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A Study of the Water Content of a Silica-Alumina Catalyst and its Component Oxides

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The water content of silica-alumina cracking catalyst, of silica gel and of activated alumina has been measured over the temperature range 100 to 500° as a function of the prior exposure to water vapor, and for the silica-alumina catalyst as a function of the presence or absence of base-exchanged potassium or barium ions. The residual water content after evacuation for several hours at 500° was 0.79, 0.64 and 0.73%, respectively, for silica-alumina catalyst and for samples base exchanged with 0.58 milliequivalent of K⁺ or 0.46 milliequivalent of Ba⁺⁺ per gram. Water retained by exposing samples to a few mm. of water vapor at 110° for an hour after an initial evacuation at 500°, and then evacuating them for an hour at this same temperature was found to be 0.2% by weight for silica-alumina catalysts, 0.6% for activated alumina and ~0.0% for silica gel. The results are interpreted as indicating that most of the active sites on silica-alumina catalysts are, after an evacuation at 500°, in the form of Lewis acids rather than Brönsted acids.

During the last five years, a number of papers²⁻⁴ have been published relative to the exchange of D₂O and of H₂O¹⁸ with silica-alumina cracking catalysts and also relative to the exchange of the light hydrogen of typical hydrocarbons with the D₂O, OD and D⁺ content of deuterated cracking catalysts.⁵⁻⁷ These experiments have thrown a great deal of light on the possible structure of the surface of a cracking catalyst and on the rapidity of the diffusion of hydrogen as H₂O (OH groups or H⁺) through the body of the catalyst. They have also given indications that the nature of the surface of a cracking catalyst depends greatly on the prior treatment, the water content⁸ and the conditions under which the water is added to or taken from a catalyst sample. In further elucidating the behavior of cracking catalysts, the work described in the present paper recounts in detail experiments on the water content of a cracking catalyst in the temperature range 150 to 500° as a function of the

detailed temperature and water vapor cycle to which the sample was subjected. It will be followed by another paper in which the exchange of the hydrogen of isobutane with a deuterated catalyst is determined as a function of this same temperature-water vapor cycle.

Experimental

Materials.—Five catalysts were studied in the present investigation. These were (1) a standard synthetic silica-alumina cracking catalyst (SA), (2) a potassium base-exchanged synthetic silica-alumina catalyst (KSA), (3) a barium base-exchanged synthetic silica-alumina catalyst (BSA), (4) a silica gel (S) having porosity and surface area similar to the silica-alumina catalysts and (5) a commercial activated alumina (A). Some physical properties of these substances are presented in Table I.

The silica-alumina catalyst was obtained from the Houdry Process Corporation and was designated by them as M-46. This catalyst has the approximate composition 87.5% silica, 12.5% alumina on a water-free basis. It was treated with water for several days at 30° and dried at 110° before use. The base-exchanged catalysts were prepared by contacting M-46 with 1.5 molar aqueous solutions of the respective metal acetates for several days, washing thoroughly and drying at 110°.

The silica gel was prepared by the hydrolysis of ethyl orthosilicate, treatment with ammonia to increase the average pore size,⁹ and calcination at 600°. It was contacted with water for several days at 30° and dried at 110° before use. Spectrochemical analysis of this substance showed it contained less than 0.1% alumina.

The alumina sample was obtained from the Harshaw Chemical Company. After being calcined at 800°, it was treated with water at 30° for several days and dried at 110°. X-Ray examination of the calcined material indicated the

(1) (a) American Cyanamid Co., Stamford, Conn.; (b) John Hopkins University, Baltimore, Md.

(2) G. A. Mills and S. G. Hindin, *THIS JOURNAL*, **72**, 5549 (1950).

(3) A. G. Oblad, S. G. Hindin and G. A. Mills, *ibid.*, **75**, 4096 (1953).

(4) S. M. Karpacheva and A. M. Rozen, *Doklady Akad. Nauk. SSSR*, **75**, 55, 239 (1950).

(5) R. C. Hansford, "Advances in Catalysis," Vol. IV, Academic Press, Inc., New York, N. Y., 1952, p. 24.

(6) R. C. Hansford, P. G. Waldo, L. C. Drake and R. E. Honig, *Ind. Eng. Chem.*, **44**, 1108 (1952).

(7) S. G. Hindin, G. A. Mills and A. G. Oblad, *THIS JOURNAL*, **73**, 278 (1951).

(8) R. C. Hansford, *Ind. Eng. Chem.*, **39**, 849 (1947).

(9) W. B. Spencer, Dissertation, University of Pittsburgh, 1950.

TABLE I
 CATALYST PROPERTIES

Base catalyst	Catalyst				
	SA Silica- alumina	KSA Silica- alumina	BSA Silica- alumina	S Silica	A Alumina
Concn. base exchange ion, meq./g.	...	0.58K ⁺	0.46Ba ⁺⁺
BET surface area, m. ² /g.	249	243	244	320	80
Pore vol., cc./g.	0.41	(0.41)	(0.41)	0.40	..
Av. pore radius, Å.	33	(33)	(33)	25	..

pattern of χ -alumina. This substance is an intermediate in the dehydration of hydrargillite to γ -alumina.¹⁰ Spectrochemical analysis indicated silica and alkali metal oxides present in the range 0.1 to 1% each.

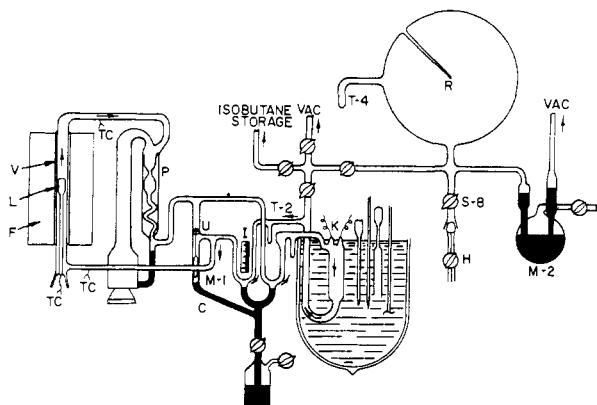


Fig. 1.—Isotope exchange system.

Deuterium oxide was obtained from the Stuart Oxygen Company and was reported by them to be at least 99.8% D₂O. The heavy water was charged, as required, to the evacuated water reservoir of the hydrogen exchange apparatus where it was frozen at -78° and evacuated several times to remove dissolved air and carbon dioxide. Laboratory distilled water was considered to consist of pure H₂O. It was charged, as required, to the evacuated water reservoir of the hydrogen exchange apparatus and purified as for D₂O.

Apparatus.—The isotope exchange equipment was used in three ways (1) to measure hydrogen exchange between water vapor and catalyst, (2) to measure volumetrically water adsorption on, and desorption from, the catalyst under various conditions in conjunction with water content studies and (3) to measure hydrogen exchange between isobutane and catalyst. The last application will be described in a later publication.¹¹

The all-glass apparatus is illustrated in Fig. 1. The usual vacuum facilities were provided (not shown). Water vapor (either H₂O or D₂O, as required) was stored in the thermally insulated vessel R. Liquid water was introduced from pipet H (shown attached in the drawing) to the evacuated reservoir through stopcock S-8. Air and carbon dioxide were separated from water vapor by repeated freezing and evacuation of the water in the side tube T-4. Vessel R was provided with a thermometer well. The pressure of water vapor was measured at manometer M-2 by use of a traveling microscope.

The main part of the exchange equipment was the gas circulation system, consisting of mercury vapor gas circulation pump P, mercury cut-off C, cell K of the hot wire gage and reactor tube V containing catalyst holder L. The normal direction of flow through the system is indicated by the arrows.

The gas circulation pump was the mercury jet type and was capable of a circulation rate of about 500 cc. per minute at a gas pressure of 20 mm. The cooling water used in the condenser was controlled at 32° to prevent condensation of the vapor in the gas circulation system.

The mercury cut-off C served a dual purpose (1) with the

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

(11) See also R. G. Haldeman, Thesis, University of Pittsburgh, 1953.

mercury level in the upper two U-tubes, a sample of gas was trapped for analysis in the cell and the circulating gas bypassed through float-operated ball check valve U. (2) In this closed position, the gas in the cell could be frozen at -78° or -195° , and the absolute pressure of the gas in the circulation system could be estimated to 0.1 mm. at scale I.

The hot wire gage was used for the analysis of samples H₂O-D₂O vapor. Its specifications and use as an analytical tool are described elsewhere.¹² The volume of the cell (K) and associated transfer lines (*i.e.*, the cell system) up to a fixed level in the mercury cut-off was accurately known and served as a buret for volumetric measurements.

The reactor tube passed through a thyatron-controlled furnace which could be maintained at a constant temperature in the range 100 to 500° to about $\pm 0.2^\circ$. The catalyst sample was held in a basket in the heart of the furnace. The basket was supported on a small diameter tube, which served also as a thermowell.

Procedure. Hydrogen Exchange between Water Vapor and Catalyst.—The catalyst was first subjected to an appropriate pretreatment, the nature of which will be evident from later discussion. To the evacuated catalyst (0.25–0.5 g.) containing but one hydrogen isotope (A)¹³ about 0.7 mmole of water containing the other isotope (B) was admitted from reservoir R. A pressure of 20–25 mm. was thereby produced in the gas circulation system. The vapor was allowed to circulate, and samples were analyzed periodically with the hot wire gage. In some of the experiments the temperature of the system was raised after a steady gas composition was attained in order to observe the effect of temperature on the equilibrium. The hydrogen of the catalyst involved in the equilibration, expressed as millimoles exchangeable water, E , was calculated as

$$E = RN - S$$

where R is the ratio of isotope A to B in the vapor at equilibrium, N is the number of millimoles of water containing isotope B initially added and S is the number of millimoles exchangeable water associated with the exchange apparatus alone, as determined by appropriate calibration experiments.

Dehydration Experiments.—In the study of the variation of catalyst water content with temperature, a dehydration procedure was frequently used. This technique involved the volumetric measurement of water evolved from the catalyst as a result of an incremental increase in catalyst temperature. The cell of the hot wire gage could be used as a burette in making these measurements. Thus, the temperature of the catalyst, after 1 hr. evacuation, was increased by increments of approximately 100° . The water evolved was frozen out at -78° after each new temperature was reached, then vaporized into the cell and measured by pressure at manometer M-1. Changes in water content could be measured to better than 0.02% by this method.

Results of Hydrogen Exchange Experiments

The analysis as a function of time and temperature of water vapor circulated over catalyst SA, in a typical experiment, is indicated by Fig. 2. Here the catalyst initially containing only light hydrogen was evacuated for 1 hr. at 110° prior to the addition of a measured amount of D₂O vapor. It will be seen that even at 110° a steady vapor composition was reached in a matter of a few hours.

(12) R. G. Haldeman, *Anal. Chem.*, **25**, 787 (1953).

(13) The catalyst could readily be altered to contain all light or all heavy hydrogen by repeated exposure at or above 100° to H₂O or D₂O as required.

Further, as temperature was increased, the vapor composition changed very little. This rapid equilibration of circulating vapor and independence of temperature change was found to occur also over the base-exchanged silica-aluminas and over the component oxides.

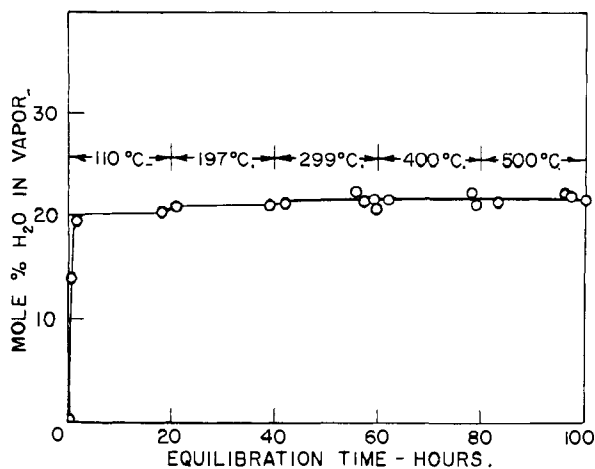


Fig. 2.—Increase in the % H_2O with time in a vapor originally pure D_2O in contact with catalyst SA containing at the start H_2O but no D_2O .

The temperature-water vapor composition data of Fig. 2, calculated as exchangeable water, are plotted in Fig. 3. The calibration data for the walls of the system are also plotted. It will be noted that the exchangeable water attributed to the catalyst is virtually independent of temperature. These data indicate that all the catalyst hydrogen is involved in the equilibration between vapor and catalyst.

Because of the rapid exchange between the added water vapor and the water, hydroxyl groups and protons in the catalyst, the latter could be completely deuterated by repeated exposure to pure D_2O . Experiments in which H_2O was circulated over the deuterated catalyst gave results analogous to those disclosed in Fig. 2 and 3. Further, for a given catalyst pretreatment, the millimoles of exchangeable water obtained by circulating H_2O over the deuterated catalyst agreed within about 0.1% with the same quantity obtained when D_2O was circulated over the catalyst containing only light hydrogen. These results also seem to indicate that all the catalyst hydrogen is involved in the equilibration and that isotope effects are small.

Proof that water contents determined by exchange represented the water equivalent to all the catalyst hydrogen was obtained by calcination of comparable samples to constant weight at 1200° . The results are given in Table II. These data indicate that the exchange technique furnishes a useful method for the *in situ* determination of catalyst water content. In fact, it is thought that the exchange method is capable of providing catalyst water contents to about 0.1% absolute.

Temperature-Composition Data.—Temperature-composition data were obtained for the five catalysts under study. The data for catalyst SA

TABLE II
WEIGHT % WATER AS H_2O

Catalyst	By exchange	By wt. loss on calcination at 1200°
SA	3.15	3.4 ^a
SA	0.79	0.7
KSA	2.42	2.3
BSA	2.92	3.1
S	0.84	0.9
A	0.94	1.1

^a Further heating to 1500° to constant weight produced a negligible change in weight.

are plotted in Fig. 4. In this plot are given five dehydration curves, each starting from a reproducible condition of catalyst hydration (letters A to E). The significance of these states is considered below.

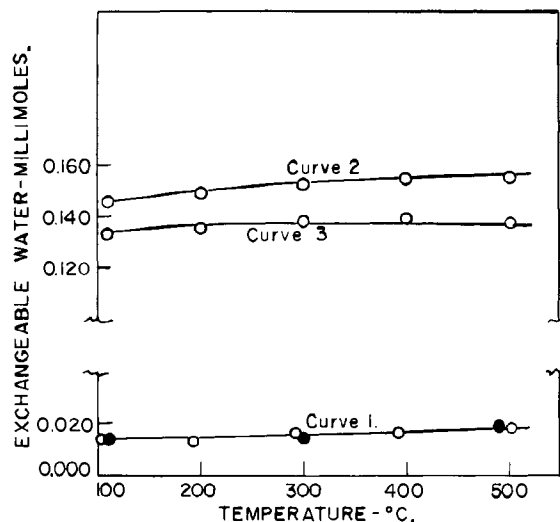


Fig. 3.—Variation of exchangeable water of catalyst SA and system with temperature; \circ , D_2O circulated; \bullet , H_2O circulated. Curve 1 is for the glass system without the catalyst; curve 2, the glass system plus 0.16 g. of catalyst SA; curve 3, the corrected curve for 0.16 g. of catalyst SA.

The points at A represent the water content of the catalyst as determined by exchange after it was soaked in water for a day, then evacuated at 110° for 1 hr. The points at B represent the water content of the catalyst after it had been cooled to 110° from 500° in 20–25 mm. of water vapor and evacuated for 1 hr. at 110° . The points at C represent the water content of the catalyst after it had been cooled from 500 to 30° in water vapor, exposed to water vapor at a relative pressure P/P_0 of about 0.7 for several days, then heated to and evacuated at 110° for 1 hr. The points at D were obtained by a process analogous to those at C, except that the P/P_0 for rehydration was approximately unity rather than 0.7. Finally, the point at E represents the water content of the catalyst after it has been evacuated at 500° , cooled to 110° *in vacuo*, exposed to excess water vapor at several millimeters pressure for 1 hr., then evacuated for 1 hr. at 110° . The water picked up by this cycle at 110° and not removed by the 1 hr. evacuation will, for convenience, be described as being "fixedly adsorbed." Its magnitude is independent of the pressure of exposure, over a con-

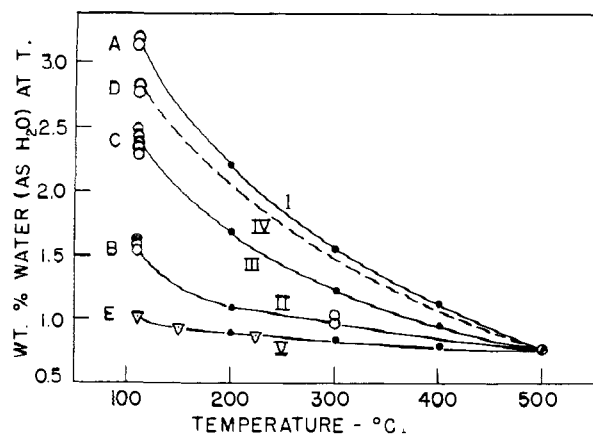


Fig. 4.—Water content *vs.* temperature for catalyst SA: ○, exchange water measurement; ●, dehydration measurement; ▽, fixed adsorption measurement; A, initial state of catalyst after evacuation at 110°; B, after cooling from 500 to 110° in water vapor and evacuating at 110° for 1 hr.; C, after rehydration at $P/P_0 \sim 0.7$ at 30° and evacuating at 110° for 1 hr.; D, after rehydration at $P/P_0 \sim 1.0$ at 30° and evacuating at 110° for 1 hr.; E, after "fixed adsorption" at 110°. Curves I to V are dehydration curves.

siderable range, as indicated by the data of Fig. 7 for measurements made at 150°.

The dehydration curves starting from points A to E form a family of curves which coalesce at 500° at a water content of about 0.8%. (The value was found also by the exchange method at 500°.)

It is interesting to note that the water expelled along curve I, when the catalyst was heated to 500° can be largely replaced by rehydration at 30° and high relative pressure of water vapor. In fact, the extent of rehydration is roughly proportional to the relative pressure.

The temperature-composition data for the base-exchange silica-aluminas, KSA and BSA, were quite similar to those of the unexchanged catalyst and need not be reproduced here. A few qualitative remarks will suffice. The water contents of KSA and BSA at 500° were 0.64 and 0.72%, respectively. Curve II for catalyst KSA was

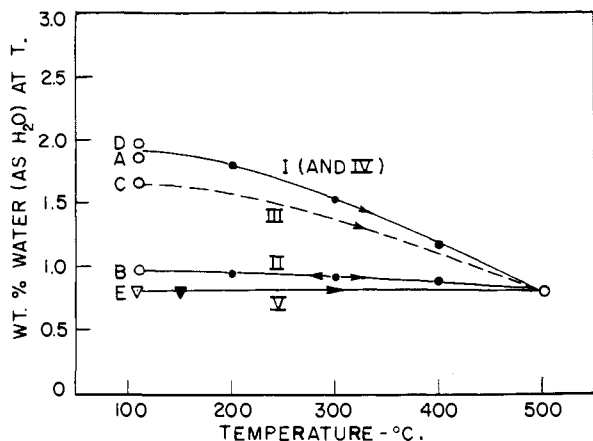


Fig. 5.—Water content *vs.* temperature for catalyst S (an ammonia-treated silica gel). For key to curve designation, see legend of Fig. 4.

nearly identical to that for SA, whereas curve II for catalyst BSA was somewhat steeper than that for SA. For the three substances, curve V was of identical slope. The spread between curves I and V was not as great for KSA and BSA as for SA.

The temperature composition data for silica gel S are represented by Fig. 5. The curves have the same meaning as for catalyst SA. Gel S had approximately the same surface area, the same average pore diameter and virtually the same kind of dependence of water content on pretreatment as that of the silica-alumina catalyst. However, the shapes of the various curves are markedly different from their silica-alumina counterparts, particularly in the low temperature region where, for a given increment of temperature, the silica gel evolves relatively little water in comparison with that given off by the silica-aluminas. It should be noted that gel S "fixedly adsorbed" virtually no water at 110 and 150° on the catalyst evacuated at 500°. The effect of pressure during exposure of catalyst to water vapor on the fixed adsorption at 150° is shown in Fig. 7.

The activated alumina (A) showed relatively little dependence of water content on pretreatment conditions. The results are given in Fig. 6. Most of the water evolved from the catalyst in its initial state (after soaking in water and evacuation at 110°) on heating to 500° (curve I) was found to be reabsorbed on cooling to 110° in water vapor and evacuation at that temperature. Further, fixed adsorption at 110 and 150° was strong on the catalyst evacuated at 500°. The effect of pressure during exposure to water vapor on fixed adsorption at 150° is shown in Fig. 7.

Discussion

During the past ten years, a great many papers¹⁴⁻¹⁸ have been published relative to the question of the types of acid sites that exist upon

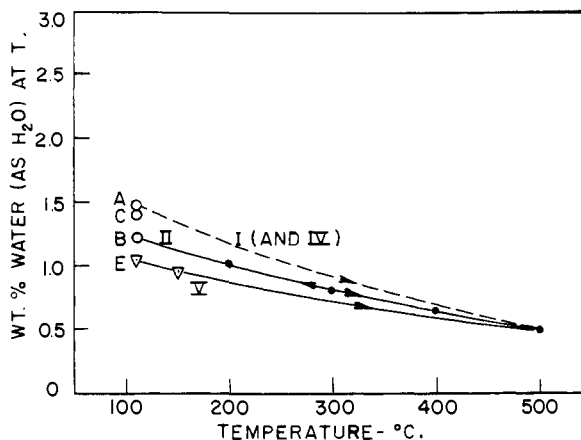


Fig. 6.—Water content *vs.* temperature, catalyst A (Harschaw activated alumina). For key to curve designation, see legend to Fig. 4.

(14) T. H. Milliken, Jr., G. A. Mills and A. G. Oblad, *Disc. Faraday Soc.*, **8**, 279 (1950).

(15) C. L. Thomas, *Ind. Eng. Chem.*, **41**, 2564 (1949).

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

(17) A. Grenall, *Ind. Eng. Chem.*, **41**, 1485 (1949).

(18) R. L. Hansford in "Advances in Catalysis," Vol. IV, Academic Press, Inc., New York, N. Y., 1952, p. 1.

silica-alumina cracking catalysts and that are responsible for the catalytic activity of these materials. Two general pictures of these surfaces have evolved. One group of workers¹⁷ has suggested that an aluminum ion is able to coordinate with four oxygen ions and thus form a complex with silica such that one proton per coordinated aluminum ion is necessary to preserve electrical neutrality. This picture of the silica-alumina catalysts would postulate the existence of protons on the surface of the silica-alumina complex as the active centers for catalytic cracking and for other reactions capable of being catalyzed by the silica-alumina catalysts. Another picture has been presented by Milliken, Mills and Oblad.¹⁴ They suggest that the silica-alumina structure in which the aluminum ions are coordinated with four oxygen ions is unstable in the acid form; they propose that, in the absence of added bases or hydrocarbons, the aluminum ions in silica-alumina catalysts are actually six coordinated as they are in some of the various forms of alumina. At the interface between silica and the six coordinated alumina groups, they believe a rapid rearrangement of atoms can take place whenever the silica-alumina groups are approached by a base such as quinoline or ammonia or even by hydrocarbon molecules. In other words, they visualize the alumina as being present in the usual calcined silica-alumina as a Lewis acid rather than a Brönsted (proton donating) acid. No general agreement exists in the literature as to which of these two pictures is more nearly correct.

The work outlined in the present paper, though not conclusive in distinguishing between these two possible pictures, does contribute several new bits of experimental data that seem to have a definite bearing on the question. These may be summarized as follows.

(1) The isotope exchange experiments as illustrated for example in Fig. 4 seem to establish that this typical silica-alumina catalyst retains about 0.8% water after it is evacuated at 500°. This is in good agreement with similar values published by other authors.^{8,14} In view of the fact that a gram of a catalyst containing 12.5% aluminum oxide consists of about 14.6 mmoles of SiO₂, 1.2 mmoles of Al₂O₃ and 0.45 mmole of H₂O, it is evident that even if all of the hydrogen of this water were present as protons, it would not be sufficient to furnish one proton for each aluminum atom or ion in the catalyst. It seems necessary, therefore, to admit at once that at least some of the aluminum must be incorporated in the silica-alumina catalyst in some form other than the one proposed by the first picture above in which the aluminum is coordinated with four oxygens, each such coordination group being accompanied by a single proton.

(2) A comparison of the total water content of the unexchanged silica-alumina catalyst and catalyst KSA (exchanged with potassium ion) and catalyst BSA (exchanged with barium ion) seems to indicate that the sites occupied by potassium and barium ions in the base-exchanged structures would not be occupied by the protons in the

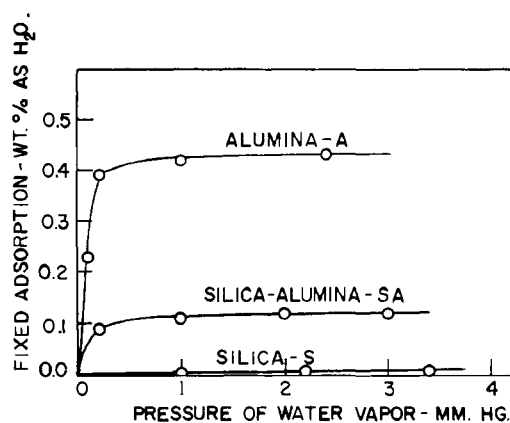


Fig. 7.—Fixed adsorption of water at 150° on silica-alumina, silica and alumina after evacuation at 500°.

absence of these ions after the catalyst has been evacuated at 500°. The basis for this evidence is summarized in Table III. It will be noted that the total water content of catalyst SA, catalyst KSA and catalyst BSA are, respectively, 0.79, 0.64 and 0.73%. In milliequivalent, these water figures interpreted as protons are equivalent to 0.89, 0.74 and 0.84 milliequivalent of hydrogen ions per gram. It is evident, therefore, that the 0.58 milliequivalent of potassium ion in catalyst KSA and the 0.46 milliequivalent of base-exchanged barium in catalyst BSA do not cause a decrease of more than 0.15 and 0.05 milliequivalent of hydrogen ion, respectively. This result certainly seems to suggest that a silica-alumina cracking catalyst evacuated at 500° does not have a very large fraction of acid sites occupied by protons.

TABLE III
EXCHANGE ION AND HYDROGEN CONTENT AT 500°

(1) Catalyst	(2) Exchange ion, meq./g. ^a	(3)	(4) Water content, wt. % as H ₂ O	(5) Hydrogen content, as meq./g. ^a	(6) Total hydrogen equiv., as meq./g. ^b
SA	none	...	0.79	0.89	0.89
KSA	K ⁺	0.58	0.64	0.74	1.32
BSA	Ba ⁺¹	0.46	0.73	0.84	1.30

^a Per gram of SiO₂ + Al₂O₃. ^b The total hydrogen equivalent is the sum of the exchangeable ion and hydrogen contents.

(3) The water content picked up on cooling catalyst KSA or BSA from 500 to 110° and not removed by 1 hr. of evacuation at 110° is the same within experimental error as for catalyst SA both when the exposure to water vapor is continuous during the cooling process from 500 to 110° (such as in Curve 2, Fig. 4, for catalyst SA), and when the exposure to water vapor occurs only at 110° (such for example as in curve 5, Fig. 4, for catalyst SA). This seems to indicate that most of this adsorbed water is picked up by portions of the catalyst other than the particular sites which during a base exchange procedure become occupied by potassium ions or barium ions. It must, however, be admitted that certain small portions of the added water vapor in the case of the SA catalyst must be going to active acid sites. This is clearly demonstrated by the experiments of Hindin, Mills

and Oblad¹⁷ in which the rate of exchange of isobutane with a deuterated cracking catalyst, the rate of isomerization of hydrocarbons over a cracking catalyst¹⁹ or the rate of cracking of hydrocarbons over a cracking catalyst are all increased by as much as twenty-five fold by the addition of as little as 0.05% H₂O or D₂O to a cracking catalyst previously evacuated at 500°. In view of these experimental results, presumably one must conclude that no more than about 0.01 milliequivalent per gram of hydrogen from water (corresponding to $\pm 0.02\%$ maximum difference between "fixed adsorption" of water at 110° on catalyst SA as compared to catalysts KSA and BSA) goes on to the particular Lewis acid sites that, in the base-exchanged catalyst, would be covered with potassium ions or barium ions. This point will be discussed in more detail at the end of the next paper which presents our own extensive measurements on the influence of different types of adsorbed water on the exchange between isobutane and deuterated cracking catalysts.

(4) The data of the present paper seem to require that the picture proposed by Milliken, Mills and Oblad¹⁴ is more nearly representative of the facts than the picture in which it is visualized that the active acid sites are protons located in the neighborhood of four-coordinated aluminum ions in alumina-silica complexes. However, there is certainly no way of precluding the possibility of a small fractional covering of the surface with Brönsted acid sites.

(19) S. G. Hindin, A. G. Oblad and G. A. Mills, *THIS JOURNAL*, **77**, 535 (1955).

A few further items should perhaps be pointed out in connection with the data in the present paper. The results plotted in Fig. 4 and 5 indicate that for both silica gel and silica-alumina catalysts about half of the water removed by evacuation at 500° cannot be restored to the catalysts until they are soaked in liquid water or exposed to a high relative pressure of water vapor at some low temperature. The data suggest that this portion of the water that is taken up by the catalyst penetrates deeply into the tiny crystallites or blocks of amorphous silica or silica-alumina that make up the silica and the silica-alumina catalysts, respectively. Apparently this penetration takes place principally from water held by capillary condensation in the pores of the silica gel or the silica-alumina catalyst. It seems reasonable to assume that much of it can be assigned to the excess silica gel in the silica-alumina catalysts. On the other hand, the "fixedly adsorbed water" indicated by curve 5 of Fig. 4 for silica-alumina and curve 5 of Fig. 6 for alumina can be taken up from the vapor phase by the catalyst at 110° with a sufficiently high heat of adsorption to avoid removal during the subsequent evacuation for 1 hr. at 110°. It should be noted in this connection that the silica gel itself apparently does not take up any "fixedly adsorbed" water. Accordingly, this type of water sorption presumably must be attributed either to the silica-alumina complex or to some residual alumina on the surface of the silica-alumina catalyst.

PITTSBURGH 13, PA.

[CONTRIBUTION FROM THE MULTIPLE FELLOWSHIP OF GULF RESEARCH & DEVELOPMENT COMPANY, MELLON INSTITUTE]

Exchange of Hydrogen between Isobutane and a Deuterated Cracking Catalyst

BY R. G. HALDEMAN AND P. H. EMMETT¹

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The exchange of the hydrogen of isobutane with the deuterium of various deuterated materials has been studied at 150° as a function of their D₂O contents; these materials include silica-alumina, silica gel, alumina and silica-alumina base-exchanged with potassium and barium ions. For silica-alumina evacuated at 500° prior to a test run, the exchange rate at 150° was found to be very small. The exchange rate increased with increasing water content of the solid, going through a maximum at a value which depended upon the prior history of the sample. Water contents greater than this optimum amount caused a decrease in the exchange rate. In general, the total amount of deuterium transferred to the isobutane during a run was found to depend primarily on the temperature of final evacuation of catalyst, regardless of prior history or absolute amount of water in the catalyst. The base-exchanged catalyst and the component oxides were comparatively inert for hydrogen exchange. Apparently, water molecules must be added to or be available at some type of silica-alumina Lewis acid site before isobutane will undergo "activated adsorption" on the catalyst surface.

Introduction

Several groups of workers²⁻⁴ have studied the exchange of hydrogen atoms in hydrocarbons with the deuterium content of deuterated silica-alumina cracking catalysts. They have also demonstrated that the water content of a catalyst has an important bearing on the rate of the exchange reaction. With a view to further elucidating the

structure and behavior of cracking catalysts, we recently explored the sorption of water vapor by silica gel, by alumina and by silica-alumina cracking catalysts.^{4,5} As a continuation of this study, the present paper summarizes our experimental results relative to the rather complex interrelation between the water sorption and the rate of exchange of the hydrogen atoms of isobutane with silica, alumina, active silica-alumina cracking catalysts and silica-alumina catalysts in which K⁺ and Ba⁺⁺ have been incorporated by base exchange.

(1) Johns Hopkins University, Baltimore, Md.
 (2) R. C. Hansford, P. G. Waldo, L. C. Drake and R. E. Honig, *Ind. Eng. Chem.*, **44**, 1108 (1952).
 (3) S. G. Hindin, G. A. Mills and A. G. Oblad, *THIS JOURNAL*, **73**, 278 (1951).

(4) S. G. Hindin, G. A. Mills and A. G. Oblad, *ibid.*, **77**, 538 (1955).

(5) R. G. Haldeman and P. H. Emmett, *ibid.*, **78**, 2917 (1956).