehydration, the geometry of the catalyst bed, and the rate of heating of the alumina to its final dehydration temperature were all found to influence the apparent activity of the catalyst for double-bond isomerization. For this reason, the standard experimental procedure outlined in the preceding section of this paper was adopted and rigorously followed with each sample. By this means it was possible to obtain consistent and reproducible activity measurements. As will be discussed presently, there was some tendency for alumina samples dried at temperatures in excess of 500°C to exhibit a gradual loss of activity with time, but since catalyst activities were measured at relatively short, constant throughputs, this aging effect did not have an appreciable effect on the comparative activity data. These data, presented in Fig. 1, indicated that eta alumina was considerably more active as a catalyst for double-bond isomerization at 150°C than was gamma alumina. In general, the activity of both aluminas increased with increasing catalyst pretreatment temperature, although there was some indication of a slight drop in activity upon drying at the highest pretreatment temperature (900°C).

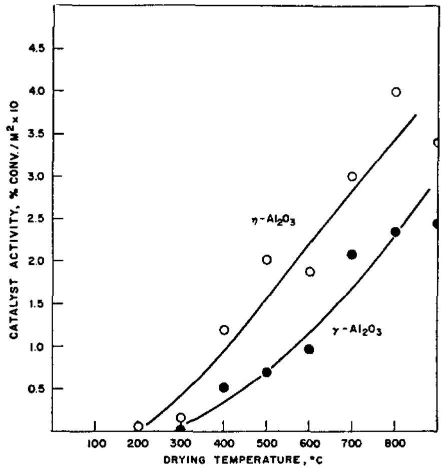

FIG. 1. Double-bond isomerization of 1-pentene over eta and gamma alumina at 150°C.

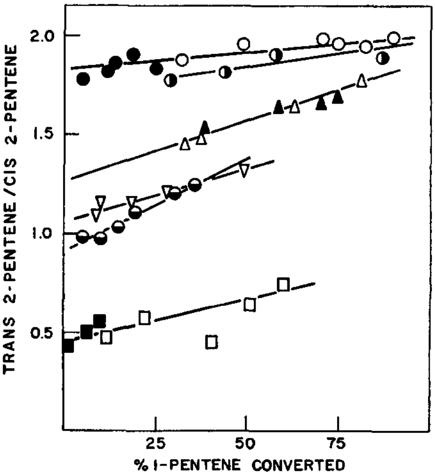

FIG. 2. Selectivity of 1-pentene to 2-pentene reaction at 150°C: γ-Al_2O_3 (●) and η-Al_2O_3 (○) dried at 500°C; γ-Al_2O_3 (■) and η-Al_2O_3 (□) dried at 250°C; SiO_2-Al_2O_3 dried at 250° (△), 500° (▲), and 900 (▽) °C; AlF_3 dried at 500°C (◒); H_3PO_4-Kieselguhr dried at 170°C (◑).

As noted by several workers (*5–8*), the double-bond isomerization of olefins over acidic catalysts such as alumina may be stereoselective in that the rate of formation of *cis*-2-alkene may be greater than that of the more stable *trans* isomer. The results of the present study, shown in Fig. 2, were consistent with these observations, and, in agreement with the results of Brouwer (*8*), it was found that the degree of stereoselectivity depended strongly upon the temperature at which the alumina had been dried. For comparative purposes, similar data were obtained on several other typical solid catalysts, namely, aluminum trifluoride, which has been considered by some workers to be a Lewis acid when thoroughly dried, supported phosphoric acid, which is a Bronsted acid, and finally, silica-alumina, a catalyst which has been described as having both Lewis and Bronsted acidity (*9*). The results, presented in Fig. 2, show that the change of stereoselectivity with the water content of alumina was greater than the change obtained by varying the chemical nature of the acid catalyst. It is interesting to note that although there was a considerable difference in the activity of eta and gamma alumina for double-bond isomerization, the stereoselectivities of the two aluminas were the same at each drying temperature.

As indicated above, it was difficult to obtain a very high degree of reproducibility in the measurement of isomerization activity of alumina and, as a result, no attempt was made to carry out a detailed kinetic study of the reaction. A few experiments were made, however, in which the flow rate was varied over a sufficient range to permit, by extrapolation to infinite space velocity, the determination of initial differential reaction rates (r°) for the formation of *cis*-2-pentene ($r_c{}^\circ$) and *trans*-2-pentene ($r_t{}^\circ$). As noted by previous workers (*5, 8*) both the *cis* and the *trans* isomers were obtained as true primary products of the reaction. By varying the temperature from 120° to 180°C, apparent activation energies corresponding to the rates of formation of the two isomers (E_c and E_t) were determined, and these data, along with the differential reaction rates, are presented in Table 1. The superiority of eta alumina, compared to gamma alumina, as a catalyst for double-bond isomerization is readily apparent, as is also the pronounced stereoselectivity of the reaction. Within the limits of experimental accuracy, the activation energies for *cis*-2-pentene formation and for *trans*-2-pentene formation were the same and did not appear to vary with the pretreatment temperature of the alumina. The observed activation energies of 12 to 14 kcal/mole can be compared with the value of 12.3 to 14.3 kcal/mole obtained by other workers (*7, 8*) in the case of 1-butene to 2-butene isomerization. It may also be mentioned that, over the range of conversions studied, the isomerization of 1-pentene to 2-pentene obeyed first order kinetics.

As mentioned above, when eta or gamma alumina had been dried above 500°C, the activity for double-bond isomerization decreased with increasing throughput, in contrast to the constant activities obtained at drying temperatures below 500°C. This is illustrated by Fig. 3, which presents aging data for the two aluminas and, in addition, provides comparative data for phosphoric acid-on-kieselguhr and aluminum trifluoride. With respect to these latter two catalysts, it should be noted that while the activity of the Bronsted acid, H_3PO_4, did not change with throughput, the Lewis acid, AlF_3, aged quite severely.

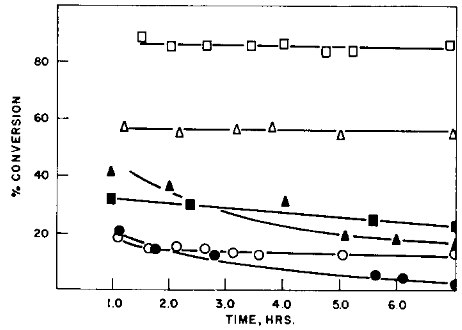

FIG. 3. Double-bond isomerization activity at 150°C: γ-Al_2O_3 dried at 500°C (○) and 900°C (●); η-Al_2O_3 dried at 500°C (□) and 900°C (■); H_3PO_4–kieselguhr dried at 170°C (△); AlF_3 dried at 500°C (▲).

TABLE 1
PENTENE DOUBLE-BOND ISOMERIZATION RATES AT 150°C[a]

Catalyst	Drying temp. (°C)	$r_t{}^\circ \times 10^8$ (moles/min m²)	$r_c{}^\circ \times 10^8$ (moles/min m²)	E_t (kcal/mole)	E_c (kcal/mole)
γ-Al_2O_3	250	0.57	1.02	14	14
γ-Al_2O_3	500	2.47	1.25	14	14
γ-Al_2O_3	900	35.0	21.0	—	—
η-Al_2O_3	250	3.60	7.25	15	14
η-Al_2O_3	500	81.0	41.0	12	12
η-Al_2O_3	900	255	170	—	—
H_3PO_4	170	930	467	—	—
SiO_2–Al_2O_3	500	263	187	6	6

[a] $r_t{}^\circ$, $r_c{}^\circ$ = rate of formation of *trans* (*t*)- and *cis* (*c*)-2-pentene.

The second reaction included in this investigation was the skeletal isomerization of 1-pentene, a reaction requiring a stronger acidity than the double-bond isomerization (*4*). The activities of the two aluminas, pretreated at temperatures from 400° to 900°C, are given in Fig. 4 for the total conversion of 1-pentene to 2-methyl-1-butene, 2-methyl-2-butene, and 3-methyl-1-butene at 390°C and space velocities of 0.48 and 0.10 mmoles/min. As in the case of double-bond isomerization, eta alumina was more active than gamma alumina. However, while the activities for double-bond isomerization increased continuously with temperature of dehydration, the activities for skeletal isomerization passed through a maximum at a drying temperature of 600–700°C. This maximum was very pronounced in the case of eta alumina and was similar to the maximum previously reported by Pines and Haag (*10*) for the isomerization of cyclohexene to methylcyclopentene. With gamma alumina behavior is quite similar even though the maximum seems less pronounced. The smaller values obtained with gamma alumina make its curve seem flatter. The percentage changes are, however, similar.

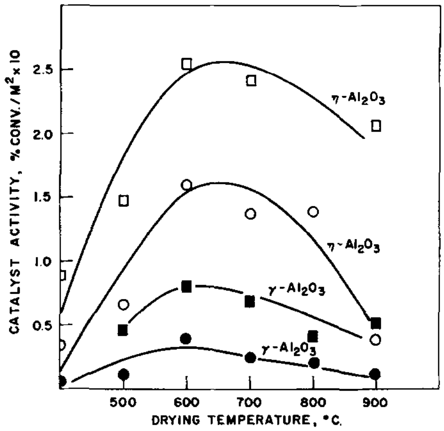

FIG. 4. Skeletal isomerization of 1-pentene over eta and gamma alumina at 390°C; flow rate = 4.8×10^{-4} moles/min, circles; flow rate = 1.0×10^{-4} moles/min, squares.

It has been noted (*11*) that when an acidic oxide surface, such as silica-alumina, is "reduced" with hydrogen at elevated temperatures, a finite amount of tenaciously held oxygen is removed. The removal of this oxygen influences certain surface properties of silica-alumina, and, in particular, it decreases the extent of formation of radical cations of polynuclear aromatics on the catalyst surface. This observation suggested the possibility that an alumina surface might also be sensitive to treatment with hydrogen, and, for this reason, several experiments were carried out in which the standard pretreatment was varied by inserting between the 16 hr–25°C argon drying and a 22 hr–500°C argon drying either a 1-hr exposure to flowing oxygen at 500°C or a sequence of exposures at 500°C successively to oxygen flowing for 1 hr, to argon for ½ hr, and to hydrogen for 1 hr. Catalytic activities for the double-bond and skeletal isomerization of 1-pentene were then determined in the usual fashion. The results, given in Table 2, seem to indicate that the double-bond isomerization is sensitive to the "oxidation state" of the alumina surface, while the skeletal isomerization is not.

TABLE 2
EFFECT OF PRETREATMENT ON THE CATALYTIC ACTIVITY OF ETA AND GAMMA ALUMINA[a]

Alumina	Pretreatment	Double-bond isom. activity at 150°C	Skeletal isom. activity at 390°C
Gamma	Oxidation	0.37	0.12
Gamma	Reduction	0.74	0.11
Eta	Oxidation	1.84	0.75
Eta	Reduction	2.52	0.84

[a] Activities measured at flow rate = 2.9×10^{-4} moles/min and given in % conversion/m².

The catalytic cracking of paraffins, like the isomerization of olefins, is catalyzed by acidic surfaces, such as silica-alumina, but requires a "stronger" acidity than does the olefin isomerization (*12*). As a measure of such acidity, the cracking of 2,4-dimethylpentane was chosen as the test reaction. This reactant, because of its molecular symmetry, tends to crack rather simply to

C_3 and C_4 fragments without undergoing secondary reactions, such as isomerization, to any great extent. The data, given in Table 3, indicate, once again, that eta alumina, dried at 500°C, is a more active catalyst than gamma alumina and, in fact, compares quite favorably with silica-alumina. Gamma alumina, while a relatively poor catalyst, was, nevertheless, more active than silica-magnesia. Upon heating to 900°C both aluminas lost their ability to crack 2,4-dimethylpentane at 500°C.

TABLE 3

CRACKING OF 2,4-DIMETHYLPENTANE[a]

Catalyst	Drying temp. (°C)	Activity (% conversion/m²)
η-Al_2O_3	500	0.013
η-Al_2O_3	900	0
γ-Al_2O_3	500	0.006
γ-Al_2O_3	900	0
SiO_2–Al_2O_3	500	0.015
SiO_2–MgO	500	0.001

[a] Temperature, 500°C, LHSV = 1.0, catalyst volume, cc = 12.0.

The final reaction studied was the isomerization of *p*-xylene. The data obtained are plotted in Fig. 5 where it can be seen that eta alumina was a more active catalyst than was gamma alumina. The two active catalysts, eta alumina, dried at 500°C, and silica-alumina, dried at 500°C, exhibited decreasing activity with increasing throughput. Because of this aging effect, eta alumina, which was initially more active than silica-alumina, eventually became inactive. As was the case in the cracking reaction, heating eta alumina to 900°C greatly lowered its catalytic activity.

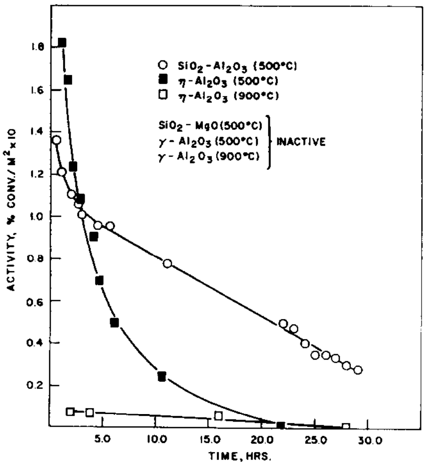

FIG. 5. Isomerization of *para*-xylene at 500°C. Catalyst pretreatment temperatures given in parentheses.

DISCUSSION

The results presented above indicate that the two aluminas under consideration had different catalytic properties, and, since the aluminas were structurally dissimilar (*1*), it is suggested that the structure of an alumina can be a significant factor governing its catalytic behavior. With respect to this point, it should be mentioned that, while Pines and Haag (*10*) have shown that the catalytic activity of alumina can be severely modified by relatively small amounts of certain impurities (i.e., alkali metal ions), the present results cannot be explained on this basis since, as shown earlier (*1*), both aluminas were quite pure and had essentially the same chemical composition. It has been concluded by other workers (*13*) that silica-alumina is a stronger acid than silica-magnesia, and the fact that the differences in catalytic properties between eta and gamma alumina are as great as those between silica-alumina, on one hand, and silica-magnesia, on the other, agrees with the indication (*1*), based on a somewhat arbitrary handling of ammonia chemisorption data, that eta alumina has a stronger surface acidity than gamma alumina.

The double-bond isomerization of olefins is, perhaps, the simplest acid-catalyzed hydrocarbon reaction (*4*) and proceeds readily over most acidic solids under relatively mild conditions. The catalysis of this reaction by alumina has been studied by Brouwer (*8*), who has shown that both the activity and selectivity of the reaction are a function, *inter alia*, of the state of hydration of the alumina. The present work substantiates these observations and, in addition, provides some evidence that, while the isomerization activities of various aluminas can differ considerably, the over-all mechanism of the reaction may be essentially the same in each case. This latter conclusion is based, in part, on the fact that, for a given drying temperature, the selectivities of the two aluminas for conversion to the *cis*- and *trans*-2-pentenes are the same. If, as suggested by previous work (*5, 8*), the selectivity of the reaction reflects its mechanism, then, presumably, the mechanistic reaction paths over eta and gamma alumina are similar. In contrast to this, the data of Fig. 2 show that a change in the chemical identity of the catalyst surface and, hence, the nature of the reactant–catalyst interaction apparently causes a change in the selectivity of the reaction. Thus phosphoric acid gave essentially an equilibrium ratio of *cis* and *trans* primary reaction products while aluminum trifluoride was strongly *cis* specific, a situation which presumably reflects a difference in the over-all mechanisms operative in the two cases. It may also be noted that the activation energy for double-bond isomerization was the same over both eta and gamma aluminas, as would be expected if these two materials were functioning in a mechanistically similar fashion.

In the preceding paper (*1*) it was shown that eta and gamma alumina evolved considerable amounts of water when heated at elevated temperatures and that this dehydration was accompanied by the development of surface acidity, as defined in terms of the extent of ammonia chemisorption. In particular, it was indicated that gamma alumina, after a preliminary drying at room temperature, had a water content in excess of that of eta alumina, and that it was necessary to remove this excess water by heating to 200–300°C before appreciable surface acidity was obtained. As can be seen from Fig. 1 the double-bond isomerization activity of gamma alumina did not become appreciable until the alumina was dried at 300°C, while eta alumina was active when dried at lower temperatures. This observation is consistent with the idea expressed earlier (*1*) that the excess water of gamma alumina is associated with the surface and, in effect, acts as a catalyst poison. During the initial stages of dehydration the desorption of this water apparently exposes certain catalytically active sites; as the dehydration proceeds any "molecular" water present on the surface may participate in the hydroxylation reactions described by Peri and Hannon (*14*) and further change the acidic properties of the alumina; finally, the last stages of the dehydration consist of the condensation of surface hydroxyl groups (*14*), giving rise to what has been regarded by some workers (*15*) as a highly "strained" and, hence, highly reactive surface. Unfortunately, the chemical nature of these thermal transformations of an alumina surface are not sufficiently well defined at the present time to permit any detailed discussion of their relationships to catalyst activity.

It is interesting to note that the phosphoric acid catalyst, a Bronsted acid, and the aluminas dried at 500°C, were similar in that their activities for double-bond isomerization did not vary with throughput. When dried at 900°C, however, the aluminas resembled the Lewis acid, aluminum trifluoride, in that activity decreased with increasing throughput. Since it has been postulated (*10*) that alumina surfaces, dried at elevated temperatures, may develop a Lewis acid character, it may be reasonable to associate these aging effects with Lewis, rather than Bronsted acid sites. Rooney and Pink (*16*) have suggested that Lewis acid sites are responsible for the polymeric deposits or "coke" which tend to deactivate a catalyst for such reactions as cracking and isomerization.

The skeletal isomerization of 1-pentene is catalyzed more by eta alumina than by gamma alumina, a fact which presumably reflects the stronger average acid strength of eta alumina (*4*). As noted earlier, the plots in Fig. 4 of activity versus drying temperature are quite similar for the two types of alumina if percentage changes are considered.

The facts that the double-bond isomerization activity of alumina was sensitive to pretreatment of the surface with hydrogen or oxygen while the skeletal isomerization activity was not, and that the activities of the alumina for catalysis of the two reactions did not show the same dependence upon the drying temperature of the alumina, indicate rather strongly that the catalytic requirements were not the same for both reactions. Evidently, the double-bond isomerization proceeds, at least in part, over sites which are not very active in the skeletal isomerization reaction, and, in terms of the classical carbonium ion mechanisms for these reactions, those sites which are active for double-bond isomerization but inactive for skeletal isomerization are presumably weak acid sites. On this basis, if one considers the olefin isomerization activity patterns of the two aluminas as a function of dehydration one concludes that at drying temperatures in excess of 500–700°C strong acid sites are destroyed while weak acid sites are created. For the case of gamma alumina, this conclusion is qualitatively consistent with earlier data obtained via ammonia chemisorption *(1)* wherein it was shown that heating to 900°C caused a decrease in the average acid site strength of the alumina, but it is not compatible with the observation *(1)* that the strong acidity of eta alumina, as defined by ammonia chemisorption, was actually increased when it was dried at 900°C. Pines and Haag *(10)* concluded from their results that there was no correlation between the olefin isomerization activity of an alumina and its total acidity as measured by the chemisorption of a strongly basic nitrogen compound (in their case, trimethylamine). The present research substantiates this conclusion and seems to indicate further that the acid site strength distribution of alumina as given by ammonia chemisorption is not related in any simple manner to catalyst activity. Perhaps there is some factor other than simple acid strength which determines the olefin isomerization activity of alumina, but in the absence of an established mechanism for the reaction, speculation beyond this point does not seem warranted. It is sufficient for present purposes simply to point out that the phenomenological relationship between ammonia chemisorption and olefin isomerization activity is not the same with both eta and gamma alumina. This is indicative of the presence of what seems to be a fundamental difference in the surface properties of the two aluminas.

The isomerization of xylene, which is the most difficult to catalyze of the three isomerization reactions employed in the present study, has been used previously *(17, 18)*, as a measure of catalyst acidity. According to the carbonium ion mechanism for this reaction *(4)*, the initial step involves the addition of a proton to the aromatic nucleus, and experimental data have been cited *(4, 19)* supporting the idea that a proton source (i.e., a Bronsted acid) is essential to the catalysis. If this concept were correct, then, presumably, activity for xylene isomerization would be an indication of Bronsted acidity. In order to evaluate this possibility, several experiments were carried out using aluminum trifluoride, supposedly a Lewis acid, as the catalyst, and, in each case, rapid isomerization of the xylene was observed. This fact, if taken at face value, would suggest that, contrary to what has sometimes been stated in the literature, the presence of a protonic acid is not necessary for the catalysis. Unfortunately, the experiment just cited cannot be taken as conclusive since the possibility of traces of protonic cocatalysts (i.e. water) associated with the aluminum trifluoride cannot be excluded. Thus it seems questionable at the present time whether any definitive statements can be made regarding the xylene isomerization catalysis other than that it apparently requires a strong acid as evidenced by the fact that, under the conditions employed in the present study, silica-alumina was an active catalyst while silica-magnesia was not.

As is apparent from the data of Fig. 5, the xylene isomerization activity demonstrates a sharp distinction between eta and gamma alumina in that while eta alumina was a very active catalyst, gamma alumina was completely inert. Of particular interest is the fact that heating eta alumina to 900°C caused a great decrease in catalyst activity as compared to heating at 500°C. If a proton source was, indeed, required for catalysis, then this observation would be rationalized on the basis that, when heated at elevated temperatures, an alumina surface consists primarily of Lewis-type acid sites rather than Bronsted acids, a concept which has been advanced by other workers (*10*). It will be noticed that eta alumina, dried at 500°C, was even more active initially than silica-alumina for xylene isomerization, but, at the same time, it aged more rapidly, so that after a few hours it became less active than silica-alumina, and, eventually, it lost all activity. This rapid deactivation could be associated either with the deposition of carbonaceous deposits on the surface of the alumina or with the influence of trace impurities, especially water, in the reactant charge, although every effort was made to reduce such impurities to a minimum. In any case, it could be postulated that the low activity of gamma alumina in this catalysis is due to an extreme sensitivity of this alumina to the deactivating agent. The present study does not really provide any experimental clarification of this point, but, on the basis of the results obtained with the other test reactions, it seems reasonable to maintain that the difference between the abilities of eta and gamma alumina to catalyze the xylene isomerization reaction reflects a primary difference in the detailed chemical nature of these sites rather than in the susceptibility of these sites to catalyst poisoning.

As the data in Table 3 indicate, certain forms of alumina can function as active paraffin cracking catalysts, and, in fact, the sample of eta alumina employed in the present study compared favorably with silica-alumina in this respect. Due to the uncertainty which, despite a considerable amount of research, still remains as to the detailed mechanism of this reaction and, in particular, to the nature of the initial step, it is not possible to attribute, unambiguously, the difference in the cracking activities of eta and gamma alumina to any specific chemical feature. The most that can be said is that, accepting the usual carbonium ion mechanism, the higher activity of eta alumina again reflects the fact that it has a stronger acidity than gamma alumina; the chemical nature of this acidity remains in doubt. Note also that here as with xylene isomerization the activity of eta alumina is less at 900° than at 500°C while the reverse is true for acid strength.

In summary, the results of the present research demonstrate the possible existence of certain basic catalytic differences among the various forms of high area aluminas, differences which do not seem to be immediately attributable to the deleterious effects of chemical impurities such as alkali metal ions. This is not to say that these impurities are not an important factor in the catalytic chemistry of alumina but rather to point out the existence of a second important, and independent, variable, namely, the structural form of the alumina. The reasons why eta and gamma alumina differ catalytically cannot be directly deduced from the present results. Certainly, the role of catalyst hydrogen content seems an important one, as would be expected from the nature of the reactions being catalyzed, and it seems reasonable to suppose that the chemical situation of this hydrogen would vary from one type of alumina to another. Another manner in which catalyst structure can influence activity is suggested by the studies of Pines and Pillai (*20*) on the dehydration of alcohols over various aluminas. These workers have concluded that in the dehydration of menthol and other alcohols, a combination of catalyst sites acting simultaneously upon the adsorbed species is required and that these active sites must presumably bear a certain geometric relationship to each other in order to realize maximum catalyst activity. It seems reasonable to postulate similar geometric requirements for other acid-catalyzed reactions. In their consideration of the double-bond isomerization of olefins, for example, Turkevich and Smith (*21*) have suggested a mechanism involving the simultaneous donation and acceptance of protons by the surface. The operation of such a mechanism would be expected to be strongly dependent upon surface geometry. Regardless, however, of the details of how such geometric constraints operate, structural factors in catalysis are not unexpected, and the present results strongly suggest the presence of such factors in the alumina system.

ACKNOWLEDGMENTS

The authors wish to express their thanks to Mr. R. T. Barth and Mr. R. Pinchok for help in obtaining some of the data.

REFERENCES

1. MacIver, D. S., Tobin, H. H., and Barth, R. T., *J. Catalysis,* **2,** 485 (1963).
2. Bridges, Joanne M., Rymer, G. T., and MacIver, D. S., *J. Phys. Chem.* **66,** 871 (1962).
3. Kaiser, J. R., Moore, L. D., and Odioso, R. D., *Ind. Eng. Chem. Prod. Res. Develop.* **1,** 127 (1962).
4. Condon, F. E., *in* "Catalysis" (P. H. Emmett, ed.), Vol. VI, Chap. 2. Reinhold, Baltimore, Maryland, 1958.
5. Haag, W. O., and Pines, H., *J. Am. Chem. Soc.* **82,** 2488 (1960).
6. Lucchesi, P. J., Baeder, D. L., and Longwell, J. P., *J. Am. Chem. Soc.* **81,** 3235 (1959).
7. Cvetanovic, R. J., and Ogasawara, S., *J. Catalysis* **2,** 45 (1963).
8. Brouwer, D. M., *J. Catalysis* **1,** 22 (1962).
9. Ryland, L. B., Tamele, M. W., and Wilson, J. N., *in* "Catalysis" (P. H. Emmett, ed.), Vol. VII, Chap. 1. Reinhold, Baltimore, Maryland, 1960.
10. Pines, H., and Haag, W. O., *J. Am. Chem. Soc.* **82,** 2471 (1960).
11. Hall, W. K., *J. Catalysis* **1,** 53 (1962).
12. Voge, H. H., *in* "Catalysis" (P. H. Emmett, ed.), Vol. VI, Chap. 5. Reinhold, Baltimore, Maryland, 1958.
13. Benesi, H. A., *J. Phys. Chem.* **61,** 970 (1957).
14. Peri, J. B., and Hannon, R. B., *J. Phys. Chem.* **64,** 1526 (1960).
15. Cornelius, E. B., Milliken, T. H., Mills, G. A., and Oblad, A. G., *J. Phys. Chem.* **59,** 809 (1955).
16. Rooney, J. J., and Pink, R. C., *Trans. Faraday Soc.* **58,** 1632 (1962).
17. Myers, C. G., Sibbett, D. J., and Ciapetta, F. G., *J. Phys. Chem.* **63,** 1032 (1959).
18. Holm, V. C. F., and Clark, A., *J. Catalysis* **2,** 16 (1963).
19. Baddeley, G., Holt, G., and Voss, D., *J. Chem. Soc.,* p. 100 (1952).
20. Pines, H., and Pillai, C. N., *J. Am. Chem. Soc.* **83,** 3270 (1961).
21. Turkevich, J., and Smith, R. K., *J. Chem. Phys.* **16,** 466 (1948).