To a stirred suspension of 11.582 g. (0.0343 mole) of (−)-*sec*-butylmercuric bromide, $[\alpha]^{22}\mathrm{D}$ −6.49°, was added 25 ml. of the Grignard solution dropwise, over a period of two hours. The addition was conducted under a nitrogen atmosphere and the reaction vessel was placed in a water-bath at 23°. The reaction was exothermic and appeared to occur very rapidly.

A cold water-bath was placed around the flask and 200 ml. of water was added while stirring. The ether layer was separated and washed with 50 ml. of water. The water solutions were extracted with two 5-ml. portions of methylene chloride and the organic solutions were combined. After distilling the solvents at atmospheric pressure, the residue was distilled at reduced pressure to give 9.318 g. (86.1%) of (−)-*sec*-butylmercury, b.p. 63° (3 mm.), $[\alpha]^{22}\mathrm{D}$ −5.52° (*c* 5.3, ethanol). Upon redistillation, the sample had the identical rotation.

Cleavage of (−)-*sec*-Butyl-(±)-*sec*-butylmercury by Mercuric Bromide.—A mixture of 0.5330 g. of (−)-*sec*-butyl-(±)-*sec*-butylmercury, $[\alpha]^{22}\mathrm{D}$ −5.52°, and 0.621 g. of mercuric bromide was dissolved in 15 ml. of ethanol. The solution was allowed to stand at room temperature for 40 hours and then heated to 50° for 30 minutes. After cooling to room temperature, water was slowly added until a precipitate formed. The solution was cooled to give white crystals, 1.033 g. (90.7%), of (−)-*sec*-butylmercuric bromide, m.p. 40.2–42.8° and $[\alpha]^{22}\mathrm{D}$ −3.36° (*c* 5, ethanol).

In several experiments the cleavage reaction was carried out in a polarimeter tube, and it was found that a constant rotation was obtained very rapidly. A yield of 88.7% was obtained when the reaction mixture was allowed to stand for 20 minutes at room temperature (expt. 4).

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[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Alumina: Catalyst and Support. I. Alumina, its Intrinsic Acidity and Catalytic Activity[1]

BY HERMAN PINES AND WERNER O. HAAG[2]

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Evidence has been gathered showing that pure alumina has intrinsic acidity. This acidity could be demonstrated in various ways: (a) The reactions catalyzed by alumina are typically acid catalyzed, such as dehydration of alcohols and skeletal isomerization of 3,3-dimethylbutene and cyclohexene. The relative ease with which different compounds react, and the nature of the products, are in accord with a carbonium ion mechanism. (b) Trimethylamine is strongly chemisorbed on alumina. (c) Indicators, which give colored complexes with typical Lewis acids, produce the same colors when adsorbed on alumina. The various test methods gave the same picture of the acidity for certain aluminas, but not for all. The lack of correlation results from the fact that the various methods respond in a different way to the two aspects of acidity—the quantitative and the qualitative aspect. Amine chemisorption and alcohol dehydration are primarily a function of the number of acid sites; both can be caused by relatively weak acids. The color change of Lewis indicators and the isomerization of cyclohexene both occur only on acid sites of considerable strength. Therefore, no correlation between the acidity, as determined by amine chemisorption, and the activity for cyclohexene isomerization is found. The total conversion of 3,3-dimethyl-1-butene is a somewhat less satisfactory measure of the number of acid sites than amine chemisorption, but the product distribution is a sensitive indication of the strength of the acids. Pure alumina from aluminum isopropoxide or from nitrate and ammonia, and calcined at 700°, showed optimum activity on a weight and on a unit surface area basis. Heating at higher temperatures decreased the number of acid sites as well as their acid strength. Impregnation of pure alumina with either sodium hydroxide or sodium chloride was shown to lead to a partial poisoning of the active sites without appreciably changing the acid strength of the remaining sites. With increasing amount of alkali, there is a parallel decrease in the activity for cyclohexene conversion, for butanol dehydration, and for amine chemisorption. Aluminas from sodium or potassium aluminate contain alkali in an amount which depends on the way of precipitation and the number of washings. Samples with 0.08–0.65% sodium have a large amount of weakly acid sites, as was indicated by the value for amine chemisorption, and were therefore excellent dehydration catalysts. At the same time they did not isomerize cyclohexene, showing the absence of strong acid sites. From the poisoning studies, the upper limit of the total number of acid sites (capable of dehydrating butanol) and of the number of strong sites (capable of isomerization of cyclohexene) was found to be 10×10^{13} and 0.8×10^{13} sites per cm.², respectively. Chemisorption of trimethylamine at 300° led to a value of 2.5×10^{13} sites/cm.².

Introduction

The importance of alumina as a catalyst or support has been widely recognized. As a support or co-catalyst it is used in many catalytic processes of industrial importance such as isomerization, alkylation, catalytic cracking, hydroforming, etc.

In spite of the extensive use of alumina, the literature reveals surprising discrepancies with respect to its catalytic activity. For example, the dehydration of primary alcohols such as 1-butanol[3a–f] and others was reported by many authors to give pure 1-olefins, whereas others found mixtures of double bond isomers. It was further reported that olefins such as *n*-hexenes[4a,b] undergo only double bond shift without skeletal rearrangement over alumina in agreement with the widespread belief that alumina is not a catalyst for the skeletal isomerization of hydrocarbons.[5a–c]

On the other hand, rearrangement of the carbon skeleton has been observed in a few cases as in the isomerization of 1-hexene[6] or in the interconversion of cyclohexene and methylcyclopentenes.[7]

(1) Presented in part before the Division of Colloid Chemistry at the Symposium on "Recent Approaches in the Study of Contact Catalysis," American Chemical Society Meeting, San Francisco, Calif., April 13–18, 1958; and before the Gordon Research Conferences in Catalysis, June 23–27, 1958, New London, N. H.

(2) Predoctoral Fellow Toni Co., 1957–1958; Universal Oil Products Co., 1956–1957.

(3) (a) H. Pines, THIS JOURNAL, **55**, 3892 (1933); (b) V. N. Ipatieff, H. Pines and R. E. Schaad, *ibid.*, **56**, 2696 (1934); (c) C. Matignon, H. Moureu and M. Dode, *Compt. rend.*, **196**, 973 (1933); *Bull. soc. chim.*, [5] **2**, 1169, 1181 (1935); (d) J. C. Balaceanu and J. C. Jungers, *Bull. soc. chim. Belg.*, **60**, 476 (1957); (e) A. Gillet, *ibid.*, **29**, 192 (1920); (f) J. A. Norton, *Chem. Revs.*, **31**, 319 (1942).

(4) (a) E. A. Naragon, *Ind. Eng. Chem.*, **42**, 2490 (1950); (b) R. G. Hay, C. W. Montgomery and J. Coull, *ibid.*, **37**, 335 (1945).

(5) (a) C. R. Noller, "Chemistry of Organic Compounds," W. B. Saunders Co., Philadelphia, Pa., 1951, p. 91; (b) H. N. Dunning, *Ind. Eng. Chem.*, **45**, 551 (1953); review of olefin isomerization with 89 references; (c) K. V. Topchieva, K. Yun-Pin and I. V. Smirnova, "Advances in Catalysis," Academic Press, Inc., New York, N. Y., Vol. IX, 1957, p. 799.

(6) S. Goldwasser and H. S. Taylor, THIS JOURNAL, **61**, 1762 (1939).

(7) (a) N. D. Zelinsky and J. A. Arbusov, *Compt. rend. Acad. Sci. (U.R.S.S.)*, **23**, 794 (1939); *C. A.*, **34**, 3696 (1940); (b) H. Adkins and A. K. Roebuck, THIS JOURNAL, **70**, 4041 (1948); (c) Nobuto Ohta,

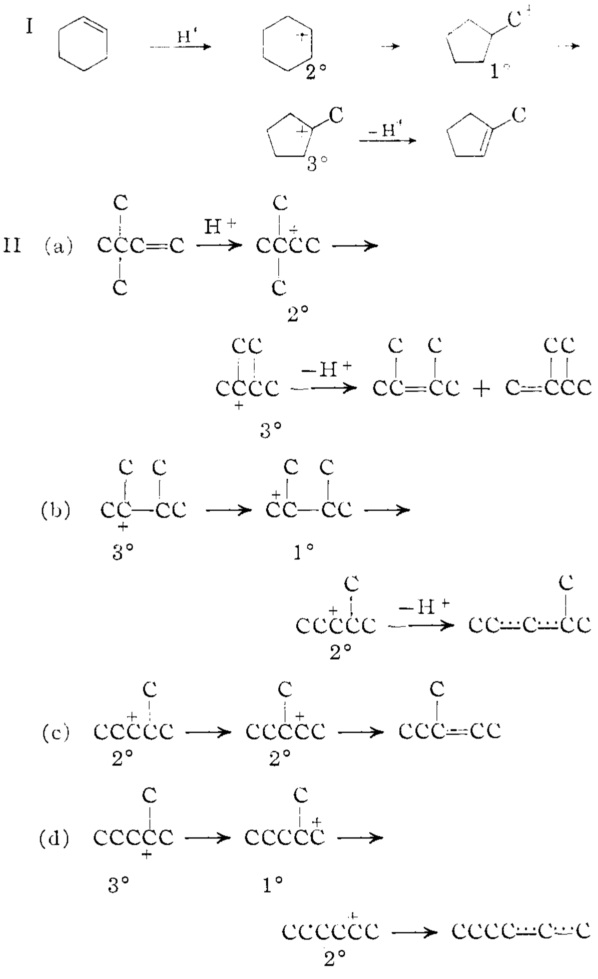
While double bond migration in olefins might arise from base[8a–h] as well as acid catalysis[5b] the occurrence of skeletal isomerization under these conditions can be attributed to acid catalysts. This presumption would attribute acidic properties to the alumina.

Several physical methods have been used to study the acidity of alumina. Titration with butylamine,[9] dioxane[10] and aqueous potassium hydroxide[11] as well as chemisorption of gaseous ammonia[11] gave apparent acidity values which approximated those of silica–alumina. On the other hand, the indicator method for testing the acidity of solids as developed by Walling[12] showed no indication of even weak acids.[13a,b] Similarly, no exchangeable protons could be detected with ammonium acetate.[9,10]

The present paper describes the use of a series of catalytic tests for the evaluation of the relative acidities of aluminas. These catalytic acidities are compared with the chemisorption of trimethylamine. Furthermore, the presence on the surface of alumina of Lewis acid sites is demonstrated using special indicators. The aluminas investigated were characterized by alkali analysis, water content, surface area and X-ray structure measurements.

The model reactions involve the isomerization of cyclohexene (CH) and 3,3-dimethyl-1-butene (3,3-DMB) and the dehydration of 1-butanol. The olefins were selected on the basis that the alumina-catalyzed reactions can best be described by a carbonium ion mechanism.

Although the energy barriers separating isomeric carbonium ions are not known and depend strongly on the nature of the attached anions, the relative rates of carbonium ion rearrangements can be estimated from the relative stability of the carbonium ions involved which is tertiary > secondary > primary (3° > 2° > 1°). Accordingly, the isomerization of cyclohexene (I) involving the rearrangement of a secondary to a less stable primary carbonium ion can be expected to proceed with greater difficulty than that of 3,3-DMB (IIa) which involves the rearrangement of 2° to 3°. The 2,3-DMB formed according to IIa can in turn form 2-methylpentene (2-MP) (IIb) by steps which involve an unstable primary carbonium ion. Therefore IIb should proceed more slowly than IIa or require stronger acid sites. For similar reasons the conversion of 2-MP to *n*-hexenes (IId) should also proceed slowly. In view of the above not only the total conversion of 3,3-DMB is important but also the depth of isomerization.



Rearrangements proceeding formally through 1° carbonium ions (step I, IIb, IId) are believed to occur with reasonably fast rates only on relatively strong acid sites, whereas those involving 2° or 3° carbonium ions take place on both strong and weak acid centers. The dehydration of alcohols should require only relatively weak acids, since alcohols are stronger bases than olefins and, therefore, are more easily protonated.

The relative activities of different alumina catalysts for the above-described reactions were used as a measure of their relative acidities. For simplicity, the catalytic activity is based on total conversion under a certain set of experimental conditions rather than on reaction rates.

Experimental Part

I. Alumina Catalysts. 1. Preparation of Alumina Catalysts.—A variety of alumina catalysts were prepared in different ways using controlled conditions. The designation of the samples and their methods of preparation are listed in Table I.

Method A.—Aluminum isopropoxide was distilled twice and hydrolyzed with distilled water. The precipitated aluminum hydroxide was washed, filtered, dried at 120° for 72 hours and screened to obtain 8-10 mesh particles.

Method B.—Aluminum hydroxide was precipitated from a solution of aluminum nitrate by a slow addition of ammonium hydroxide at 90°. The precipitate was filtered, washed, and dried at 120° for 36 hours.

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[11] A. N. Webb, *Ind. Eng. Chem.*, **49**, 261 (1957).

[12] C. Walling, THIS JOURNAL, **72**, 1164 (1950).

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TABLE I

METHODS OF PREPARATION AND DESIGNATION OF ALUMINA CATALYSTS

Catalyst	Method of prepn.	Temp., °C.	Conditions hr. Atm.	Wt. % Na or (K)	Area, m^2./g.	Crystal phase[f]
1	A	400	4 (10 mm.)		246	30% α-mo,[g] 70% η; no χ
2	A	600	4 (10 mm.)		147	η^h
3	A	700	4 (10 mm.)		152	η
4	A	800	4 (10 mm.)		131	η and θ
5	A	900	4 (10 mm.)		84	θ and trace of κ^i (?)
6	A	1000	4 (10 mm.)		44	θ and little α
7	A	600	12			
8	A	350	16 Air			
9-0	A	600	4 N_2	0	287	η and little θ
9-1	A impreg. with NaOH	600	4 N_2	0.11	280	
9-2	A impreg. with NaOH	600	4 N_2	.2		
9-3	A impreg. with NaOH	600	4 N_2	.4		
9-4	A impreg. with NaOH	600	4 N_2	.6	275	
9-5	A impreg. with NaOH	600	4 N_2	1.0		
9-6	A impreg. with NaOH	600	4 N_2	1.5		η
10-1	A impreg. with NaCl	600	4 N_2	0.2		
10-2	A impreg. with NaCl	600	4 N_2	0.6	215	
10-3	A impreg. with NaCl	600	4 N_2	1.5		
11(2)[a]	C (in NaOH)	600	4 N_2	0.65	371	
11(4)[a]	C (in NaOH)	600	4 N_2			
11(6)[a]	C (in NaOH)	600	4 N_2			
11(8)[a]	C (in NaOH)	600	4 N_2	.08	254	
12	A[b]	750	4 Air	.001		η and some θ
13	A	750	4 N_2			η (?) and α
14	B	650	4 N_2			
15	B	700	4 vacuum			γ and some δ^j
16	B	900	4 vacuum			θ and κ^k
17	C (in KOH)	500	2 Air	(1.0)	218	η
18	C (in KOH)	360	16 N_2			
19	C(7)[a] (in KOH)	360	16 N_2	(0.09)	384	
19a	C(7)[a] (in KOH)	700	4 N_2		298	
20	C(11)[a] (in KOH)	360	16 N_2	(.03)		
21	Harshaw,[c] 1/8" pills			.36		γ
22	Harshaw,[c] 1/8" pills	600	4 Air			γ
23	Alcoa[d]			.07		γ and χ
24	Houdry[e]			.38		γ and χ
25	A	1250	4 Air			α

[a] Number of washings in parentheses. [b] Hydrolyzed with an equal volume solution of ethanol and water. [c] Lot No. AL-0104 T 1/8", 580-005-45, The Harshaw Chemical Co., Cleveland 6, Ohio. [d] Activated alumina, grade F-10, Aluminum Co. of America, Pittsburgh 1a, Pa. [e] Hard alumina, grade 100, Houdry Process Corp., Philadelphia, Pa. [f] β-tri-I = β-trihydrate I (bayerite I); β-tri-II = β-trihydrate II (bayerite II); α-mo = α-monohydrate (böhmite). [g] Small crystalline böhmite. [h] Broad peak at 4.6 Å., becoming sharper and more intense in sample $3 < 12 < 4$. [i] 1 κ-peak at 2.12 Å. is missing. [j] Assignment based on 2 broad lines at 2.75 and 1.54 Å. [k] Typical line: 2.12 and 2.58 Å.

Method C.[14]—Aluminum shavings which were prepared from an aluminum bar, 99.99% pure,[15] were dissolved in an aqueous solution of potassium hydroxide. The bulk of the base was neutralized with nitric acid, and the aluminum hydroxide was precipitated by carbon dioxide at room temperature. The precipitate was washed and dried at 110° for 16 hours. The powder was compressed at 120,000 pounds per sq. inch and the material obtained broken up to give 8-14 mesh particles.

Impregnation.—To samples of alumina, previously pilled and calcined at 500°, was added a solution of sodium chloride or sodium hydroxide in just enough water to be completely absorbed. After 10 minutes the samples were dried at 110° and calcined in nitrogen for 4 hours at 600°.

2. **X-Ray Measurements.**—The instrument used was a Geiger-counter X-ray spectrometer type no. 12021, North American Phillips Co., Inc.

3. **Surface Areas.**—The surface areas of the alumina samples were determined by the standard BET method[16] using a high vacuum system[17] as described in detail in the literature.[18] Before each determination the samples were evacuated for one hour at 300°. Nitrogen was used as the adsorbate at the temperature of liquid nitrogen. The temperature was measured with an oxygen thermometer, using the values of oxygen pressure given by Farkas and Melville.[19]

4. **Chemisorption of Trimethylamine.**—The apparatus and procedure used were the same as described by Richardson and Benson.[20]

II. **Catalytic Reactions.**—The catalytic reactions were performed by passing the liquid reactant over the catalyst in a Pyrex tube, which was heated in a vertical furnace. The temperature was maintained constant by an automatic temperature controller. The liquid feed was pumped into the

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(14) P. W. Selwood, "Advances in Catalysis," Vol. III, Academic Press, Inc., New York, N. Y., 1951, p. 41.

(15) Obtained from the Aluminum Company of America through the courtesy of Dr. J. A. Nock, Jr.

(16) H. Brunauer, P. H. Emmett and E. Teller, THIS JOURNAL, 60, 309 (1938); H. Brunauer, "The Adsorption of Gases and Vapours," Oxford University Press, New York, N. Y., 1945.

(17) The apparatus was made available to us through the courtesy of Professor R. L. Burwell, Jr.

(18) W. E. Barr and V. J. Anhorn, "Scientific and Industrial Glass Blowing and Laboratory Techniques," p. 257.

(19) A. Farkas and H. M. Melville, "Experimental Methods in Gas Reactions," Macmillan and Co., London, 1939, p. 104.

(20) R. L. Richardson and S. W. Benson, *J. Phys. Chem.*, 61, 405 (1957).

TABLE II

ISOMERIZATION OF 3,3-DIMETHYL-1-BUTENE AND OF CYCLOHEXENE OVER VARIOUS ALUMINA CATALYSTS

				3,3-Dimethyl-1-butene						Cyclohexene
					Products, %[h]					
Expt.	Catalyst no.[a]	Temp., °C.	LHSV	Conversion, %	3,3-DMB	2,3-DMB	2-MP	3-MP	Selectivity[b]	Conversion, %
1	3	350	6.0	79.0	21.0	73.0	6.0	..	92	
2	5	350	6.0	52.6	47.4	52.1	0.5	..	99	
3	6	350	6.0	39.9	60.1	39.9	..	..	100	
4	3	410	2.0	..	..	..	..	..	..	82.9
5	5	410	2.0	94.1	5.9	69.6	20.1	4.4	74	3.8
6	17	410	2.0	5.5	94.5	5.4	0.1	..	99	0
7	19	410	2.0	87.1	12.9	70.6	15.1	1.4	81	..
8	20	410	2.0	95.9	4.1	70.6	21.9	3.4	74	..
9	15	410	2.0	..	..	..	..	..	..	70
10	16	410	2.0	..	..	..	..	..	..	38
11	12	350	2.0	97.3	2.7	39.3	37.2	19.8[c]	40	43
12	17	350	2.0	0	100	..	..	..	..	0
13	19	350	2.0	78.9	21.1	69.5	9.4	..	88	4.3
14	19a	350	2.0	84.0	16.0	72.9	9.7	1.4	87	11.6
15	20	350	2.0	91.9	8.1	83.2	7.3	1.4	91	9.9
16	11(2)	350	2.0	63.0	37.0	60.5	2.5	..	96	0
17	11(4)	350	2.0	58.3	41.7	57.1	1.2	..	98	0
18	11(8)	350	2.0	75.5	24.5	72.9	1.6	..	97	0
19	9-0	350	2.0	97.3	2.7	39.3	37.2	19.8	40	43
20	9-1	350	2.0	87.0	13.0	56.3	23.0	7.7	65	32
21	9-2	350	2.0	76.2	23.8	47.7	19.8	8.7	63	..
22	9-3	350	2.0	66.2	32.8	49.8	13.5	3.9	75	17
23	9-4	350	2.0	62.6	37.4	49.8	10.0	2.8	80	..
24	9-5	350	2.0	34.3	65.7	23.2	8.9	2.2	68	4
25	9-6	350	2.0	0	100.0	..	..	..	..	..
26	10-1	350	2.0	86.3	13.7	67.9	14.8	3.6	79	21
27	10-2	350	2.0	62.0	38.0	56.2	5.8	..	91	2
28	10-3	350	2.0	0	100.0	..	..	..	..	..
29	12	350	0.5	98.1	1.9	23.0	42.6	31.0[d]	23	..
30	23	350	.5	96.9	3.1	74.8	20.2	1.9	77	..
31	21	350	.5	19.5	80.5	19.5	..	..	100	0.9[g]
32	24	350	.5	15.7	84.3	15.4	0.3	..	98	..
33	24[e]	350	.5	0	100.0	..	..	..	..	0
34	24[e]	410	.5	3.2	96.8	3.2	..	..	100	..
35	24[f]	350	.5	46.6	53.4	46.6	..	..	100	..

[a] See Table I for detailed description of the catalysts. [b] Selectivity ratio of (2,3-DMB/2,3-DMB + 3-MP + H) × 100. [c] In addition 1% of *n*-hexenes (H) were formed. [d] In addition 1.5% of *n*-hexenes were formed. [e] Same catalyst as used in expt. 32, but one catalyst pellet of different size out of about 150 was removed. [f] Same catalyst sample as used in expt. 33; this catalyst was used for isomerization and dehydration reactions at 410° and was regenerated several times at 550°. [g] The reaction was carried out at 410° and LHSV 0.50. [h] DMB = dimethylbutene; MP = methylpentene.

reaction tube by means of a stainless steel, syringe-type displacement pump of 40-ml. capacity. The flow rate could be continuously changed from 0.2 to 40 ml. per hour by means of a Zero-Max variable speed torque converter (Revco, Inc., Minneapolis, Minn.). The liquid products were condensed in a water-cooled liquid receiver, followed by a small trap cooled in ice-water, and gases were collected over saturated salt water.

In the isomerization reactions, the liquid products were usually analyzed directly as received, although in a few cases they were distilled through a 3-inch Vigreux column, using a high boiling liquid as a chaser. In the dehydration of cyclohexanol, the two layers obtained were separated, and the organic layer was dried over sodium sulfate. For the catalyst evaluations, from 2 to 10 ml. of liquid material was passed over 5 to 20 ml. of catalyst. Larger amounts of reactants were used when it was intended to separate the products by distillation. Analytical distillations were carried out, using a Podbielniak Whirling Band column (W. J. Podbielniak, Inc., Chicago, Ill.).

III. Analytical Procedure.—The products obtained were partially identified by infrared analysis. The infrared absorption spectra were obtained using a Baird recording infrared spectrophotometer, equipped with rock salt optics (Baird Atomic Inc., Cambridge, Mass., formerly Baird Associates, Inc.).

Most of the analyses were performed by gas chromatography, using a Podbielniak Chromacon model 9475-3A vapor phase chromatography analytical apparatus (W. J. Podbielniak, Inc., Chicago, Ill.). The following columns were used: tricresyl phosphate (6 ft. for cyclohexene and methylcyclopentenes, 34 ft. for *n*-butenes), β,β'-oxydipropionitrile (40 ft. for hexenes) and silver nitrate in ethylene glycol (12 ft.). The latter column gave the following order of elution (relative retention volumes in parentheses): *trans*-2-butene (1.00), ethylene (1.66), isobutylene (2.27), *cis*-2-butene (4.20), 1-butene (4.78). The order of elution of *cis*- and *trans*-2-butene is opposite to that reported in the literature.[21]

IV. Materials. Cyclohexanol, 1-butanol and cyclohexene were reagent grade commercial products. They were distilled on an 8-inch Vigreux column, the center cut only being used. Their purity was established by boiling point, refractive index, infrared absorption spectrum and vapor phase chromatography.

3,3-Dimethyl-1-butene was obtained from 3,3-dimethylbutanol[22] by dehydration over alumina (Harshaw Chemical Co.) at 400° and at an hourly liquid space velocity of 0.6. The 3,3-dimethyl-1-butene distilled at 41.0-41.4°, n^{20}D 1.3759. It constituted 80% of the total olefins formed, the remainder being 2,3-dimethylbutenes.

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(21) B. W. Bradford, D. Harvey and D. F. Chalkley, *J. Inst. of Petr.*, **41**, No. 375, 80 (1955).

(22) V. N. Ipatieff, W. W. Thompson and H. Pines, THIS JOURNAL, **73**, 553 (1951).

The trimethylamine used for the amine adsorption was Eastman Organic Chemicals Department, white label purity. It was distilled into the storage bulb and degassed by repeated freezing and evacuating.

Results and Discussion

A. Catalytic Activity. (1) Isomerization of Cyclohexene.—The results of the isomerization of cyclohexene (CH) over various alumina catalysts are presented in the last column of Table II. It becomes immediately apparent that some aluminas give a high conversion of CH to methylcyclopentenes (MCP), while others are completely inactive. Equilibration experiments at 410° (not shown) starting with either CH or 1-methylcyclopentene produced identical mixtures consisting of 9% CH and 91% MCP.

The highest activity is exhibited by catalysts 3 and 15, prepared from carefully purified aluminum isopropoxide and reagent grade aluminum nitrate, respectively. These catalysts are free of alkali or halogens. In view of the method of preparation they are also assumed to be free of silica, although no analytical data to support this are available. It is therefore believed that the high isomerization activity of these high purity catalysts is an intrinsic property of alumina and is indicative of the presence on the surface of acidic sites of considerable acid strength. All the catalysts which had little or no activity for CH conversion contained alkali.

(2) Isomerization of 3,3-Dimethyl-1-butene.—Contrary to reports in the literature[23] 3,3-dimethyl-1-butene was isomerized over most of the alumina catalysts tested, the conversions ranging from 0 to 98%. Mixtures containing up to at least eleven hexene isomers were obtained, in a few cases accompanied by small amounts of lower boiling material.

The alumina-catalyzed skeletal isomerization of 3,3-DMB proceeds by consecutive reaction steps[24] according to scheme II above.

In spite of the complexity of products 3,3-DMB proved a very useful and sensitive model compound for evaluating the acidity of catalysts. As can be seen from the results in Table II, all the catalysts gave a higher conversion of 3,3-DMB as compared to CH, in agreement with the expectations based on carbonium ion intermediates. For instance, catalyst 5 gave a 94% conversion of 3,3-DMB at 410° (expt. 5), while under the same conditions it isomerized CH only to an extent of 3.8%. Catalyst 17 (expt. 12) and cat. 11(8) (expt. 18), both of which were inactive toward CH, revealed their quite different catalytic characteristics toward the much more sensitive 3,3-DMB, in that the first one was also inactive for conversion of 3,3-DMB while the latter gave a 75% conversion. The significance of the product distribution will be discussed below.

(3) Dehydration of 1-Butanol.—1-Butanol was dehydrated over various alumina catalysts with the results summarized in Table III. As in the olefin isomerization, large differences in dehydration activity are apparent (3 to 93% dehydration). The product distribution likewise differs greatly. While some catalysts gave almost pure 1-butene (catalysts 10-2 and 17), others gave a mixture of all the *n*-butenes. Experiments with catalyst 9-0 at longer contact time produced equilibrium mixtures of the *n*-butenes with additional formation of isobutylene. It will be noted that the 2-butenes are formed in a stereoselective way as indicated by the ratio *cis/trans*, which shows values of 0.9 to 2.3 as compared to the equilibrium value of 0.6.

TABLE III

DEHYDRATION OF 1-BUTANOL OVER ALKALI CONTAINING ALUMINAS[a]

Expt.	Cat.	Dehydration, %	Butenes, % 1-	Butenes, % 2-*trans*-	Butenes, % 2-*cis*-	Ratio *cis*/*trans*
36	9-0	82	35.1	33.6	31.3	0.9
37	9-1	51	59.4	19.6	21.0	1.1
38	9-2	45	63.1	19.3	17.6	0.9
39	9-4	28	71.5	13.2	15.3	1.2
40	9-5	14.5	..	..	..	..
41	9-6	3	71.8	9.8	18.4	1.9
42	10-1	65	68.2	12.3	19.5	1.6
43	10-2	31	92.5	2.3	5.2	2.3
44	10-3	6	79.6	7.8	12.6	1.6
45	19a	81	59.6	16.2	24.2	1.5
46	11(4)	86	87.6	3.8	8.6	2.3
47	11(8)	93	80.0	6.4	13.6	2.1
48	17	17	96.5	1.4	2.1	1.5

[a] The experiments were carried out at 350°, HLSV 2.0.

(4) Factors Influencing the Catalytic Activity of Aluminas. (a) Calcination Temperature and Water Content.—A series of aluminas was prepared from the same batch of alumina hydrate which had been made from aluminum isopropoxide. The hydrate samples were heated for four hours at 400°, 600°, 700°, 800°, 900°, and 1000° (catalysts 1–6, Table I), and tested for catalytic activity with cyclohexene under identical conditions; the results, presented in Fig. 1, indicate that maximum catalytic activity occurs at a calcination temperature of 600–700°. The specific isomerization activity, expressed in percentage methylcyclopentene per unit surface area was calculated and plotted against the calcination temperature (Fig. 1, broken line). It is immediately apparent that the low isomerization activity of the aluminas calcined at 400 and 900° is not due to a smaller surface area. The sample calcined at 800° has about the same specific activity as those calcined at 600 and 700°. The qualitative change of the alumina surface on thermal treatment appears to be much more pronounced than the change in area. A similar dependence of the catalyst activity on the calcination temperature was found in the isomerization of 3,3-DMB (expt. 1, 2, 3; Table II).

It seems that this very drastic dependence of the specific isomerization activity upon the calcination temperature has not been observed previously. However, similar activity changes have been reported for the dehydration activity of aluminas[25] although the results are contradictory. With an increase in the calcination temperature from 600 to 1000° Brey and Krieger[26] reported a *decrease*

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(23) P. L. Cramer and A. L. Glasebrook, THIS JOURNAL, **61**, 230 (1939).

(24) W. O. Haag and H. Pines, *ibid.*, **82**, 2488 (1960).

(25) J. B. Senderens, *Bull. soc. chim.*, [4] **3**, 197 (1908).

(26) W. S. Brey and K. A. Krieger, THIS JOURNAL, **71**, 3637 (1949).

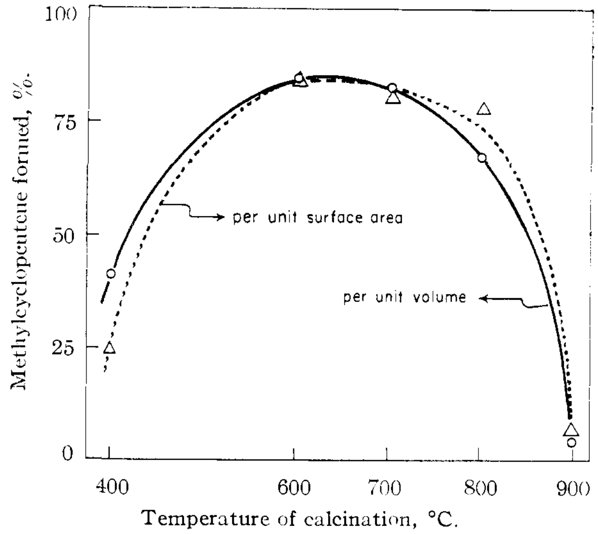

Fig. 1.—Isomerization of cyclohexene (410°, HLSV 2.0): as a function of calcination temperature of alumina ———, isomerization activity per unit volume; --------, isomerization activity per unit surface area.

and Boreskov and co-workers[27] an *increase* in the specific activity, whereas Cremer[28] found a maximum in the dehydration activity at 700° pretreatment.

Since cracking catalysts require a small concentration of water for maximum activity, it was of interest to look for a possible relationship between isomerization activity (Fig. 1) and water content of the alumina catalysts.

Table IV lists the results. The water in these catalysts is present in the form of hydroxyl groups.[29] From the number of oxygen ions on the surface of alumina (14.7×10^{14} per cm.^{2})[30] the amount of water corresponding to complete surface coverage with hydroxyl groups can be calculated. Comparison with the experimental value gives the fraction of the surface oxygens which are present in the form of hydroxyl groups (Table IV, last column). It has been proposed[30] that alumina enhances typically acid-catalyzed reactions when its surface is saturated with water. From the present data it appears, however, that high activity is associated with a surface only partially covered with water (in the form of hydroxyl groups). It is believed that the low activity of the 400° sample is at least partly due to the presence of too much water. After removing part of the excess water by passing air over the sample for 16 hours at 360°, the cyclohexene conversion increased from 41.3 to 75.7%. Thus, large amounts of water on the catalyst act as a poison. However, other factors are of importance too, as can be inferred from the fact that the low activity 900° sample (no. 5) has about the same water content per unit area as the high activity catalysts obtained at 600–800°. The activity of sample 5 improved from 3.8 to 11% cyclohexene conversion after it had been used and regenerated repeatedly. It has been suggested[30,31] that the catalytic activity of dehydrated oxides might result from surface strain sites which tend to "heal" at higher temperature. If this picture is correct then annealing of surface strain in alumina occurs between 800 and 900°. The increased activity after use of the 900° sample at 400–500° would then indicate formation of new strain sites at the lower temperatures. Similar changes with time were observed with other catalysts (*cf.* expt. 35).

TABLE IV

WATER CONTENT OF ALUMINA AS A FUNCTION OF CALCINATION TEMPERATURE

Catalyst no.	Calcd. temp., °C.	Water content, % Exptl.[a]	Calcd. for monolayer[b]	Fraction of surface covered
1	400	6.57	5.41	1.21
2	600	1.75	3.23	0.54
3	700	1.30	3.32	.40
4	800	1.15	2.88	.40
5	900	0.80	1.85	.43
6	1000	0.80	0.97	.82

[a] Determined from the loss of weight on heating for four hours (constant weight) at 1250° in a platinum crucible. [b] See text.

(b) **Alkali Metal Ions.**—Recent data in the literature[32] indicate that the activity of alumina for the dehydration of ethanol is markedly decreased by adsorbed sodium hydroxide. Other authors[33] claimed that only the particle size distribution in connection with the surface area has a relationship to the catalytic activity of aluminas (for dehydration of 2-propanol), whereas the analytical composition is only of minor importance. No information with regard to the isomerization activity seems to be available in the literature.

A series of aluminas containing varying amounts of sodium was prepared under identical conditions by impregnating samples of pure alumina with aqueous solutions of sodium hydroxide (cat. 9) and sodium chloride (cat. 10) of various concentrations. After drying and calcining, the various catalysts were tested for isomerization activity with CH and 3,3-DMB, and for dehydration activity with 1-butanol. For comparison, alkali-containing aluminas obtained from sodium and potassium aluminate were also tested. The results are included in Tables II and III, and presented in Fig. 2.

The data in Fig. 2 indicate that the activity of alumina for alcohol dehydration as well as for olefin isomerization is poisoned by impregnation with sodium hydroxide or sodium chloride. The approximately parallel decrease in conversion with increasing sodium content indicates that the catalytic centers for dehydration are the same as those for isomerization, contrary to a recent report.[5c] Sodium chloride appears to be a somewhat more effective poison for CH and gives a more selective

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(27) G. K. Boreskov, V. A. Dzis'ko, M. S. Borisova and V. N. Krasnopol'skaya, *Zhur. Fiz. Khim.*, **26**, 492 (1952); *C. A.*, **47**, 957 (1953).

(28) E. Cremer, *Z. Elektrochem.*, **53**, 269 (1949).

(29) O. Glemser and G. Rieck, *Angew. Chem.*, **68**, 182 (1956).

(30) G. A. Mills, S. Weller, S. G. Hindin and T. H. Milliken, *Z. Elektrochem.*, **60**, 823 (1956).

(31) A. G. Oblad, S. W. Weller and G. A. Mills, "Solid/Gas Interface," Proceedings of the Second International Congress of Surface Activity, Butterworth, London, 1958, p. 309.

(32) G. K. Boreskov, V. A. Dzis'ko and M. S. Borisova, *Zhur. Fiz. Khim.*, **27**, 1172 (1953); *C. A.*, **48**, 5627*i* (1955).

(33) G. Rienäcker and K. Wencke, *Angew. Chem.*, **66**, 749 (1954); K. Wencke and G. Rienäcker, *Chem. Techn.* (*Berlin*), **6**, 577 (1954).

product distribution from 3,3-DMB than sodium hydroxide does, while the reverse is observed for dehydration.

About 1.5% sodium is required to render the impregnated catalysts inactive for olefin isomerization and nearly so for dehydration (Fig. 2). By contrast, if alkali is incorporated into the alumina during precipitation ("aluminate" catalysts 11 and 17–20), alkali concentrations of more than an order of magnitude smaller are sufficient to completely poison the isomerization of cyclohexene. For example, as little as 0.08% Na (cat. 11(8)) lowered the conversion of cyclohexene from 43% (cat. 12) to 0% (expt. 18).

The aluminate catalysts were surprisingly active for the dehydration of 1-butanol (Table III, expt. 45–47) and for the isomerization of 3,3-DMB, yet at the same time highly selective (Table II, expt. 13–18).

(c) **Ammonia.**—A few experiments were carried out in which the catalytic activity of aluminas was tested before and after exposure of the catalysts to an atmosphere of ammonia at elevated temperature (Table V). While ammonia had no effect on the weakly acidic catalyst (expt. 49), it strongly influenced the pure alumina catalyst (expt. 50 and 51). Although the total conversion of 3,3-dimethyl-1-butene was only partially reduced, the selectivity was greatly increased. Similarly, the isomerization of cyclohexene to methylcyclopentene dropped after exposure of the catalyst to gaseous ammonia to 12% of the original value.

(d) **X-Ray Structure.**—The literature of alumina structures is complicated by the discrepancies in names. The terminology used here is essentially that proposed by Stumpf and coworkers[34] with the addition of a newly discovered crystalline form of aluminum trihydrate ("bayerite-II").[35] The crystal phases of the various aluminas are given in Table I.

TABLE V

INFLUENCE OF AMMONIA ON ISOMERIZATION ACTIVITY OF ALUMINAS

Expt.	Catalyst	NH_3 treated	Conversion, %	Products,[g] % 3,3-DMB	 2,3-DMB	 2-MP	 3-MP	Selectivity[f]
			Isomerization of 3,3-dimethyl-1-butene					
49[a]	24	No	55.3	44.7	55.3	..	..	100
		Yes[b]	52.1	47.9	52.1	..	..	100
50[c]	12	No	97.7	2.3	34.9	45.6	17.2	36
		Yes[b]	81.3	18.7	66.8	13.6	0.9	82
			Isomerization of cyclohexene Methylcyclopentenes, %					
51[e]	12	No	45.5					
		Yes[d]	5.4					

[a] Reaction carried out at 410°, HLSV 0.5. [b] A slow stream of ammonia was passed over the catalyst for 4 hours at 410° and atmospheric pressure, followed by a rapid stream of nitrogen for 10 minutes. [c] 410°, HLSV 2.0; presence of *n*-hexenes possible. [d] Ammonia treatment as in *b*, but only for 2 hours. [e] 400°, HLSV 2.0. [f] Table II, footnote *b*. [g] Table II, footnote *h*.

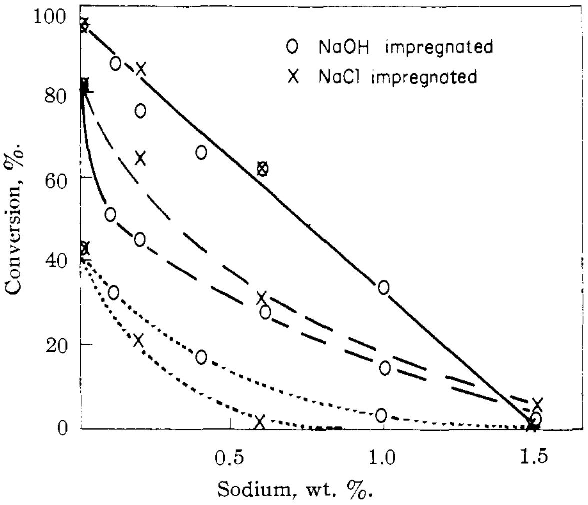

Fig. 2.—Isomerization of cyclohexene (---------) of 3,3-dimethyl-1-butene (———) and dehydration of 1-butanol (– – – –) over impregnated aluminas (350°, HLSV 2.0).

The decomposition sequence observed for the aluminas was essentially that reported in the literature.[34]

Eta as well as γ-alumina are good catalysts for isomerization as long as they are free of alkali metals (expt. 4 and 9, respectively). Trace amounts, 0.05%, of alkali severely affect the catalytic activity of aluminas, but these cannot be detected by the usual X-ray analysis. The pronounced decrease in cyclohexene conversion occurring between 800 and 900° calcination temperature (Fig. 1) could result from a phase transition of the catalyst from predominant η- to nearly pure θ-alumina.

(5) **Evaluation of Acidity of Aluminas from Model Reactions.**—The activity of pure alumina for isomerization and dehydration is believed to be due to the presence of acid centers on the catalyst surface. High catalytic activity can result from (a) a large number of acid centers or (b) high acid strength of the sites.

According to the principles outlined in the introduction, the conversion of cyclohexene is a measure of strong acid sites, while the dehydration activity of 1-butanol is an indicator for strong *and* weak acids. A catalyst can therefore be fingerprinted for number and strength of acid sites with these two reactions. A similar result can be obtained from the isomerization of 3,3-DMB alone. Overall conversion measures total acidity, whereas the depth of isomerization reflects the strength of the acids: weak acids produce only the primary rearrangement product (2,3-DMB) (selectivity 100), while stronger acids cause further isomerization to 2- and 3-MP (lower selectivity).

Application of these principles to the catalysts tested indicate: aluminas without alkali contain a large number of strong acid sites; aluminas prepared from sodium or potassium aluminate contain a large number of weak acid sites; impregnation of pure alumina with sodium hydroxide reduces the total number of sites without appreciably changing the acid strength distribution of the remaining sites; impregnation with sodium chloride has a

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[34] H. C. Stumpf, A. S. Russell, J. W. Newsome and C. M. Tucker, *Ind. Eng. Chem.*, **42**, 1398 (1950).

[35] R. A. Van Nordstrand, W. P. Hettinger and C. D. Keith, *Nature*, **177**, 713 (1956). The name "Nordstrandite" was proposed for this structure: J. H. deBoer, *Angew. Chem.*, **70**, 383 (1958).

similar effect, but the remaining acid sites are reduced in strength. The commercial catalysts (expt. 30–35) ranged from moderately strongly acidic (cat. 23, Alcoa Alumina) to weakly acidic (cat. 21, Harshaw Alumina). The non-acidic Houdry catalyst 24 (expt. 33) developed weakly acid sites with prolonged use (expt. 35).

The striking differences in catalytic behavior between impregnated aluminas (I) and those obtained from aluminate solutions (A) are summarized in Table VI, where two catalysts (one of each group) with similar sodium contents are compared. For reference, a pure alumina catalyst (P) is also included. Catalyst A has a larger number of acid sites than catalyst I (conversion of 1-butanol 93% *vs.* 51%), but they are of low acid strength (no isomerization of cyclohexene, high selectivity in the isomerization of 3,3-DMB), whereas the sites in catalyst I are much stronger.

The results obtained on poisoning with ammonia (Table V) can also conveniently be accounted for by suggesting that ammonia is chemisorbed at 400° only on strongly acid surface centers. There was no effect of ammonia on catalyst 24 (expt. 49, Table V), which the excellent selectivity had characterized as containing no strong acid sites. On the other hand, ammonia blocked the strongly acid sites of catalyst 12 with a resulting decrease in cyclohexene conversion (expt. 51) and an increase in selectivity (expt. 50).

TABLE VI

COMPARISON BETWEEN IMPREGNATED AND ALUMINATE CATALYSTS[a]

	P	I	A
Catalyst no.	9-0	9-1	11(8)
Sodium content, %	0	0.1	0.08
Surface area, m.^{2}/g.	287	280	254
Conversion			
of cyclohexene, %	43	32	0
of 3,3-dimethyl-1-butene, %	97	87	76
of 1-butanol, %	82	51	93
Isomerization of 3,3-DMB, selectivity	40	65	97
Dehydration of 1-butanol			
2-Butene, %	65	41	20
Ratio *cis-/trans*-butene	0.9	1.1	2.1

[a] P = pure alumina, I = impregnated, A = aluminate catalyst.

The impregnation method did not lead to a similar selective poisoning of the strongly acid centers. This is most likely due to the method of impregnation. When a sodium hydroxide solution of low concentration penetrates the pores of the alumina pellets, the solute is apparently strongly and non-selectively adsorbed causing a rapid depletion of the solution before the total pore volume is filled. Since the solvent was removed at this stage, a redistribution of sodium hydroxide was not possible through the solution and apparently did not take place to a great extent by surface migration during the calcination period which followed. For this reason part of the internal surface contains acid sites in approximately the original acid strength distribution (selectivity of 3.3-DMB increased only moderately, Table II).

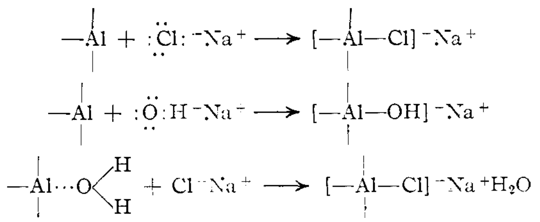
Only when the amount of sodium hydroxide in the impregnating solution is raised sufficiently to allow adsorption of sodium hydroxide by the total internal surface, does the catalyst become inactive for the isomerization of cyclohexene. At the same time the catalyst (9-6) is inactive for the isomerization of 3,3-dimethylbutene and nearly so for the dehydration of 1-butanol.

The impregnation with sodium chloride proceeds in a similar way although the slight differences which were observed are of significance. Sodium chloride is apparently adsorbed in a more selective way than sodium hydroxide is, showing some preference for the stronger acid sites. This is reflected in its higher poisoning efficiency for cyclohexene conversion (Fig. 2) and also in the considerably increased selectivity observed in the isomerization of 3,3-DMB (Table II, expt. 27 as compared to expt. 23).

The approximately linear decrease of catalytic activity for the conversion of 3,3-DMB and 1-butanol with increasing sodium content (Fig. 2) suggests that sodium hydroxide and sodium chloride are adsorbed on the acid sites of the catalyst. At least in the case of sodium chloride, the adsorption of sodium ions does not seem to be due to ion exchange with protons on the surface

$$\text{Cat}^-\text{H}^+ + \text{Na}^+\text{Cl}^- \longrightarrow \text{Cat}^-\text{Na}^+ + \text{H}^+\text{Cl}^-$$

since no exchange was found to occur even with ammonium acetate.[9,10] It is however possible that the adsorption takes place on incompletely coördinated aluminum ions on the surface (Lewis acid sites = —Al).



$$\text{—Al} + :\ddot{\underset{..}{\text{Cl}}}:^-\text{Na}^+ \longrightarrow [\text{—Al—Cl}]^-\text{Na}^+$$

$$\text{—Al} + :\ddot{\underset{..}{\text{O}}}:\text{H}^-\text{Na}^+ \longrightarrow [\text{—Al—OH}]^-\text{Na}^+$$

$$\text{—Al}\cdots\text{O}\langle^{\text{H}}_{\text{H}} + \text{Cl}^-\text{Na}^+ \longrightarrow [\text{—Al—Cl}]^-\text{Na}^+ + \text{H}_2\text{O}$$

The more selective adsorption of sodium chloride as compared with sodium hydroxide could result from the lower basicity (or lower nucleophilicity) of the chloride anion relative to the hydroxide anion.

B. Surface Concentration of Alkali Metal Ions.—If one assumes that both types of aluminas contain the alkali metal ions on the surface rather than in the bulk, upper values for the surface concentration of the alkali metal ions can be calculated from the known surface area. Table VII lists the values for various catalysts in units of atoms per cm.^{2}; the area per atom is also included. In the aluminate catalysts, as little as 8.5×10^{12} sodium atoms per cm.^{2} are sufficient to completely inhibit the isomerization of cyclohexene. This corresponds to a surface coverage of considerably less than 1%. If one assumes that pure alumina develops the same number of active centers during calcination as one containing alkali, and that each alkali metal atom deactivates one acid site, one arrives at the conclusion that a pure alumina catalyst has about 10^{13} strongly acid sites per cm.^{2}. This figure might be compared with those

TABLE VII

MAXIMUM SURFACE CONCENTRATIONS OF ALKALI METAL IONS

Catalyst no.	Type[a]	No. of alkali atoms per cm.^{2}	Area per atom (A.^{2})	Cyclohexene isomerization, %	Butanol dehydration, %
9-1	I	10×10^{12}	970	32	51
9-3	I	38×10^{12}	270	17	..
9-5	I	95×10^{12}	110	4	14
9-6	I	104×10^{12}	71	0	3
19a	A	4.7×10^{12}	2100	11	81
11(8)	A	8.5×10^{12}	1200	0	93
17	A	75×10^{12}	133	0	17

[a] I = impregnated, A = aluminate.

estimated for silica–alumina cracking catalysts for which surface densities of 10^{14} sites/cm.^{2} (base exchange capacity[36]) and 10^{13} sites/cm.^{2} (quinoline adsorption[37]) have been reported. In addition to the strong acid centers, more than 7.5×10^{13} weak sites are present, capable of dehydrating 1-butanol (catalyst 17).

Adding alkali by absorption from aqueous solution, on the other hand, requires about 10^{14} atoms per cm.^{2} to inhibit cyclohexene isomerization. Apparently, no selective deactivation of the strongly acid sites takes place. Since the same amount of sodium also deactivates the catalyst for the dehydration of 1-butanol (Table II, cat. 9-6), one may conclude that alumina has about 10^{14} sites/cm.^{2} active for dehydration, 10% of which are active for the isomerization of cyclohexene.

C. Trimethylamine Adsorption (Amine Index).—The activity of certain solid substances to catalyze hydrocarbon reactions, such as polymerization, isomerization and cracking, which can most conveniently be described in terms of carbonium ion mechanisms, is generally attributed to the acidity of such catalysts.

While the acidities of the cracking catalysts have been studied extensively by various methods, only a few investigations of aluminas have been published. Trambouze[10] determined the Lewis acidity by titration with dioxane, and Webb[11] carried out acidity measurement by ammonia chemisorption. The Tamele method,[38] using *n*-butylamine, was employed by Bailey and co-workers.[9]

The adsorption of trimethylamine was selected for the quantitative determination of the acidity of aluminas since this method permits the study of the effect of temperature. This acidity is expressed as "Amine Index" (AI) and is equivalent to millimoles of trimethylamine adsorbed per gram of catalyst.

In the present study the amount of trimethylamine adsorbed after pumping for one hour at 300° is considered to be representative of chemisorption. Values at lower temperatures probably contain considerable amounts of physical adsorption. Higher temperatures of measuring adsorption could not be used on account of side reactions resulting in coke formation.

The amine index of the various aluminas is given in Table VIII. The ratio of 300/200 does not reflect a difference in acid strength since silica–alumina catalyst has about the same ratio as aluminas. The absolute values of trimethylamine adsorption at 300° corrected for surface area are shown in the last column; they are expressed in units of 10^{13} molecules per cm.^{2}.

TABLE VIII

ADSORPTION OF TRIMETHYLAMINE ON ALUMINAS (AMINE INDEX)

Units	mmoles per gram						10^{13} molec. per cm.^{2}
Press., mm.	150	10^{-4}					10^{-4}
Temp., °C.	25	25	100	200	300		300
Catalyst[a]						Ratio[c]	
1	1.12	0.45	..	0.133	0.067	0.50	1.6
2	0.57	.29	0.15	.086	.050	.58	2.0
3	.61	.30	.16	.080	.033	.41	1.4
5	.30	.13	.06	.024	.005	.21	0.3
9-0	1.00	.55	.31	.18	.120	.67	2.6
9-1	0.79	.52	.31	.18	.11	.61	2.5
9-2	.80	.37	.22	.14	.07	.50	1.5
9-3	.90	.39	.23	.13	.07	.54	1.5
9-4	.98	.44	.25	.15	.07	.50	1.5
9-5	1.02	.42	.21	.11	.04	.36	0.9
9-6	0.62	.15	.05	.02	.01	.50	0.2
10-1	.90	.48	.30	.18	.10	.65	2.1
10-2	.87	.41	.25	.14	.06	.43	1.3
11(2)	1.27	.50	.30	.19	.13	.69	2.1
11(8)	1.05	.50	.31	.20	.13	.65	3.0
17	0.90	.38	.15	.08	.025	.31	0.7
18	0.87	.10	.04	.02	.004	.20	0.1
19	1.52	.62	.31	.17	.085	.50	1.3
19a	1.19	.55	.34	.20	.12	.60	2.4
20	1.47	.62	.33	.19	.095	.50	
22	0.31	.16	.08	.04	.012	.30	0.9
24	0.08	.04	.017	.005	...	...	0.0
Si–Al[b]	1.55	.76	.33	.18	.095	.54	1.5

[a] Table I. [b] UOP silica-alumina cracking catalyst type B. [c] Ratio of the amount of trimethylamine adsorbed at 300° to that at 200°.

The aluminas with high alkali content have a low amine index (catalysts 9-6, 17 and 18). The AI indicates that pure alumina has 2×10^{13} acid sites per cm.^{2}; this calculation is based on the assumption that each adsorbed molecule corresponds to one acid site.

This value is in good agreement with that obtained by titration with *n*-butylamine[9] (1.1 to 2.5×10^{13} sites/cm.^{2}), but considerably lower than the values of 1×10^{14} and 2×10^{14} found by ammonia chemisorption[11] and dioxane titration,[10] respectively. The reason for these differences is not apparent. Steric factors may play a role, since it has been shown[38] that on silica–alumina the "irreversible" adsorption of ammonia is about three times larger than that of ethylamine. The effective molecular areas are about 10 A.^{2} for ammonia and 19 A.^{2} for ethylamine,[39] and about 32 A.^{2} for trimethylamine.[40] On this basis, a factor

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(36) D. S. MacIver, P. H. Emmett and H. S. Frank, *J. Phys. Chem.*, **62**, 935 (1958).

(37) G. A. Mills, E. R. Boedeker and A. G. Oblad, THIS JOURNAL, **72**, 1554 (1950).

(38) M. W. Tamele, *Disc. Faraday Soc.*, **8**, 270 (1950).

(39) S. E. Voltz and S. W. Weller, *J. Phys. Chem.*, **62**, 574 (1958).

(40) Adsorption isotherms on alumina were obtained using trimethylamine at 25°. The isotherms corresponded to the type "II" [S. Brunauer, L. S. Deming, W. E. Deming and E. Teller, THIS JOURNAL, **62**, 1723 (1940)]. Comparing the volume of gas corre-

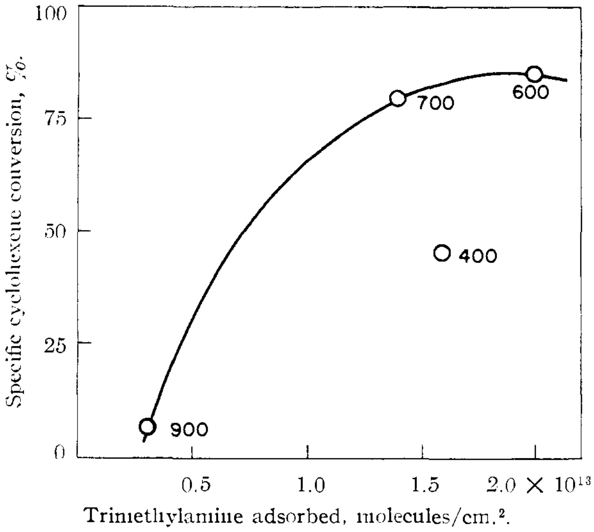

Fig. 3.—Comparison between trimethylamine adsorption and isomerization of cyclohexene (410°, HLSV 0.5).

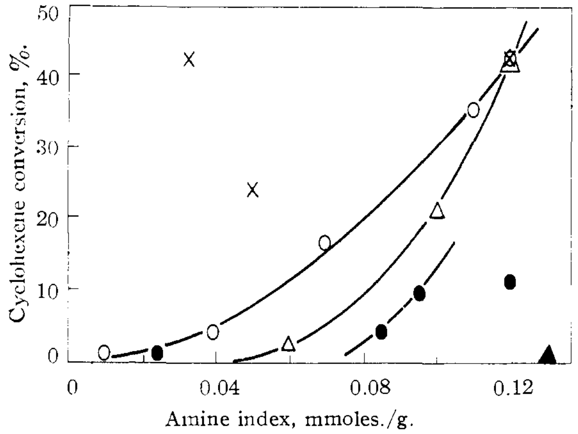

Fig. 4.—Cyclohexene conversion (350°, HLSV 2.0) *vs.* acidity; aluminas: O, NaOH impregnated; ●, from potassium aluminate; △, NaCl impregnated; ▲, from sodium aluminate; ×, from isopropoxide.

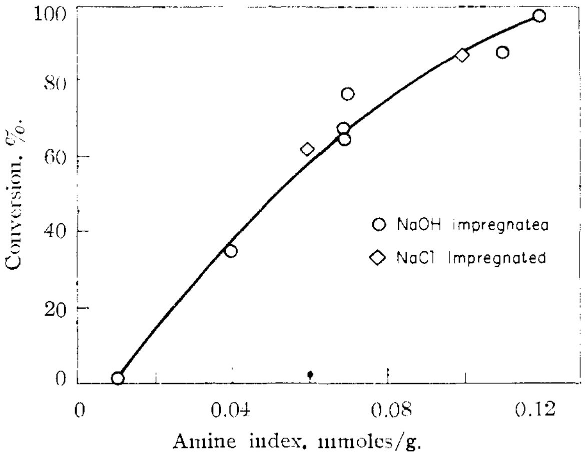

Fig. 5.—Conversion of 3,3-dimethyl-1-butene (350°, HLSV 2.0) *vs.* acidity; alumina from isopropoxide: O, NaOH impregnated; ◇, NaCl impregnated.

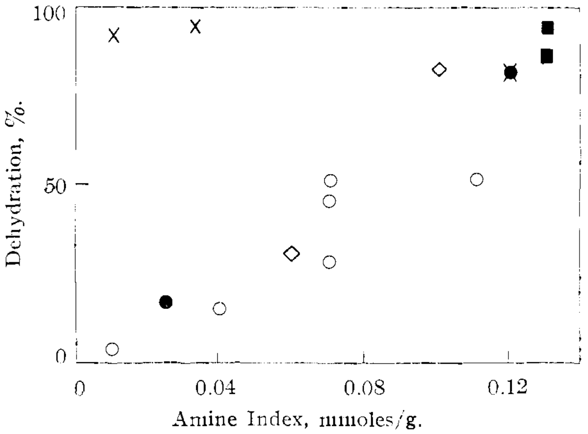

Fig. 6.—Dehydration of 1-butanol (350°, HLSV 2.0) *vs.* acidity; alumina: ×, from isopropoxide; ●, from potassium aluminate; ■, from sodium aluminate; O, NaOH impregnated; ◇, NaCl impregnated.

of five between the apparent acidities as determined by chemisorption of ammonia[11] and trimethylamine (present study) is reasonable.

D. Amine Index and Catalytic Activity.—It is one of the purposes of the present investigation to determine whether the amine index of aluminas can give a true picture of their catalytic activity.[20,38,41a,b]

The correlations between amine index and catalytic activities of aluminas for isomerization and dehydration are given in Figs. 3, 4, 5 and 6. From the results obtained the following general conclusions can be drawn: a. There is a satisfactory correlation between catalytic activity and amine index for catalysts from the same source[42]; *both measure "acidity"* (Figs. 3, 4 and 5). b. There is no satisfactory correlation between catalytic activity and amine index of aluminas obtained from different sources (Figs. 4 and 6).

These seemingly conflicting results are due to the heterogenicity of the surface of aluminas, which contain centers of different acid strength. Since catalytic activity is known to depend on acid *strength* and amine chemisorption apparently does not depend on acid strength, a direct correlation can be expected only when the acid strength distribution of the acid centers on the different aluminas is the same.

Figure 4 indicates that at the same amine index (same number of acid sites) the sites are stronger in the case of sodium hydroxide (higher conversion of CH), weaker in the case of sodium chloride impregnation, and even weaker in the catalyst prepared from potassium aluminate. This is in good agreement with the conclusion reached from the

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sponding to a monolayer (point "B") and the surface area by nitrogen adsorption one obtains an effective area of the trimethylamine molecule of 38 A². This compares with the value of 32 A². calculated [W. E. Garner, "Chemistry of the Solid State," Butterworths Scientific Publ., London, 1955, p. 96] from the density of liquid trimethylamine [E. Swift, Jr., and H. P. Hochanedel, THIS JOURNAL, **67**, 880 (1945)].

[41] (a) T. H. Milliken, Jr., G. A. Mills and A. G. Oblad, *Disc. Faraday Soc.*, **8**, 279 (1950); (b) C. J. Plank, *Anal. Chem.*, **24**, 1304 (1952).

[42] The 400° calcined alumina (Fig. 3) has low catalytic activity in relation to trimethylamine adsorption. The relatively large amount of water present on this catalyst apparently inhibits the catalytic reaction without interfering appreciably with amine chemisorption.

isomerization of 3,3-dimethylbutene where the selectivity increased in the same order (Table II): NaOH < NaCl < K-aluminate. Thus, 3,3-DMB gives the same information as the more tedious method of determining total acidity with trimethylamine and strong sites with cyclohexene. *Trimethylamine chemisorption method alone is of no value for predicting catalytic behavior of unknown aluminas.*

The fact that satisfactory relations between amine adsorption measurements and catalytic activities were obtained with cracking catalysts,[13a,20,38,39,41,43] indicates that either these catalysts do not differ greatly in their acid strength or that all the sites on silica–alumina are sufficiently strong acids to be catalytically active.

E. Nature of Acidity. (1) **Brönsted Acidity.**—Synthetic cracking catalysts and natural clays give the acid color with a variety of indicators.[12,21,38] On the other hand, alumina gives no color change with any of the indicators (ref. 13 and our results). This is surprising, since the activity for isomerization of cyclohexene shown by pure alumina classifies it as a relatively strong acid. Several reasons might be cited for this apparent discrepancy. If one assumes that the catalytic activity of alumina is due to protonic acids on the surface, then it is conceivable that alumina is a strong acid only at the high temperatures of the catalytic reactions, but not at room temperature where the color tests are made. However, performing the color test in refluxing *o*-xylene (b.p. 144°) did not give the acid color with neutral red. Thus it appears that Brönsted acids on alumina, if present at all, are of very low acid strength. The same conclusion was reached from the failure of alumina to undergo cation exchange with ammonium acetate.[9,18]

(2) **Lewis Acidity.**—The catalytic acidity of alumina could also be due to the presence of Lewis acid sites.

In the present study, evidence has been obtained that the change of color, which certain compounds undergo when adsorbed on alumina or silica alumina, is due to the presence of Lewis acid sites on the surface of the solid catalysts.

The following indicators were used: crystal violet leuko base (I), malachite green leuko base (II), *p,p'*-methylidenebis-[N,N-dimethylaniline] (III) and phenolphthalein (IV). They were purified by repeated crystallizations from ethanol (I and III) or benzene (II). Compounds I–III are slowly oxidized by air, especially in solution, to produce the corresponding carbinol bases, which on acidification with acetic acid produce the highly colored salts. Consequently, the compounds were purified until a solution in acetic acid stayed completely colorless. For the color tests, fresh solutions in dry benzene were used. Unless specified otherwise, the color tests were made by placing about 0.3 g. of the solid catalyst either in powdered or in pelleted form into a test-tube, adding 1 ml. of dry benzene and then adding 0.5 ml. of a 0.5% solution of indicator in benzene (saturated solution in benzene in the case of IV). The samples were generally calcined for two hours at 500° immediately before use.

(a) **Triphenylmethane Derivatives.**—A pure alumina catalyst, prepared from aluminum isopropoxide and calcined at 700° (cat. 12, Table I), gave the following colors with: I: blue after 10 sec., changing to violet-blue after 10 min.; II: green after 10 sec., slowly increasing in intensity, bluish-green color developed fully after 15 min.; III: pale green after 1 min., bluish-green after 30 min. Thus, the difficulty to form color increases from I to III.

The same colors, yet more intense, were produced by silica–alumina, silica–magnesia, aluminum chloride and stannic chloride, but not by boron fluoride, boron fluoride–hydrogen fluoride, concentrated sulfuric acid, silicophosphoric acid, aluminum isopropoxide, and α-alumina. They were likewise not given by those alumina catalysts which had been found to be inactive for the isomerization of cyclohexene (catalyst 17, 21 and 24). Catalyst 11 (2), containing weak acid sites, gave the blue color with I, but only a pale green color with II and no color with III. Of the impregnated catalysts, all except those with the highest concentrations of sodium (9-6 and 10-3) gave the expected colors with I, II and III. Alcoa alumina (cat. 23) gave quite intense colors in a short time.

Exposure of the catalysts to the humidity of the atmosphere before testing inhibited the development of color in the aluminas. The active centers apparently are poisoned by the strong adsorption of water which is removed by heating at high temperatures.

A fresh surface can also be formed by crushing the solid. Thus, a pellet of pure alumina, which had not been freshly calcined, gave no color with a solution of crystal violet leuco base. When the pellet was crushed with a glass rod while it was still covered with the solution, a violet-blue color immediately formed. Addition of water now, however, had no effect. When a drop of concentrated sulfuric acid was added, the color changed to green; more sulfuric acid produced a yellow color. Additions of aqueous ammonia or sodium acetate brought the color back to green and then to violet.

These observations clearly indicate that when a molecule like crystal violet leuco base (I) is adsorbed on alumina, it undergoes not only a reversible physical change in the sense of Weitz, *et al.*,[44] or de Boer, *et al.*,[45] but rather an irreversible chemical change.

The nature of the color produced, and the behavior toward acids, points to the formation of the corresponding color salts: By removal of a hydride ion from the central carbon of I, the crystal violet ion A is formed, which owes its violet color to resonance between three identical structures A'. If the electron pair on one of the dimethylamino groups is tied up by protonation, the resonance system (B) typical for the malachite green ion C is formed. A similar conjugated system is produced from II or III by hydride removal. Fur-

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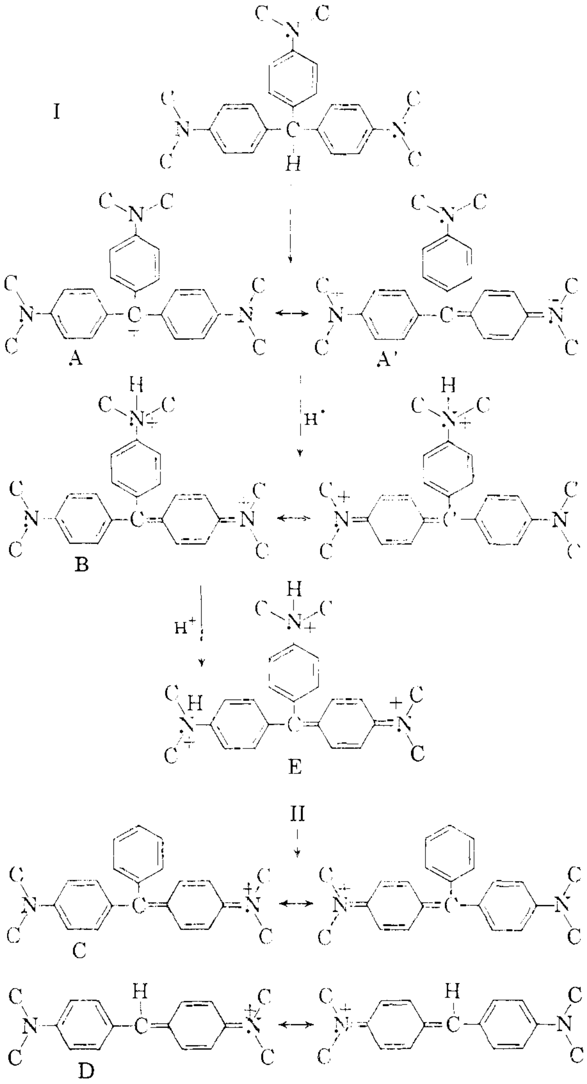
(43) V. C. F. Holm, G. C. Bailey and A. Clark, *J. Phys., Chem.*, **63**, 129 (1959).

(44) E. Weitz, F. Schmidt and J. Singer, *Z. Elektrochem.*, **46**, 222 (1940); **47**, 65 (1941), and references cited there.

(45) J. H. de Boer and G. M. M. Houben, *Proc. Koninkl. Nederland. Akad. Wetenschap.*, **54B**, 421 (1951); *C. A.*, **46**, 10875 (1952).



ther protonation of B ties up a second dimethylamino group to produce the yellow ion E.

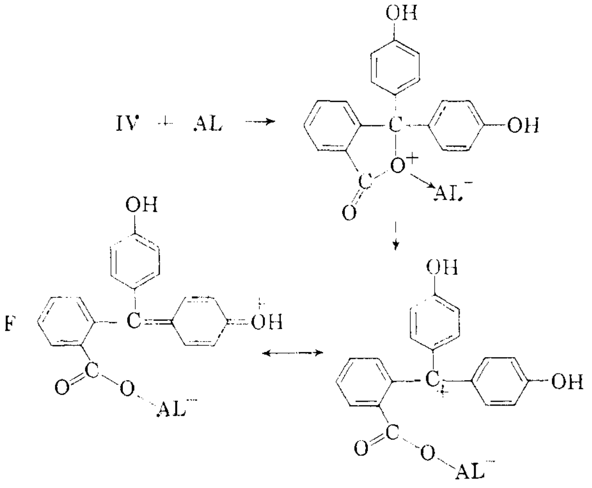
There are several ways in which ions such as A, C and D can be formed from their corresponding leuco bases.

Oxidation by air is possible and does take place slowly. A solution of I in benzene stays colorless when boiled for 15 minutes. In an atmosphere of carbon dioxide, no color was formed within one hour. With the solid catalysts mentioned above, however, the color formation even proceeded in an atmosphere of carbon dioxide or nitrogen, using carefully degassed solutions. It appears that air oxidation is not responsible for the observed color formation.

More difficult to eliminate is oxygen on the surface. It is known that dehydrated silica gel has oxidizing properties, probably due to the presence of chemisorbed oxygen in the form of O_2^-, an unstable superoxide ion, as was observed by Weyl,[46] and recently by Bentur[47] and Krasil'nikov.[48] Indeed, silica gel oxidized the leuco bases I and II to crystal violet (A) and malachite green (C), respectively. It also formed free iodine from aqueous potassium iodide. However, it is believed that in the case of alumina, the formation of color salts from the leuco bases is *not* due to similar oxidizing properties. First of all, preadsorbed water strongly interferes with the color formation on alumina, but not on silica. Second, there is no indication of an oxidation of iodide to iodine by alumina. Thirdly, hydrogen treatment destroys the ability of silica, but not that of alumina, to form crystal violet from I.

It is believed that the formation of A from I is a result of a direct hydride abstraction by the Lewis acid centers on the surface of alumina. Typical Lewis acids, like aluminum chloride and stannic chloride, produce the same effect, whereas Brönsted acids, like concentrated sulfuric acid and hydrochloric acid, dissolve I under formation of colorless salts. From these solutions, the unchanged leuco base can be recovered by dilution with water. The failure of BF_3-gas in benzene to produce any color from I is unexpected. A possible explanation is that boron fluoride forms a strong complex with the nitrogen atoms of the dimethylamino groups of I, a reaction which might not be possible for the sterically hindered Lewis sites on alumina. Steric hindrance is known to prevent the formation of stable complexes between triphenylboron and dimethylaniline,[49] but not between triphenylboron and aniline.

(b) **Phenolphthalein.**—It was found that phenolphthalein was adsorbed on alumina with a red color of a shade distinctly different from the well-known purple color of IV in basic media. It is believed that the lactone ring of IV is opened by the Lewis acid sites (AL) of the catalyst to form the red color salt F.



Analogous reactions of phenolphthalein or related compounds have been reported to occur with aluminum chloride,[50] stannic chloride,[50,51 -c] boron

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(46) W. A. Weyl, "A New Approach to Surface Chemistry and to Heterogeneous Catalysis," The Pennsylvania State College, State College, Penna., 1951, p. 25.

(47) S. Bentur, *Bull. Research Council Israel*, **7B**, 16 (1957); *C. A.*, **52**, 6890 (1958).

(48) K. G. Krasil'nikov, V. F. Kiselev and E. A. Sysoev, *Doklady Akad. Nauk S.S.S.R.*, **116**, 990 (1957); *C. A.*, **52**, 6889 (1958).

(49) E. Krause, *Ber.*, **57**, 813 (1924); see also H. C. Brown and M. D. Taylor, THIS JOURNAL, **69**, 1332 (1947).

(50) K. H. Meyer and H. Hantzsch, *Ber.*, **40**, 3479 (1907).

(51) (a) R. V. Rice, S. Zuffanti and W. F. Luder, *Anal. Chem.*, **24**, 1022 (1952); (b) G. N. Lewis and J. Bigeleisen, THIS JOURNAL, **65**, 1144 (1943); (c) G. Sachs and L. Ryffel-Neumann, *ibid.*, **62**, 993 (1940).

trichloride,[51b] fuming sulfuric acid[51b] and calcium and barium fluoride.[52] It was found that boron fluoride in benzene also produced an insoluble red precipitate. According to Kortüm,[53] all these reactions can be considered Lewis acid–base reactions.

There is a pronounced relationship between the sensitivity of the samples toward water and the strength of their Lewis acid sites. Silica–alumina gave crystal violet from I even after it was soaked with water, while alumina is rendered inactive by 5 minutes exposure to the humidity in the atmosphere. Similar observations were made by Kortüm.[53]

(3) **Conclusions.**—The present study shows that the intrinsic acidity of alumina, which manifests itself in certain catalytic reactions, can indeed be measured by chemical means. There is a good correlation between catalytic activity and the color formation. The leuco bases of crystal violet and malachite green are sensitive indicators of Lewis acid sites existing on the surface of alumina. However, their sensitivity toward oxidation requires some precaution. Test substances of the phenolphthalein type do not have this limitation.

Catalysts which are not active for the isomerization of cyclohexene give no color with IV when freshly calcined (5 hours at 500°), even if they contain sizable amounts of alkali. The basic aluminas do give a red color with phenolphthalein when they contain larger amounts of water. The two types of color are readily distinguished: adding water to the colored sample causes a slow fading of color in the case of the truly acid catalysts, while the basic aluminas give an intense purplish red color in the water layer. Substituting the hydroxyl group in IV by methoxy groups should eliminate this difficulty altogether. It should certainly be possible to select from the rich resources of organic chemistry a series of indicators which combine sensitivity with specificity.

All the alumina samples gave a positive test for acidity with I, II and IV when crushed in the presence of the indicator solutions. This shows that the nascent surfaces contain Lewis acid sites.

Acknowledgment.—The authors extend their appreciation to the California Research Corporation for the analyses of aluminas, to Dr. R. A. Van Nordstrand for the advice given in the interpretation of the X-ray data and to Mr. Ed M. Lewicki for carrying out some of the experimental work.

Evanston, Ill.

[52] J. H. de Boer, *Z. Elektrochem.*, **44**, 488 (1938).

[53] G. Kortüm, J. Vogel and W. Braun, *Angew. Chem.*, **70**, 651 (1958).

[Contribution from the Ipatieff High Pressure and Catalytic Laboratory, Department of Chemistry, Northwestern University]

Alumina: Catalyts and Support. II.[1a] Hydroisomerization and Aromatization of Hydrocarbons in the Presence of Molybdena–Alumina Catalysts. Effect of Aluminas[1a,b]

By Herman Pines and Gaston Benoy[2]

Received June 11, 1959

Extensive research has been reported on the catalytic action of molybdena–alumina hydrocarbons. In none of the reported investigations was there a mention made that alumina *per se* may have intrinsic acidic properties which may influence the hydroisomerization and aromatization properties of the molybdena–alumina catalyst. The object of this study was to determine the catalytic effect of molybdena–alumina catalysts having aluminas of increasing acid character. The catalytic activity was tested using as model hydrocarbons: *n*-octane, methylcyclopentane, cyclohexane, 1,2- and 1,4-dimethylcyclohexane and ethylcyclohexane. In each case it was noticed that with increasing acidity of the alumina the extent of hydroisomerization increases. The hydroisomerization of 1,2-dimethyl-C^{14}-cyclohexane was studied. Ethylcyclohexane upon hydroisomerization yielded *n*-propylcyclopentane as the principal single hydrocarbon. The mechanism of hydroisomerization is discussed.

Extensive research has been reported in the literature on the catalytic action of the oxides of transition metals supported on alumina. It has been shown that molybdena–alumina catalyst in the presence of hydrogen under pressure aromatizes and/or hydroisomerizes saturated hydrocarbons.[3–7]

In none of the cited investigations was it indicated that alumina *per se* may have intrinsic acidic properties which might influence the hydroisomerization and aromatization properties of the molybdena catalyst. It was, however, recognized that the incorporation of small amounts of silica to alumina increased the hydroisomerization activities of the molybdena–alumina catalyst and this was attributed to the acidity of the support.[8,9]

Pines and Haag[1] have demonstrated that the catalytic behavior of alumina depends upon its method of preparation. Alumina prepared by the hydrolysis of aluminum isopropoxide showed

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[1] (a) For paper I see H. Pines and W. O. Haag, This Journal, **82**, 2471 (1960). (b) Presented in part before the Gordon Research Conferences in Catalysis, June 23–27, 1958, New London, N. H.

[2] Vladimir N. Ipatieff Postdoctoral Fellow, 1957–1958. Present address: Gevaert Photo-Producten, Mortsel (Antwerpen), Belgium.

[3] A. S. Russell and J. J. Stokes, Jr., *Ind. Eng. Chem.*, **38**, 1071 (1946).

[4] A. S. Russell and J. J. Stokes, Jr., *ibid.*, **40**, 520 (1948).

[5] G. M. Webb, M. A. Smith and C. H. Ehrhardt, *Petrol. Processing*, **2**, 836 (1947).

[6] B. S. Greensfelder, R. C. Archibald and D. L. Fuller, *Ind. Eng. Chem.*, **43**, 561 (1945).

[7] B. S. Greensfelder and D. L. Fuller, This Journal, **67**, 2171 (1945).

[8] A. Clark, M. P. Matuszak, N. C. Carter and J. C. Cromeans *Ind. Eng. Chem.*, **45**, 803 (1953).

[9] R. M. Dobres, D. S. Henderson, S. J. Lucki and B. W. Rope in "Catalysis," Vol. 6, edited by P. H. Emmett, Reinhold Publishing Corp., New York, N. Y., 1958, p. 513.