JOURNAL OF CATALYSIS 3, 512–527 (1964)

Studies of the Hydrogen Held by Solids

VI. The Hydroxyl Groups of Alumina and Silica-Alumina as Catalytic Sites

W. KEITH HALL, F. E. LUTINSKI, AND H. R. GERBERICH
From the Mellon Institute, Pittsburgh, Pennsylvania

Received March 31, 1964

The microcatalytic technique was used in evaluating the ability of silica-alumina and alumina catalysts to crack 2,3-dimethylbutane and to isomerize cyclopropane; observations were also made of the coke formation during cracking and of the chemisorption of ammonia at several temperatures. Hydrogen contents (measured by exchange with D_2) were varied by carefully controlling the dehydration conditions and by substitution of fluorine for the hydroxyl groups of alumina. "Base exchange" of silica-alumina with alkali metal ions lowered the catalytic activity but did not materially affect the hydrogen content. With catalysts dehydrated at temperatures above the cracking range, the rate of decomposition of 2,3-dimethylbutane was independent of hydrogen content, but the activities of catalysts dehydrated at only 550° were somewhat higher. With alumina, the specific activities for cracking actually increased slightly as the hydrogen content was lowered. Alumina was as active as silica-alumina for cracking. Apparently the principal difference in the behavior of these two materials is that alumina is more readily poisoned by traces of H_2O and/or reaction products than silica-alumina. Substitution of the hydroxyl groups of alumina with fluorine greatly enhanced its activity and otherwise rendered it more like silica-alumina. Samples of fairly pure *eta* and *gamma* alumina, as well as members of a series of mixtures of *eta* and *gamma* alumina, were found to vary in activity independently of hydrogen content; *eta* alumina was the more active.

The amount of ammonia chemisorbed per unit area in the range of 175° to 500° was not a function of the catalyst hydrogen content. When the alumina or silica-alumina was extensively dehydrated, several times more ammonia was chemisorbed, even at 500°, than the amount of residual hydrogen. It is therefore apparent that the strong acid sites presumed to chemisorb ammonia are not of the Bronsted type.

The rate of isomerization of cyclopropane correlated with the hydrogen contents of alumina and of silica-alumina catalysts. In both cases, the activities could be further increased by added-back water; with silica-alumina, the rate increased continuously with H_2O content, but a maximum activity occurred with alumina. As with cracking, base exchange of silica-alumina or substitution of F for OH in alumina decreased and enhanced the activity, respectively. Evidently, the two reactions proceed by different mechanisms although possibly involving the same aprotic sites.

INTRODUCTION

It is variously thought that the intrinsic acid sites of silica-alumina and alumina catalysts are Lewis or Bronsted or that both of these coexist on the same surface. Although this matter recently has been under intensive investigation, it remains unsettled. In earlier work (*1–3*) we sought and found evidence for strongly electrophilic centers capable of oxidizing triphenylmethane to the triphenylcarbonium ion, and polynuclear aromatic hydrocarbons and phenylated amines to their corresponding cation radicals. Although the exact nature of these sites remains open to question (*4*), it was established that the tertiary hydride ion from triphenylmethane, 1,1-diphenylethane, and cumene was transferred to the silica-alumina surface; it was not transferred to an existing carbonium ion nor was H_2 generated. More recently, we examined the hydrogen remaining on acidic catalysts after evacuation at elevated temperatures (*5*) in a search for evidence of protonic acidity in the total hydrogen content. The results of this work (NMR and kinetic D_2 exchange studies) were entirely negative. The indications were that the hydrogen was more alcoholic than acidic in nature. Using the experimental error to estimate an upper limit, it was concluded that no more than $3 \times 10^{13}/\text{cm}^2$ protons could possibly be present. The present work was carried out in the same vein, using acid-catalyzed reactions as the proton probe.

When the catalytic activity (*6*), total hydrogen content (*5*), and the *n*-butylamine acidity (*7*) were plotted vs surface area for a series of silica-alumina catalysts all having the same chemical composition but varying in surface area, Fig. 1 resulted. Since all three of these properties vary linearly with surface area, it follows that each will correlate with any other. Such correlations do not necessarily imply relationships, however, as all three properties may correspond to different sites which are uniformly, but independently, distributed over the catalyst surface. To establish relationships, or lack of them, it was necessary to vary the hydrogen content at constant surface area and to evaluate the resulting catalytic activity and ability to chemisorb amines. This was the experimental basis of the present work.

Reference to Fig. 1 shows that if amines are chemisorbed by reaction with catalyst protons, as supposed by Hirschler (*4*) and Benesi (*7*), then roughly one-third of all the hydrogen must be acidic. This value ($5 \times 10^{13}/\text{cm}^2$) is only a little larger than the upper limit for protonic acidity mentioned above. The total hydrogen held by the solid can readily be lowered below this value.

Until the recent work of Pines and coworkers (*8*), alumina was thought to be not as active as silica-alumina for acid-catalyzed reactions; to date, few valid

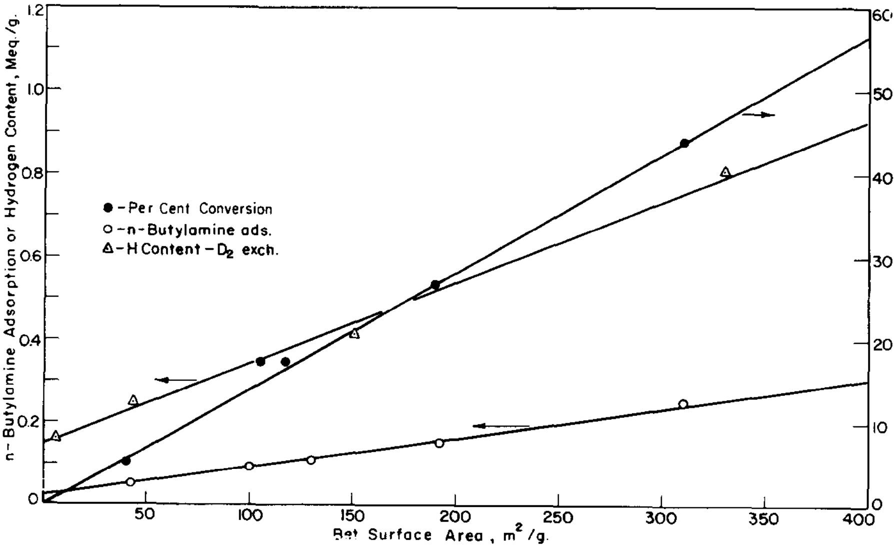


FIG. 1. Correlation between acidity, hydrogen content, or activity for decomposition of 2,3-dimethylbutane and surface area.

comparisons of these materials exist. Our microcatalytic experiments suggest that alumina is intrinsically more active for cracking than silica-alumina, but that it is more readily poisoned. Its activity for cyclopropane isomerization was, however, lower than that of silica-alumina.

The activity of silica-alumina for cracking (*9, 10*), cumene dealkylation (*11*), and propylene polymerization (*12*) is reported to be considerably increased by the addition of as little as 0.05% H_2O. The effects on the exchange reaction between isobutane and deuterated cracking catalysts are well documented (*13–16*), but the chemistry involved is not understood. Similar effects of water on the rates of cyclopropane isomerization are described herein for both alumina and silica-alumina.

EXPERIMENTAL

Procedures. Except as otherwise noted, aliquots of 20–50-mesh fractions of the catalysts were sealed into glass (or quartz where required) reactors fitted with stopcocks and given a *standard pretreatment.* This involved evacuation for 1 hr at 27°C before raising the temperature gradually (4.5 hr) to 550°, where it was stabilized; the sample was then treated for 2 hr in a high flow of O_2 and evacuated overnight at the same temperature. This procedure was intended to free the surface of any adsorbed organic compounds and to dehydroxylate the catalysts to the same extent as in our earlier work (*5, 17*). For additional dehydroxylation, the catalyst tubes were surrounded by a linearly programmed, rising temperature furnace following the standard pretreatment, and evacuated as the temperature was raised from room temperature to 700° (5 hr), to 800° (6.5 hr) or 900° (8 hr); the evacuations were continued at the final temperature for an additional 16 hr. These procedures effected large changes in catalyst hydrogen content without greatly altering the surface areas. As required, water was added back to catalysts using a procedure of Haldeman and Emmett (*15*): After pretreatment, the catalyst was allowed to cool in water vapor (25 mm Hg) from 550° to a predetermined temperature at the normal cooling rate of the furnace, and then it was evacuated for 1 hr. Final temperatures used were 400°, 300°, 225°, and 150°.

Duplicate samples were prepared for some of the work. The hydrogen content of one of these was determined by exchange with D_2 and its surface area was measured. This sample was then used for ammonia chemisorption measurements and discarded. The 2,3-dimethylbutane cracking experiments were carried out on the other sample. Aliquots of this catalyst were used for carbon analysis (Pregl micromethod) and for surface area measurements (following regeneration in O_2 at 550°). The two surface area measurements were always in good agreement; averages are reported herein. Occasional redeterminations of hydrogen contents for samples made by a given procedure also agreed quite well. Checks on reproducibility of activity measurements are noted in the tables and graphs.

New and smaller samples were prepared for the cyclopropane isomerization experiments. Hydrogen contents were measured before the activity tests were made; surface areas were determined after the tests, following regeneration in flowing O_2 (2 hr at 550°). It was necessary to prepare duplicate samples for hydrogen content and activity measurements in those instances where water was added back.

The method of catalyst activity evaluation, using our semiautomatic microreactors, has been detailed elsewhere (*6*). Small slugs of reactant gas were carried in a He stream over catalysts at a series of temperatures selected to effect from 5 to 85% reaction. These tests were repeated in a cyclic manner and the fraction of the reactant converted was plotted vs slug number. Data taken at the same temperature formed curves called conversion isotherms. Arrhenius plots could be constructed from these data at any particular slug number. The slug size was about 8 cc (NTP) for cyclopropane and 19 cc (NTP) for 2,3-dimethylbutane. The former consisted of pure cyclopropane whereas the latter was a helium-hydrocarbon mixture containing 4.3 cc (NTP) of 2,3-dimethylbutane; this mixture was made by saturating a helium stream with the hydrocarbon at 18°C.

Hydrogen contents were calculated from the isotope dilutions when the catalysts were exchanged with D_2. As it was known (*5, 17*) that the total hydrogen of alumina and silica-alumina could be equilibrated with D_2 in a few hours at 550°, this temperature was used for most of this work. In a few cases, however, the rising temperature (DHA) method was employed (*5*). In those cases where water had been "added-back," helium was circulated over the catalyst (at 550°) and through a liquid nitrogen trap, where the desorbed water was collected. This water was measured in the BET system. The amount so determined was then added to the residual hydrogen content measured in the usual way. Surface areas could be determined *in situ* from the adsorption of nitrogen using the BET method.

The ammonia adsorption data were determined by the method of Barth and Ballou (*18*). The adsorption at 100 mm Hg was measured at 175° and at a series of temperatures up to 500°; the path was reversible.

Treatment of data. Franklin and Nicholson (*19*) reported that the rate of cracking of pure paraffins is between first and second order in hydrocarbon pressure. As preliminary work in our laboratory suggested that the decomposition of 2,3-dimethylbutane was first order with inhibition by products, the present data have been treated using the first order law. Accordingly, the data for low and intermediate conversions were weighted where necessary in the construction of Arrhenius plots; generally, however, the fit was quite good over the whole range. In our earlier work (*6*), we computed activities as per cent conversions at 525° (as in Fig. 1). Whereas such comparisons are valid at a particular temperature, the temperature coefficient of the per cent conversion is not a proper activation energy (*20*). Moreover, first-order Arrhenius plots were found to provide a better fit of the earlier data (*6*) than the zero-order law, but the activation energies so obtained were from 8 to 10 kcal higher, i.e., ~30 kcal/mole for catalytic cracking over silica-alumina and about 45 kcal/mole for thermal cracking.

In those instances where the conversion isotherm is nearly independent of slug number (Fig. 2), the Arrhenius plot will be insensitive to where the data are selected, and the conversion at a particular temperature is a measure of the *inrinsic* activity of the catalyst. Where strong poisoning occurs, as with the alumina catalysts, this is not true and the data must be treated in a somewhat arbitrary way. We have elected to derive the Arrhenius plots from the data at the 25th slug, i.e., after the alumina curves have started to flatten. Even so, the activation energies derived from these data are of questionable validity. The conversion isotherms from the cyclopropane data were generally more horizontal than those obtained for cracking (Fig. 2) over the same catalysts. The dehydrated aluminas poisoned slowly with slug number, whereas the conversions for the dehydrated silica-aluminas actually increased slightly during the first few slugs and then flattened. In both cases, the catalysts with added-back water were independent of slug number.

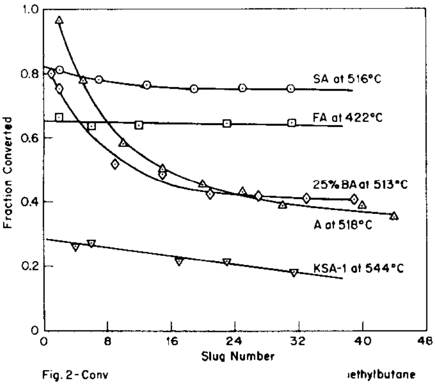


FIG. 2. Conversion isotherms for cracking of 2,3-dimethylbutane on various catalysts.

According to Bassett and Habgood (*20*), the rate constant product, kK, can be calculated from isothermal data for a first order microcatalytic reaction according to the relation

$$kK = (F^\circ/273RW)\ln[1/(1-x)], \quad (1)$$

where F° is the flow rate in cc (NTP)/min, R the gas constant, W the catalyst weight in grams, and x is the fraction converted; k is the kinetic factor and K is the coverage factor of the apparent rate constant. These workers also showed how K and the heats of adsorption could be determined from retention time measurements using the catalyst as a chromatographic column. In the present work, this technique was adopted in order to ascertain whether variations in kK corresponded to variations in K or in k; an argon tracer was used as suggested by Owens and Amberg (*21*). Retention times for cyclopropane could be measured with fair accuracy between 0° and 25°C with the sample size required for the isomerization experiments (1 cm diam × 2.5 cm). When the same amount of catalyst was distributed in a long narrow column (*ca.* 4 mm × 27 cm), the retention times were not affected. In order to make the measurements near 100° where isomerization occurs, it was necessary to use larger catalyst weights; 1-cm diameter tubes of appropriate length were used for this work. All of these results were in fair agreement when normalized to unit surface area.

Catalysts. The silica-alumina preparations were made from a single batch of Houdry M-46 catalyst (12.5% Al_2O_3). The pellets were crushed and sieved, and the 20–50-mesh fraction was retained. Portions of this were "base-exchanged" by soaking in solutions of KOAc and $Ba(OAc)_2$, reproducing the procedure of Haldeman and Emmett (*15*); a control was prepared by soaking in distilled water. The control (SA) was further modified by dehydroxylation *in vacuo* to several temperatures in excess of the standard pretreatment temperature (550°) as described above. The base-exchanged catalysts were given only the standard pretreatment. These samples, KSA-1, KSA-2, and BSA, contained 0.25, 0.53, and 0.41 meq of potassium (K) and barium (B) per gram of catalyst, respectively. Spark spectra analysis of the control indicated the presence of 0.1% Fe, 100 to 300 ppm of Na, Ti, and Zr, and smaller amounts of other elements.

The data shown in Fig. 1 were collected from a series of preparations made from a Houdry S-65 catalyst. The procedures used to vary the surface area, the hydrogen contents, and activities are described elsewhere (*5, 6*). The *n*-butylamine titration data were determined by the method of Benesi (*7*), titrating to the butter-yellow endpoint.

The control alumina, A, was a very pure material furnished by the MK Research and Development Co., Pittsburgh, Pa. Its preparation and properties are described elsewhere (*17*). X-ray measurements of the alumina hydrate and of samples removed on heating it in steps to 650° indicated that the finished catalyst was probably a mixture of *eta* and *gamma* alumina. The fluorided alumina (FA) was from the same source (*17*); it was made by soaking Catalyst A in 0.035 *M* TransistAR Grade H_2F_2. Acid, equivalent to 1.5% F, was present; 1.22% was found by quantitative analysis. Spark spectra analysis revealed that these preparations had total metallic impurity levels of less than 50 ppm. Catalyst A was further modified by dehydroxylation to elevated temperatures in the same way as the silica-alumina series. Very little transformation occurred on heating to 700° or 800°, although some tendency to form theta alumina was evidenced at the higher temperature. The bulk of the material was transformed in the 900° sample. Theta alumina is an anhydrous phase; its formation is probably unavoidable when aluminas are extensively dehydroxylated.

Samples of *eta* and *gamma* alumina (*22, 23*) were furnished by Dr. D. S. MacIver of the Gulf Research & Development Co.; these are designated as ηA and γA, respectively. Samples of mixed bayerite-boehmite (or a pseudoboehmite) preparations were supplied by M. M. Stewart of GR & DC. X-ray measurements indicated approximate compositions of 25%, 50%, 75%, and 100% bayerite; these preparations are designated by %-BA. They were converted to the mixed *eta* and *gamma* aluminas by heating in air to 550°C in a muffle furnace at its normal heating rate (~16 hr, including 4 hr above 500°). Since Bayerite transforms into *eta* alumina and boehmite into *gamma* alumina under these conditions, the catalysts, as tested, should be mixtures of *eta* and *gamma* alumina of approximately the same composition. All of these materials were reasonably pure. The principal impurities in ηA and γA were 100 and 250 ppm Cu, 5 and 100 ppm Na, respectively, and about 150 ppm Fe and 200 ppm Si in each. The BA series was somewhat less contaminated. The worst case (50% BA) contained 160 ppm Fe, 250 ppm Cu, and 250 ppm Mg.

Reagents and gases. The helium-carrying gas was from Airco (nominal purity 99.997 mole %). It was passed through an activated charcoal trap (50 g) thermostated at −195° before use. Linde oxygen (99.9% pure) was passed through a glass-wool-packed, dry-ice trap to remove water. The cyclopropane was obtained from the Ohio Chemical & Surgical Equipment Co.; it had a nominal purity of 99.5%, the principal impurities being propylene and H_2. To insure removal of traces of H_2O and other oxygenated compounds, it was passed through a column of NaH. Only traces of propylene and butane appeared when this gas was chromatographed. Phillips pure grade 2,3-dimethylbutane was also passed over NaH. Its purity exceeded 99 mole %; only the parent peak appeared when chromatographed. The D_2 (General Dynamics Co.) was purified by diffusion through a Pd thimble. The NH_3 was triply distilled.

RESULTS

The data from the cracking experiments over silica-alumina catalysts are compared with the corresponding hydrogen contents and ammonia adsorptions in Table 1. Sufficient catalyst was used in each experiment to fill the 7-cc volume of the quartz reactor. The surface areas (Column 4) decreased by only about 20% during the dehydroxylation to elevated temperatures; the areas of the base-exchanged catalysts also fell within the same range. The hydrogen contents (Columns 8 and 9) could be decreased by a factor of 20 by dehydroxylation at elevated temperature, but were unaffected by base exchange (*15*). The decrease effected by raising the dehydroxylation temperature to 700° was accompanied by a corresponding decrease in rate (Columns 5 and 6); further dehydroxylation had little effect. The effects of base exchange with K^+ were unmistakable. The activities of these catalysts were evidently not directly related to their hydrogen contents.

Similar results and conclusions may be derived from the data for the alumina preparations listed in Table 2. Here the activity increased, if anything, with increasing dehydroxylation. Moreover, the *eta* alumina (although somewhat more pure) was considerably more active than the *gamma* form, a conclusion which was generally reinforced by the results from the mixed *eta* and *gamma* aluminas derived from the mixed bayerite-boehmite compostions and by the work of MacIver *et al.* (*22, 23*). These activity variations were not accompanied by corresponding alterations in hydrogen content. Nor was the reactivity of the hydrogen noticeably different; rising temperature D_2 exchange (DHA) curves (*5*) from the several forms were indistinguishable. Finally, the fluorided alumina had a lower hydrogen content and yet a much higher activity. (The high activity of Alon-C also may be attributed to small amounts of halide.)

Plots of the ammonia chemisorption vs temperature were slightly convex toward the *T* axis. Values taken at 175° and 500°C are listed (Columns 10 and 11) in Tables 1 and 2 for the silica-alumina and for some of the alumina catalysts. Straight lines drawn between these points would provide an estimate of the original data. When corrected for variation in surface area (Columns 12 and 13), the ammonia adsorption is seen to be independent of the catalyst hydroxyl content. Base exchange of the silica-alumina catalysts lowers the am-

TABLE 1

CRACKING OF 2,3-DIMETHYLBUTANE OVER SILICA-ALUMINA

Catalyst[a]	Max. pre-treatment temp. (°C)	Wt. (g)	Surf. area (m^2/g)	% Conv.[a] at 525° (100 ×)	Rate constant[a] ($kK/m^2 \times 10^8$ at 525°C[b])	Activation energy[a] (kcal/mole)	Hydrogen content		Ammonia adsorption data[c]				Carbon[d] per slug (%)
							cc(NTP) of H_2/g	$OH/cm^2 \times 10^{-14}$	cc(NTP)/g		Molecules/$cm^2 \times 10^{-14}$		
									at 175°	at 500°	at 175°	at 500°	
SA	550	3.080	270	83,76,67	5.4,4.4,3.3	33,33,30	6.86	1.4	8.5	2.7	0.84	0.27	0.0118
SA	550	3.101	—	80	5.0	24	—	—	—	—	—	—	—
SA	700	3.065	—	38	1.5	29	—	—	—	—	—	—	—
SA	700	3.080	253	37	1.6	32	3.75	0.8	7.8	2.4	0.83	0.25	0.00107
SA	800	3.080	237	41,38	1.8,1.7	28,32	2.45	0.6	6.9	2.05	0.78	0.23	—
SA	800	3.099	—	27	1.1	33	—	—	—	—	—	—	—
SA	900	2.832	213	29	1.4	33	0.31	0.08	5.4	1.95	0.68	0.25	0.00056
SA	900	3.100	214	39	1.9	29	—	—	—	—	—	—	—
BSA	550	4.337	225	44	1.5	27	7.10	1.7	6.6	2.0	0.79	0.24	0.00097
KSA-1	550	4.176	236	14	0.4	44	6.61	1.5	5.9	1.8	0.67	0.20	0.00090
KSA-2	550	4.135	236	6	0.2	38	6.20	1.4	4.5	1.2	0.51	0.14	0.00269
Blank[e]			2	~0.1		44.8							

[a] Where several figures are given, repeat runs were made with the same catalyst.

[b] kK/m^2 has the dimensions mole atm^{-1} sec^{-1} m^{-2}.

[c] Measurements made at 100 mm pressure of ammonia.

[d] Weight per cent carbon held on the catalyst divided by the number of slugs passed during the experiment.

[e] Thermal cracking over ground Vycor; 20–40 mesh; identical results were obtained with empty tube or when tube was filled with high area silica gel.

TABLE 2

CRACKING OF 2,3-DIMETHYLBUTANE OVER ALUMINA

Catalyst	Max. pretreatment, temp. (°C)	Wt. (g)	Surf. area (m^2/g)	% Conv. at 525° (100 ×)	Rate constant ($kK/m^2 \times 10^8$ at 525°C[a])	Activation energy (kcal/mole)	Hydrogen content		Ammonia adsorption data[b]				Carbon[c] per slug (%)
							cc(NTP) of H_2/g	OH/cm² × 10^{-14}	cc(NTP)/g		Molecules/cm² × 10^{-14}		
									at 175°	at 500°	at 175°	at 500°	
A	550	5.198	136	52	2.6	32	6.38	2.5	7.9	2.6	1.6	0.53	0.016
A	700	5.131	126	52	2.9	24	3.37	1.4	—	—	—	—	0.0096
A	804	4.618	127	37	2.0	26	1.82	0.77	7.3	2.5	1.5	0.53	—
A	830	4.853	127	56	3.3	13	1.82	0.77	7.3	2.5	1.5	0.53	0.010
A	915	4.599	115	61	4.5	23	0.30	0.14	6.3	1.8	1.5	0.42	0.017
γA	550	5.895	191	40	1.2	25	8.47	2.4	—	—	—	—	0.0073
ηA	550	3.516	225	85	6.3	29	10.89	2.6	—	—	—	—	0.0079
100% BA[d]	500	3.660	250	71	3.4	28	20.53	4.4	—	—	—	—	0.013
75% BA[e]	500	4.792	287	72	2.4	27	19.24	3.6	—	—	—	—	0.009
50% BA[f]	500	4.267	257	52	1.7	24	16.44	3.3	—	—	—	—	0.0094
50% BA	500	4.310	257	49	1.5	28	16.44	3.3	—	—	—	—	—
25% BA[g]	500	6.215	255	50	1.1	—	15.37	3.2	—	—	—	—	0.0065
Alon C	550	4.482	105	91	12.7	18	6.40	3.2	—	—	—	—	0.0003
FA[h]	550	4.827	143	>99	18.1	21	3.68	1.5	—	—	—	—	—

---

[a] kK/m^2 has the dimensions mole atm^{-1} sec^{-1} m^{-2}.

[b] Measurements made at 100 mm of ammonia.

[c] This is the weight per cent carbon deposited on the catalyst divided by the number of slugs.

[d] 100% bayerite.

[e] 75% bayerite – 25% pseudoboehmite.

[f] 50% bayerite – 50% pseudoboehmite.

[g] 25% bayerite – 75% pseudoboehmite.

[h] Contains 1.22 wt % F^-.

monia chemisorption, particularly at 500° but not to an extent comparable with the decrease in activity. Similarly, the difference in ammonia chemisorption behavior reported by MacIver, Tobin, and Barth (*22*) for the *eta* and *gamma* alumina of Table 2 is much too small to be correlative with the activity change shown in Table 2. It is significant that when the catalysts were dehydrated at the highest temperatures, the amount of ammonia adsorbed considerably exceeded the remaining hydrogen (hydroxyl groups).

At the end of the cracking experiments, the helium carrying gas was allowed to flow for several hours at 525°. Any hydrocarbon left adsorbed after this treatment was defined as coke. This was determined and divided by the number of slugs passed in the duration of the experiment (between 40 and 50 in all cases). These data are listed in the last column of Tables 1 and 2.

Some typical conversion isotherms are shown in Fig. 2. The data for the two alumina catalysts were taken at almost the same temperature as for the silica-alumina catalyst. It can be seen that whereas alumina appears to be intrinsically more active than silica-alumina, it poisons more readily. Moreover, since SA has the larger surface area, the difference in the specific intrinsic activities is more pronounced than indicated. Had these catalysts been tested in the steady state, however, the specific activity of SA probably would have been found greater than that of A. The much higher activity of the fluorided alumina is indicated by the much lower temperature required; similarly, the lower activity of the base-exchanged catalyst is reflected by the higher temperature.

The poisoning rate of the alumina catalysts correlated inversely with hydrogen content; the ratio of rate constants for the 5th and 26th slugs fell from about 2.6 for the catalyst given the standard pretreatment to 1.6 for the catalyst dehydrated at 900°. When this is taken into account, it is evident that the intrinsic specific activity is approximately constant for this series of catalysts.

The rate of isomerization of cyclopropane correlated with the hydrogen contents of both silica-alumina (Fig. 3) and alumina (Fig. 4) catalysts. The hydrogen content was varied in two ways, i.e., dehydroxylation at increasing temperatures (open points) and by adding back water (solid points) following the *standard* pretreatment. The data were further extended by lowering the pretreatment temperature to 450°. An activity maximum appeared with alumina but not with silica-alumina. It should be noticed, however, that it was not possible to achieve the same high hydroxyl concentrations with the latter. Surface area determinations were made on Catalyst A, before and after adding back water at 150°; the values were identical within experimental error. Therefore, the decrease in activity beyond the maximum cannot be attributed to loss of surface.

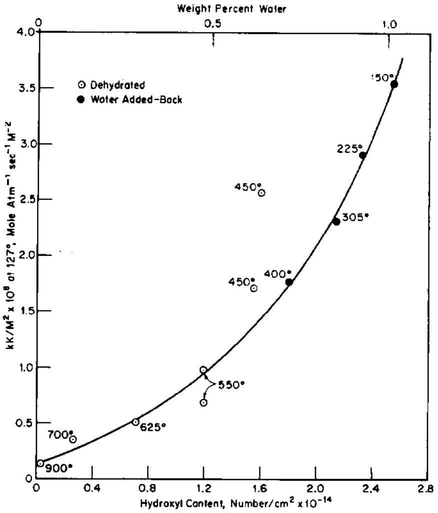


FIG. 3. Effect of water content of silica-alumina on the rate of isomerization of cyclopropane. Temperatures of dehydroxylation or treatment with water are shown.

Base exchange of silica-alumina decidedly reduced its activity. In terms of the rate constant plotted on Fig. 3, BSA, KSA-1, and KSA-2 yielded values of 0.038, 0.025, and 0.0015 $\times 10^{-8}$ mole atm^{-1} sec^{-1} m^{-2}, respectively. The lowered rate constant was at least partially attributable to

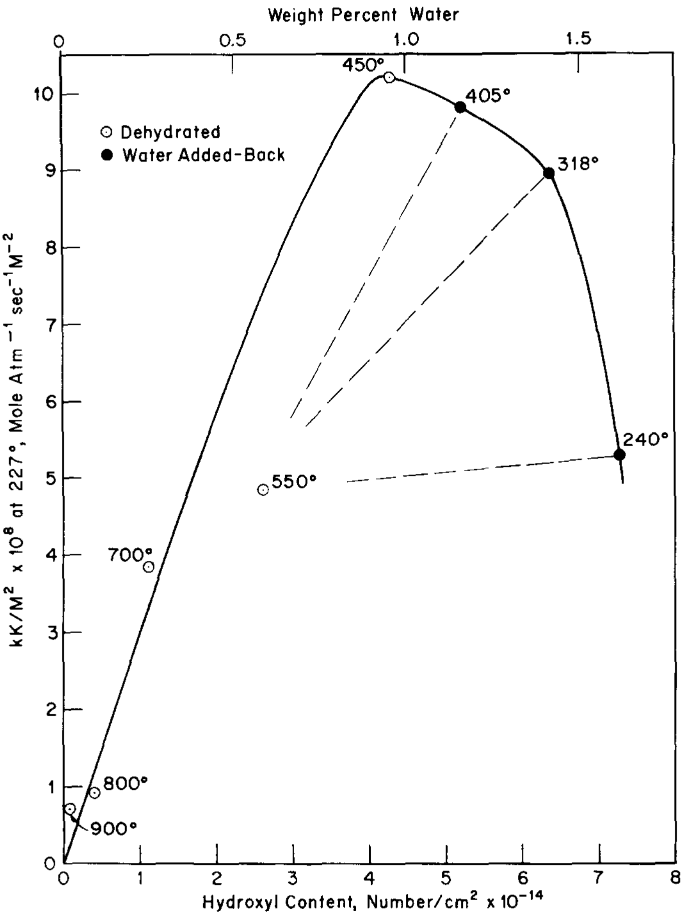


FIG. 4. Effect of water content of alumina on the rate of isomerization of cyclopropane. Temperatures of dehydroxylation or treatment with water are shown.

a higher activation energy; the values for these three catalysts were 30, 25, and 25 kcal/mole, respectively. All of the remaining silica-alumina catalysts fell in the range 18 ± 3 kcal/mole. The lowered activity of KSA and BSA could not be attributed to a decrease in catalyst hydrogen content as values of 1.4, 1.2, and 1.2×10^{14} OH/cm^2 were found for these catalysts. These values are almost identical with those found for the controls (550° points of Fig. 3). Similarly, the fluorided alumina was much more active than its control, whereas its hydrogen content was lower. Extrapolated to the conditions of Fig. 4, the rate constant of FA was 1590×10^{-8} mole atm^{-1} sec^{-1} m^{-2}. In this connection, FA was more like silica-alumina than alumina. Catalysts FA and SA effected comparable conversions nearly 100° below the temperature required for Catalyst A. (Note that the data of Figs. 2 and 3 are rate constants at 127° and 227°C, respectively.) These activity changes appeared to correlate with higher activation energies over alumina (24 ± 4 kcal/mole) than over silica-alumina or fluorided alumina (15 kcal/mole).

The sample size for the cyclopropane experiments was about 1 g; for the cracking experiments, 3 to 4 g was used. It was found that hydrogen contents of the smaller samples were consistently lower for a given pretreatment procedure (compare abscissas of Figs. 3 and 4 with the data of Tables 1 and 2). This probably indicates that the catalysts were not uniformly dehydrated; there may be considerable variability in the surface density of hydroxyl groups from one part of the bed to another, or even within a single particle.

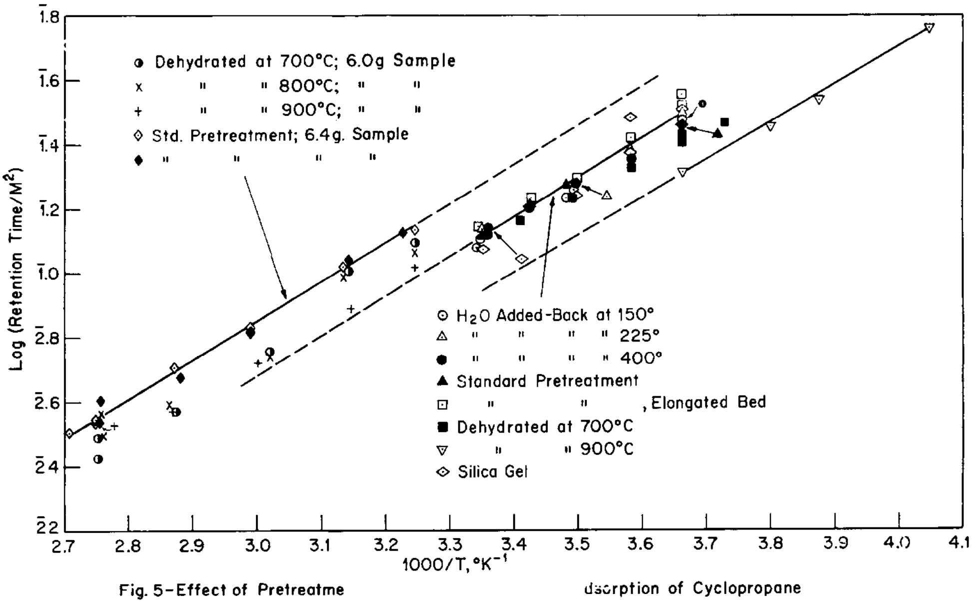


FIG. 5. Effect of pretreatment of silica-alumina on the adsorption of cyclopropane.

Since the rate constant product kK varied significantly with the catalyst water content, it was deemed desirable to separate this parameter into the kinetic factor k and the coverage factor, K. This was accomplished by retention time measurements as suggested by Bassett and Habgood (*20*). Our results are collected in Fig. 5, where the data have been normalized to unit surface area. Several sets of data are presented. Those associated with the lower two curves (lower temperatures) were obtained from samples identical with those used in the isomerization experiments. These data include: SA with the standard pretreatment, SA dehydrated at 700° and 900°, SA with "added-back" water, and silica gel. The geometry appeared to make little difference. Identical results were obtained from 1-g samples in capillary tubes and in the larger diameter tubes used in the isomerization experiments. The lowest curve was drawn through the data from the sample dehydrated at 900° and the middle curve through data for the standard pretreatment; all of the data for the 1-g samples fell between these limits. The difference between the two lines, a factor of 1.8, was not nearly large enough to account for the 25-fold change in rate. The adsorption heats derived from the lines, 5.3 and 5.7 kcal/mole, respectively, were only slightly greater than the heat of vaporization (5.2 kcal/mole) of cyclopropane (*24*).

When the sample size was increased to 6.4 g so that the retention times would be measurable in the temperature range where isomerization occurs, consistent findings resulted, but normalization to unit surface area was insufficient to bring these into perfect agreement with the remaining data. The upper line was drawn through the points for the catalyst with highest hydrogen content and its slope corresponds to a heat of adsorption of 5.6 kcal/mole. Ross *et al.* (*25*) reported heats of physical adsorption of cyclopropane on graphite of 5.5

and 6.0 kcal/mole between −29° and 130°C. It follows, therefore, that physical adsorption is being measured on silica-alumina and this is supported by the fact that properly normalized data from silica gel fall onto the same curve. Silica gel was not a catalyst for this reaction; no isomerization occurred to 540°C where the thermal reaction first became evident. Hence, these measurements do not correspond to the active *chemisorbed* intermediate. The isomerization may take place on a number of active sites which is small compared with the total adsorption, and the heat of adsorption on these sites is probably much greater than the heat of vaporization. This is illustrative of the hazards involved in the use of the chromatographic method (*26*) for the measurement of catalytically meaningful heats of adsorption.* Nevertheless, the data of Fig. 5 do indicate that the increasing activity with catalyst hydrogen content is a real catalytic effect and is not associated with the chromatographic properties of the catalyst.

DISCUSSION

In the present work, means were found to lower the hydrogen content of silica-alumina and alumina catalysts by more than an order of magnitude without a corresponding decrease in surface area. This dehydroxylation had little effect on the ability of the catalyst to chemisorb ammonia between 175° and 500°C or to crack 2,3-dimethylbutane. In agreement with the data of Fig. 1, the ammonia chemisorbed on catalysts pretreated in the standard way amounted to a large fraction of the total hydrogen present. When the hydrogen content was lowered, however, the ammonia chemisorption did not follow; in fact, the chemisorption considerably exceeded the total hydrogen content when the latter was decreased by ten-fold. It is therefore evident that not all the sites which chemisorb ammonia are protonic as frequently supposed by workers who have attempted to titrate the acidity using the amine-indicator method (*4, 7*). It is also apparent that the correlation between *n*-butylamine adsorption and hydrogen content, suggested by the data of Fig. 1, does not stem from a direct relationship; rather, it implies that both the amine adsorption sites and the catalyst hydroxyl groups are more or less uniformly distributed over the total catalyst surface. The available data are consistent with the view, but do not prove, that the sites which chemisorb ammonia are responsible for the cracking activity.

According to Peri (*27*), ammonia is chemisorbed on alumina in two ways. Ammonia molecules are held on Lewis acid sites and surface NH_2 and OH groups are formed in a process similar to rehydration of the catalyst; NH_4^+ was not observed. Ammonia was largely removed from Lewis sites by evacuation to 500°C, but the NH_2 groups were stable to much higher temperatures. Generally, raising the dehydration temperature to higher and higher temperatures tended to favor the ammonolysis process. Accordingly, it might be expected that the ammonia chemisorption on alumina at 500° in the present work resulted largely from ammonolysis of the surface and that the chemisorption at 175° was the sum of this and the ammonia held by coordination to Lewis sites. If this were the case, however, the chemisorption at 500° should have increased with the extent of dehydroxylation, because as water was removed from the catalyst, more dual acid–base sites of the type pictured by Peri were presumably created. Reaction of these sites with ammonia should lead to increasing amounts of surface NH_2 with increasing dehydroxylation. The invariance of the NH_3 chemisorption with extent of dehydroxylation is in better accord with the view that the adsorption is nonspecific, i.e., that an NH_3 molecule will adsorb on a given site on the surface in the one form or the other, depending upon the environment.

---

* Note Added in Proof. J. J. Carberry [(*Nature* **189**, 391 (1961)] has shown that the lowest value of the range of heats of absorption, which are operative, will generally be determined by this method. Thus, in most cases, a catalytically meaningful heat cannot be derived.

With dehydrated silica-alumina, Eischens and Pliskin (*28*) found relatively weak infrared bands at 3.2 and 6.9 μ which they ascribed to NH_4^+; they concluded, however, that most of the ammonia was chemisorbed on Lewis sites. Nicholson (*39*), on the other hand, estimated that the ratio of Lewis to Bronsted sites was nearly 3/2. As shown in Tables 1 and 2, the ammonia adsorption is little influenced by the hydration state of the catalyst, being similar in this respect to the cracking activity. Certainly most of the ammonia which is chemisorbed on the catalyst dehydrated at 900°C cannot be held as NH_4^+. Another feature of interest is that the amounts of ammonia chemisorbed are nearly ten-fold larger than the number of strong acid sites ($5 \times 10^{12}/cm^2$) estimated from the chemisorption of trityl derivatives (*1*) and by titration with CO_2 (*29*). As a completely satisfactory interpretation cannot yet be given, these questions obviously deserve further attention.

Alumina and silica-alumina are quite similar with respect to both ammonia chemisorption and cracking activity. The former, which appears to be intrinsically the more active, also chemisorbs more ammonia. Alumina is currently considered to be a strong Lewis acid by most workers. The data provide no reason to suppose that the cracking mechanism is any different over alumina than over silica-alumina. In fact, different forms of alumina differ from each other in activity by as much as they differ from silica-alumina. It therefore seems safe to assume that the primary act in paraffin cracking over both substances is carbonium ion formation by hydride ion abstraction (*1*). Bronsted acidity, if present, is important only in secondary reactions with the olefins formed in the primary cracking reactions.

In contrast to our results, Peri (*30*) reported that over alumina the rate of double-bond isomerization increased as the catalyst was dehydroxylated. Similarly, Hindin and Weller (*31*) found that the rates of ethylene hydrogenation and H_2–D_2 exchange increased over alumina with dehydroxylation. Kaliko (*32*) showed that lowering the structural water content by calcining a silica-alumina cracking catalyst resulted in a maximum activity for cumene dealkylation for a sintering temperature of approximately 800°C. It is curious that these reactions should proceed at higher rates when the hydrogen content is lowered whereas the rate of cracking of a paraffin molecule is relatively unaffected and the activity for cyclopropane isomerization is lowered. Dehydroxylation might be expected to increase the number or accessibility of Lewis acid sites, but evidently this does not occur. As shown by Hall (*5*) and Basila (*33*), however, hydroxyl groups adjacent to aluminum atoms tend to be preferentially removed when catalysts are evacuated for a few hours at 550°C. As postulated by Peri (*29*), the dual acid–base site resulting from dehydroxylation may be important for double-bond isomerization, hydrogenation, and other reactions, which may not involve carbonium ion intermediates.

Base exchange of silica-alumina lowers the ammonia chemisorption but not in proportion to the decrease in catalyst activity. Base exchange does not alter the catalyst hydrogen content. This raises the question as to what is meant by "base exchange." In the literature, with cracking catalysts as well as with clays, it is usually supposed that a metathesis has taken place between the alkali metal ions of an aqueous solution and the protons of the catalyst surface. On this basis, the proton concentrations of BSA, KSA-1, and KSA-2 should have been lowered by 1.1 (0.55 for $HOBa^+$), 0.64 and $1.35 \times 10^{14}/cm^2$, respectively. These values are of the same magnitude as the hydrogen content of the control catalyst (SA), yet there was no noticeable decrease in this quantity. It therefore seems reasonable to suppose that anions were incorporated into the catalyst along with the cations. This might lower the number of acid sites and/or effect a decrease in the strength of those remaining, as required by the data of Hirschler (*4*). It should be noted in this connection that the anion removed from solution will be that which is the most strongly adsorbed, i.e., KOH may be removed from a solution of KCl because the hydroxyl ion "fits" the surface lattice much more readily than a chloride ion. Cook *et al.* (*40*) reached this same conclusion a decade ago. The over-all effect is not easily distinguishable from the metathesis mentioned above.

The transformations which occur on "base exchange" can best be understood by considering the reverse process in the crystalline zeolites. Here, aluminum is tetrahedrally coordinated (formally AlO_2^-) in a silica structure; a univalent cation, or its equivalent, is required to balance the charge. The NH_4^+ ion, when present, may be decomposed into H^+ and NH_3, which is removed from the lattice site. The proton formed is unstable; it combines with a lattice O^{2-} to form OH^-. This, in turn, is lost from the catalyst by dehydroxylation on heating to elevated temperatures, and trigonally coordinated aluminum ions (Lewis acid sites) result. Base exchange of silica-alumina reverses these steps. Similarly, it is the restoration of tetrahedral coordination which is the driving force for the chemisorption of nitrogen bases and for carbonium ion formation.

Our cyclopropane results agreed quite well in general with those of Bassett and Habgood (*20*). The data fitted the first order law as shown in their Figs. 2 and 3. They reported 19 kcal/mole for the apparent activation energy over a Linde molecular sieve 13X (Na form) in the temperature range 263–378°C; this value is in agreement with that of Roberts (*34*) for a silica-zirconia-alumina catalyst between 100° and 135°. We obtained 16 ± 1 kcal/mole for SA regardless of the extent of dehydration, but when water was added back, 20 ± 1 kcal/mole was obtained. KSA and BSA yielded 25 and 30 kcal/mole, respectively. The results from the alumina catalysts were more erratic but fell in the same range. The center line of Fig. 5 may be reduced to

$$K = 1.2 \times 10^{-10} \exp(5700/RT) \text{ mole atm}^{-1} \text{ m}^{-2} \quad (2)$$

or

$$K = 3.0 \times 10^{-8} \exp(5700/RT) \text{ mole atm}^{-1} \text{ g}^{-1} \quad (3)$$

This may be compared with the result of Bassett and Habgood, i.e.,

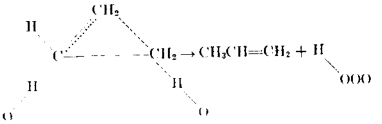
$$K = 1.7 \times 10^{-8} \exp(11000/RT) \text{ mole atm}^{-1} \text{ g}^{-1} \quad (4)$$

Evidently, the heat of adsorption on the molecular sieve exceeds that of physical adsorption. Bassett and Habgood concluded that the true activation energy for their catalyst was 19 + 11 = 30 kcal/mole. The catalyst studied in the present work which most closely approximates their sieve was KSA; the true activation energy from our data is 25 + 6 = 31 kcal/mole.

The cyclopropane results presented in Figs. 3 and 4 are generally consistent with either the Bronsted acid mechanism suggested by Roberts (*34*) or the concerted hydrogen transfer mechanism postulated by Schissler, Thompson, and Turkevich (*35*) for the double-bond isomerization of butene-1, i.e.,

$$c\text{—}C_3H_6 + H^+ \rightarrow CH_3\text{—}CH_2\text{—}\overset{\oplus}{C}H_2 \rightarrow CH_3\text{—}CH{=}CH_2 + H^+ \quad (5)$$

or



(6)

Recent tracer data (*36*) do not support either of these ideas and, in fact, rule them out unless the number of protons (active hydrogen atoms) is very much less than the hydrogen content ($\sim 10^{14}/\text{cm}^2$) as measured by D_2, viz., $\sim 10^{12}/\text{cm}^2$. Thus, although the surface hydroxyl groups may function as sites for isomerization, they evidently do not enter chemically into the reaction, as indicated by Eqs. (5) and (6). Consequently, it seemed reasonable to suppose that the enhancement of the rate with increased hydroxyl concentration was effected through an increased surface concentration of the chemical intermediate. The retention time measurements of Fig. 5 were made to test this postulate, but failed to provide the desired information as the chemisorbed species was not measured. Therefore, this remains an active possibility.

The only really convincing evidence for the existence of Bronsted acidity on silica-alumina catalysts is the observation (*37, 38*) that the pyridinium ion forms spontaneously following pretreatment similar to that used in the present work; Basila (*38*) concluded that approximately equal numbers of pyridine molecules were converted to pyridinium ions and bonded to Lewis sites, (i.e. $\sim 10^{13}/\text{cm}^2$). After weighing the evidence, Basila concluded that a strong Bronsted acid was not present initially. When a base adsorbs on Lewis sites, however, hydrogen bonding occurs between the adsorbed base and adjacent hydroxyl groups. Depending upon the strength of the Lewis acid–Lewis base interaction, this hydrogen bonding may result in hydrogen atom transfer to the adsorbed Lewis base with a concerted electron transfer to the solid as the coordinate covalent bond is broken. In this way, the pyridinium ion forms. This picture is supported by Hall's observation (*2*) that the triphenylamine radical ion readily forms on the silica-alumina surface. Presumably, a classical carbonium ion could form from an adsorbed olefin in this way, as a transient species. In the isomerization of cyclopropane, either the *induced Bronsted acid* is not important to the mechanism or else only a very small fraction of the total hydrogen atoms is involved, e.g., those hydrogens adjacent to Lewis sites strong enough to chemisorb cyclopropane. It is important to note that the maximum amount of hydrogen so involved is tenfold less than the number of pyridinium ions formed (*38*). These questions are dealt with more comprehensively elsewhere (*36*).

This picture has the advantage of consistency with information that is otherwise difficult to rationalize. Thus, Lewis acids are always present and are the sole requirement for initiation of paraffin cracking. On the other hand, an *induced Bronsted* function may be attributed to the catalyst in situations where it is required by the mechanism, e.g., in the cracking of olefins or in the dealkylation of cumene. Ammonia and pyridine adsorb on Lewis sites and are hydrogen-bonded to a portion of the otherwise inert hydroxyl groups; with pyridine, detectable amounts of pyridinium ion result. The effect of base exchange is not a metathesis with catalyst protons but an incorporation of a basic oxide into the catalyst structure resulting in a decrease in Lewis acidity, i.e., a reduction in the strength as well as the number of Lewis sites. In this way, the ammonia adsorption may be reduced by only a factor of two while the activity for hydrocarbon reactions may be lowered by many times. This is analogous to the leveling of an acid by a strong, but not by a weak, base. In the case of cyclopropane, the hydrogen bonding to the chemisorbed hydrocarbon increases the polarization of the molecule and may enhance the rate without actual proton transfer. It may also be that carbonium ion formation by hydride abstraction from this molecule is favored over proton transfer. A favored interpretation of our tracer data (*36*) involves a bimolecular mechanism in which the adsorbed cyclopropane is released from the catalyst surface either as propylene or as exchanged cyclopropane as another molecule is chemisorbed.

ACKNOWLEDGMENTS

This work was sponsored by the Gulf Research & Development Company as part of the research program of the Multiple Fellowship on Petroleum. We are indebted to W. L. Kehl and R. T. Barth of Gulf Research & Development Company for an X-ray examination of the alumina samples and for the ammonia chemisorption measurements, respectively.

REFERENCES

1. LEFTIN, H. P., AND HALL, W. K., *Actes Congr. Intern. Catalyse, 2ᵉ, Paris, 1960* **1,** 1353 (1961).

2. HALL, W. K., *J. Catalysis* **1,** 53 (1962).

3. Leftin, H. P., and Hall, W. K., *J. Phys. Chem.* **66**, 1457 (1962).
4. Hirschler, A. E., *J. Catalysis* **2**, 428 (1963).
5. Hall, W. K., Leftin, H. P., Cheselske, F. J., and O'Reilly, D. E., *J. Catalysis* **2**, 506 (1963).
6. Hall, W. K., MacIver, D. S., and Weber, H. P., *Ind. Eng. Chem.* **52**, 421 (1960).
7. Benesi, H. A., *J. Am. Chem. Soc.* **78**, 5490 (1956); *J. Phys. Chem.* **61**, 970 (1957).
8. Pines, H., and co-workers, *J. Am. Chem. Soc.* **82**, 2471 (1960); *ibid.* **83**, 2847 (1961); *ibid.* **84**, 3934 (1962); *Chem. Ind. (London)*, p. 984 (1963).
9. Hindin, S. G., Oblad, A. G., and Mills, G. A., *J. Am. Chem. Soc.* **77**, 535, 538 (1955).
10. Hansford, R. C., *Ind. Eng. Chem.* **39**, 849 (1947).
11. Prater, C. D., and Lago, R. M., *Advan. Catalysis* **8**, 293 (1956).
12. Holm, V. C. F., Bailey, G. C., and Clark, A., *J. Phys. Chem.* **63**, 129 (1959).
13. Hansford, R. C., Waldo, P. G., Drake, L. C., and Honig, R. E., *Ind. Eng. Chem.* **44**, 1108 (1952).
14. Hindin, S. G., Mills, G. A., and Oblad, A. G., *J. Am. Chem. Soc.* **73**, 278 (1951).
15. Haldeman, R. G., and Emmett, P. H., *J. Am. Chem. Soc.* **78**, 2917, 2922 (1956).
16. Larson, J. G., and Hall, W. K., *J. Am. Chem. Soc.* **85**, 3570 (1963).
17. Hall, W. K., and Lutinski, F. E., *J. Catalysis* **2**, 518 (1963).
18. Barth, R. T., and Ballou, E. V., *Anal. Chem.* **33**, 1080 (1961).
19. Franklin, J. L., and Nicholson, D. E., *J. Phys. Chem.* **60**, 59 (1956).
20. Bassett, D. W., and Habgood, H. W., *J. Phys. Chem.* **64**, 769 (1960).
21. Owens, P. J., and Amberg, C. H., *in* "Solid Surfaces and the Gas-solid Interface," p. 182. (Am. Chem. Soc. Advan. in Chem. Series, No. 33, 1961).
22. MacIver, D. S., Tobin, H. H., and Barth, R. T., *J. Catalysis* **2**, 485 (1963).
23. MacIver, D. S., Wilmot, W. H., and Bridges, J. M., in press.
24. "Handbook of Chemistry and Physics" (C. D. Hodgman, ed.), 44th ed., p. 2463. Chem. Rubber Publ. Co., Cleveland, Ohio, 1962.
25. Ross, S., Saelens, J. K., and Oliver, J. P., *J. Phys. Chem.* **66**, 696 (1962).
26. Eberly, P. E., *J. Phys. Chem.* **65**, 68, 1261 (1961); *ibid.* **66**, 812 (1962).
27. Peri, J. B., *Am. Chem. Soc. Meeting, 142nd, Atlantic City, 1962,* Abstr. of Papers, p. 9-I.
28. Eischens, R. P., and Pliskin, W. A., *Advan. Catalysis* **10**, p. 1 ff. (1958).
29. Peri, J. B., Paper No. I-72 presented at Third International Congress on Catalysis, Amsterdam, 1964.
30. Peri, J. B., *Actes Congr. Intern. Catalyse, 2^e, Paris, 1960* **1**, 1333 (1961).
31. Hindin, S. G., and Weller, S. W., *Advan. Catalysis* **9**, 70 ff. (1957).
32. Kaliko, M. A., *Zh. Fiz. Khim.* **33**, 2516 (1959).
33. Basila, M. R., *J. Phys. Chem.* **66**, 2223 (1962).
34. Roberts, R. M., *J. Phys. Chem.* **63**, 1400 (1959).
35. Schissler, D., Thompson, S., and Turkevich, J., *Discussions Faraday Soc.* **10**, 46 (1951).
36. Hall, W. K., Larson, J. G., and Gerberich, H. R., *J. Am. Chem. Soc.* **85**, 3711 (1963); *ibid.* **86**, in press.
37. Parry, E. P., *J. Catalysis* **2**, 371 (1963).
38. Basila, M. R., Kantner, T. R., and Rhee, K. H., *Am. Chem. Soc. Meeting, 145th, New York, 1963,* Abstr. Papers, p. 26-I.
39. Nicholson, D. E., *Nature* **186**, 630 (1960).
40. Cook, M. A., Cutler, I. B., Hill, G. R., Wadsworth, M. E., and Oblad, A. G., *J. Phys. Chem.* **57**, 1 (1953).