and Oblad[17] in which the rate of exchange of isobutane with a deuterated cracking catalyst, the rate of isomerization of hydrocarbons over a cracking catalyst[19] 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% H_2O or D_2O 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 ±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 Oblad[14] 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-coördinated 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.

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.

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

[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. EMMETT[1]

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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 D_2O 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 workers[2-4] 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.

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[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).

Experimental

Materials.—Research grade isobutane, obtained from the Phillips Petroleum Company, was treated for removal of olefins and moisture by passage at 65° through a bed of silica–alumina catalyst which first had been evacuated at about 400°. Inert gases were separated from the isobutane by repeatedly freezing the hydrocarbon in its storage reservoir at −195° and pumping it. The isobutane so treated was found by infrared examination to be spectroscopically pure.

The catalysts studied were a commercial (Houdry) silica–alumina catalyst, SA; two base-exchanged silica–alumina catalysts, KSA and BSA, which contained 0.58 milliequivalent (meq.) of K^+/g. and 0.46 meq. Ba^{++}/g., respectively, a silica gel, S, of surface area and average pore diameter roughly equal to that of SA and a commercial (Harshaw) activated alumina, A. These catalysts are described in greater detail in the preceding publication.[5]

The D_2O of 99.8% purity was obtained from the Stuart Oxygen Company.

Apparatus.—The apparatus consisted essentially of the gas circulation system previously described[5] with the addition of facilities for the purification, storage, metering and sampling of isobutane.

The isobutane was stored in a five-liter reservoir equipped with a side tube and a mercury manometer. The isobutane charge for an exchange experiment was measured in a doser bulb of about 1500-cc. volume connected to the storage vessel through a mercury cut-off. In use, a pressure of about 19 mm. was obtained in the doser by cooling the side tube of the isobutane reservoir to −78°. Thus, a charge of about 1.5 mmoles was trapped in the doser when the cut-off was closed.

Procedure.—The present experiments involved measurement of the exchange of hydrogen between the completely deuterated catalyst and isobutane of normal isotopic composition. In most experiments, isobutane was circulated for 3 hr. at 65 mm. over 0.5 g. of catalyst at 150°.

Prior to each experiment, the catalyst was subjected to some pretreatment of a type previously discussed by the authors.[5] (The nature of these pretreatments will become evident in later discussion.) The final step of a catalyst pretreatment usually was evacuation for 1 hr.

Following the preparation of the catalyst, cut-off C (refer to Fig. 1, reference 5 for the diagram of the apparatus) in the gas circulation system was closed, isolating the catalyst and pump system from the rest of the circulation system. The isobutane was transferred from the doser to side tube T-2 by immersing the tube in a bath at −195°. The charge was evacuated briefly, then vaporized carefully into the circulation system after cut-off C was opened. The gas, at a pressure of about 65 mm. was circulated over the catalyst by a mercury jet pump. It was found that under the experimental conditions, the extent of exchange was independent of the circulation rates employed. The isobutane pressure was measured at manometer M-1 by closing C and applying liquid nitrogen at T-2. At the end of this operation, the isobutane was vaporized, the cut-off opened and normal circulation of gas restored. The catalyst temperature was maintained at 150 ± 0.5° by means of a thyratron controlled furnace F. The furnace inlet and outlet lines were maintained at about the same temperature by means of heater windings.

At the end of the reaction time, usually 3 hr., the isobutane was frozen out in a sample bulb and the catalyst was evacuated for 1 hr. The amount of light hydrogen which had been transferred to the catalyst was estimated by circulating over it a measured amount of pure D_2O for several hours and analyzing the equilibrium vapor in a hot wire gage.[6] The calculation requires a knowledge of the total water content of the catalyst at the time of the isobutane exchange. This information was furnished from the water content studies previously described.[5]

Since the catalyst and system contained only heavy hydrogen prior to isobutane exchange and since pure D_2O was added for measurement of the extent of exchange, all the light hydrogen in the system entered by way of exchange from the isobutane. The amount of light hydrogen may be easily calculated from the total water present and the mole fraction of light water in the equilibrium vapor.

The extent of exchange thus obtained by analyses of the catalyst was expressed as a first order rate constant k_H having the units milligram-atoms of hydrogen exchanged per hour per millimeter pressure of isobutane per gram of catalyst. The assumption of first-order dependence on isobutane pressure is justified by the work of Hansford, *et al.*,[2] and by our experiments at 45 and 65 mm. for a standard catalyst pretreatment. These runs yielded rate constants consistent within 10% of each other. A small correction of the rate constants for the back reaction was made on the assumptions that re-exchange is proportional to the atom fraction of light hydrogen on the catalyst and to the average atom fraction of deuterium at primary positions in the isobutane molecules. The approximate correction is

$$C = {}^1/_2(1 + F_d - f_d)$$

where F_d is the final atom fraction of deuterium in the catalyst and f_d is the average atom fraction of deuterium at primary positions in the isobutane at the end of the experiment. The term C represents the arithmetic mean difference between F_d and f_d. (The logarithmic mean is theoretically more accurate, but differs insignificantly from the arithmetic mean for these experimental conditions. Its use in no case increased the k_H value by more than 10%.)

The isobutane products were analyzed on a Consolidated mass spectrometer, the instrument being operated at "high gain" to obtain maximum sensitivity. The isobutane conversions were small, rarely exceeding three mole % of deuterated species. While the spectra were not adequate to supply accurate conversion data, approximate agreement with the results from isotopic analyses of the catalyst were obtained by a method utilizing the relative abundance of propyl ion peaks from deuterated and non-deuterated isobutanes and the apparent average deuteration per molecule converted as derived from the mass 59 to 67 peaks. (The mass 59 peak must first be corrected for the contribution due to C^{13} in the unconverted isobutane. The mass 68 peak was found to be virtually absent.)

The apparent average deuteration A' is given by

$$A' = \frac{\Sigma n_i h_i}{\Sigma h_i}$$

where the h_i are the relative peak heights corresponding to mass numbers 59 through 67 and n_i have the values 1 through 9 for the peaks of mass numbers 59 through 67. The average computed in this way is less than the true average because of the large contribution of the fragment of mass one less than the parent ion of each deuterated isobutane. However, the error from this source in the average is thought not to exceed about 0.5 atom per molecule,[7] while the error in computing the apparent average is probably of the same magnitude. Therefore, the difference between apparent and true average is neglected in the present discussion.

The exchange data may be expressed in terms of millimoles isobutane converted per hour per mm. per gram as indicated below

$$k_1 = k_H/A'$$

Results

Different 0.5-g. portions of catalyst SA were found to have a considerable variation in activity for hydrogen exchange with isobutane after a standard catalyst pretreatment. This pretreatment consisted of heating the deuterated catalyst to 500° for several hours, cooling it to 150° in 20–25 mm. of water vapor and evacuating it for 1 hr. at 150°. The catalyst then contained 1.37 weight % water (as D_2O) as indicated by the value at 150° on curve II, Fig. 4, of reference 5. For this catalyst condition, nine portions of a sample had an average hydrogen exchange activity expressed as k_H of about 10×10^{-4} with an average deviation of 1×10^{-4} and a maximum deviation of about 4×10^{-4}.

Composite exchange data for an average portion of catalyst are given in Fig. 1. The reader should bear in mind that each exchange experiment was

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

(7) R. E. Honig, *ibid.*, **22**, 1474 (1951).

made at 150°, although for catalyst pretreatment the temperature was varied between 150 and 500°. The data of Fig. 1 are based on the isotopic analysis of the catalyst. Small, proportional corrections in the original data were made to normalize them to a reference standard activity of 10×10^{-4} milligram atoms per hour per mm. per gram. The water contents for each evacuation temperature of the plot were obtained from the corresponding curves of Fig. 4 of reference 5. The catalyst pretreatments utilized for each curve of Fig. 1 are described below.

The exchange rate data of curve I, Fig. 1, were obtained for catalyst pretreatments consisting of first cooling the catalyst from 500° to successively lower temperatures of 400, 300, 225 and 150° in 20 to 25 mm. water vapor and evacuating it for an hour at each temperature. The catalyst was then subjected to the reverse pretreatment consisting of heating it to successively higher temperatures of 225, 300 and 400°. The reaction rate in terms of hydrogen exchanged decreases rapidly with increase of the temperature of evacuation and appears to be independent of the direction from which this evacuation temperature is approached.

Prior to the determination of curve II, the catalyst was cooled to about 30° and exposed to water vapor for several days at a relative pressure of about 0.7. Exchange experiments were then made at catalyst evacuation temperatures of 150, 180, 225, 300 and 400°. The reaction rate will be observed to rise with increasing evacuation temperature to a maximum for 225° then to fall sharply with further increase of temperature.

Pretreatment conditions for curve III were similar to those for curve II except that rehydration was carried out at about 30° and unit relative pressure. A maximum in the rate corresponding to 225° evacuation will be observed, although this peak is considerably below that of curve II.

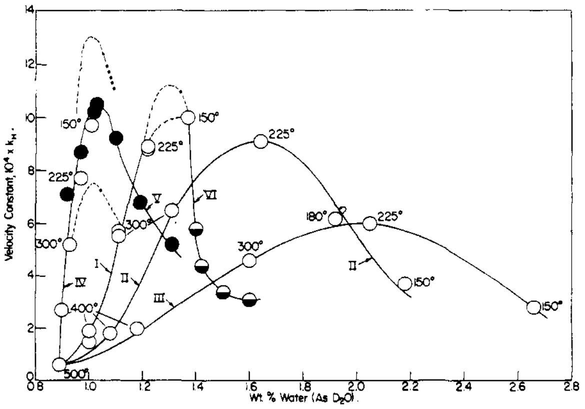

Fig. 1.—Composite data for the rate of exchange of hydrogen atoms from isobutane with the deuterium content of a deuterated silica–alumina cracking catalyst at 150° as a function of the per cent. D_2O present: ○, catalyst evacuated at indicated temperature; ●, water vapor added at 150° to catalyst evacuated at 500°; ◒, water added at 150° to catalyst evacuated at 150°. For meaning of curves I, II, III, IV, V and VI see text. k_H is expressed as milligram atoms of hydrogen exchanged per hour per mm. pressure of isobutane per gram of catalyst.

The pretreatments for curve IV were carried out in two ways. First, on the catalyst initially evacuated at 500°, water was fixedly adsorbed at temperatures of 150, 225, 300 and 400°. (By fixed adsorption is meant the residual water adsorbed on the dehydrated catalyst when it is exposed to low pressures of water vapor and then evacuated at the specified temperature for 1 hr. For a more exact definition, see our preceding publication.[5]) The second method involved addition of small quantities of water at 150° to the catalyst evacuated at 500° (the experiments by this second method are represented by the filled circles of curve IV).

Addition of water by either method to the catalyst evacuated at 500° produces an abrupt increase in exchange activity. The maximum activity occurs for the addition of about 0.13% D_2O, which corresponds to the maximum water which can be fixedly adsorbed at 150°.[5] A similar activation of dehydrated cracking catalysts for hydrogen exchange by the addition of small amounts of water was observed by Hansford and co-workers[2] and Hindin and co-workers.[3]

The effect of addition of water at 150° in excess of that which can be fixedly adsorbed on the catalyst initially evacuated at 500° is shown by curve V. This excess water which is loosely held by the catalyst will be observed to poison strongly the exchange reaction.

The position of the peak of curves IV and V has been found to vary among catalyst portions within the limits indicated by the dotted lines of Fig. 1. For most samples, the peak occurs about as indicated by the junction of solid curves IV and V.

The effect of addition of small quantities of water to the catalyst after its standard pretreatment at 150° is indicated by curve VI. A very marked poisoning of the exchange reaction will be observed to occur. Thus, the addition of 0.03 weight % D_2O reduces the reaction rate by nearly one-half, while the addition of about 0.1% reduces the rate by two-thirds.

It should be pointed out that these data seem to indicate that for evacuation temperatures of 225° and higher, on curves I, II, III and IV, Fig. 1, the total hydrogen exchanged is roughly independent of the total catalyst water content.

It is of interest now to consider the variation of deuterium distribution in the isobutane product as the experimental conditions are varied along curves I to VI. A good indication of the distribution of deuterium is given by the relative peak heights of the mass spectra in the region, mass 59 to 68. Such data are given by the curves in Figs. 2 and 3.

Figure 2A shows the change in distribution as the catalyst activity is varied according to curve I, Fig. 1. It will be seen that as the temperature of dehydration is increased, the occurrence of multiple deuteration drops rapidly. Thus, for 150° evacuation, maximum peak height occurs at mass 65 (corresponding roughly to 7 deuterium atoms per molecule), while for 500° evacuation, the maximum

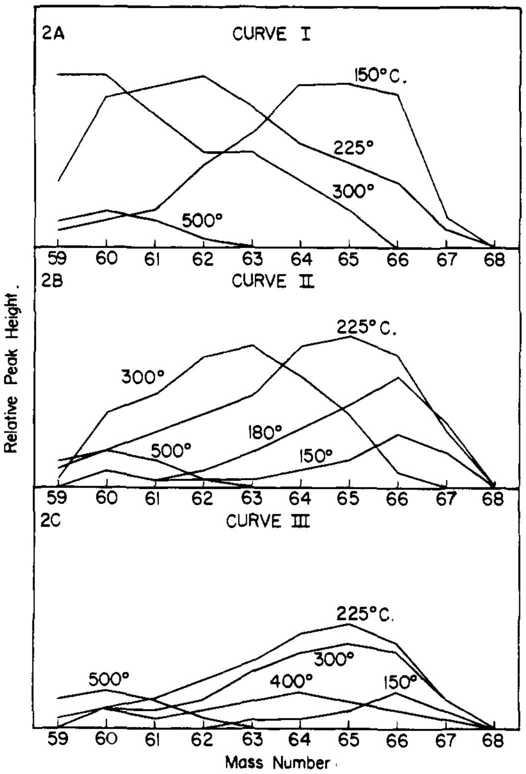

Fig. 2.—Deuterium distribution in product of isobutane exchange for curves I, II and III of Fig. 1. Temperatures of the final evacuation immediately preceding each experiment are indicated.

occurs at about mass 60 (roughly two deuterium atoms per molecule.)

Figures 2B and 2C represent the distributional variation as experimental conditions are changed along curves II and III, Fig. 1, respectively. The shift to lower deuteration with increase in evacuation temperature is much less rapid in these cases of higher catalyst water content than was observed for similar evacuation temperatures along curve I.

Figure 3A shows the effect on the distribution of deuterium in the converted isobutane resulting from the addition of small quantities of water at 150° to the catalyst that has been evacuated initially at 500°. The data correspond to points on curves IV and V of Fig. 1. It is evident that while the first water added strongly activates the catalyst for exchange, the average deuteration per molecule converted increases little until the maximum fixed adsorption is reached (0.13% D_2O). As water in excess of this value is added, the deuterium content of the isobutane increases rapidly even though the total hydrogen exchanged drops sharply.

Figure 3B indicates the effect of fixedly adsorbing maximum water at various temperatures on the catalyst evacuated at 500°. In general, addition of water in this way is roughly equivalent to the addition of small quantities of water at 150°.

Figure 3C illustrates the effect on the deuterium distribution of adding small quantities of water at 150° to the catalyst initially in its standard condition. The net effect is to increase the average deuteration per molecule, even though the total hydrogen exchanged is drastically reduced.

The data of Fig. 2 and 3 may be used to calculate the apparent average deuterium content per molecule of isobutane undergoing exchange. This average is lower than the true average deuteration by an amount thought to be not more than 0.5 atom per molecule. Since the exact correction is not known, and since the experimental error in the average is probably of the same magnitude, the difference is neglected in further consideration.

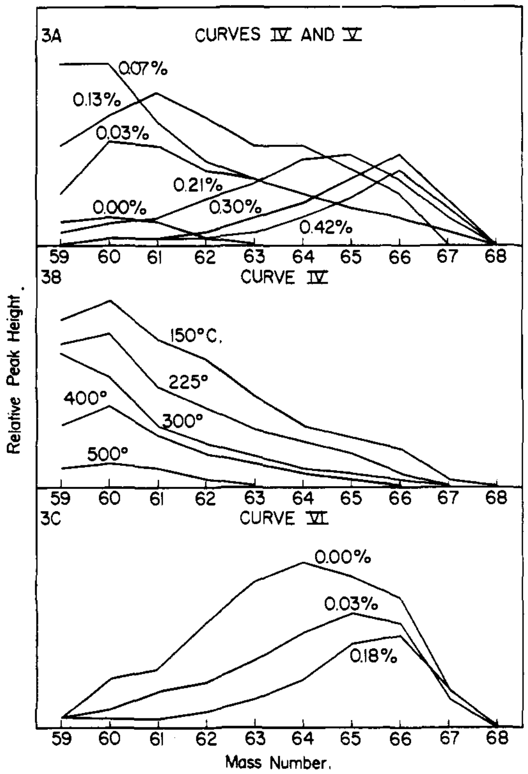

Fig. 3.—Deuterium distribution in product of isobutane exchange for runs in which water was added back in indicated amounts immediately before the exchange run (Figs. 3A and 3C) and for runs in which water was added at the indicated temperature and then partially removed by evacuation for 1 hr. at the same indicated temperature (Fig. 3B).

The apparent average values of deuteration per molecule reacting are plotted *versus* catalyst water content in Fig. 4. The observations made in the discussion of Fig. 2 and 3 regarding the effect of various changes in catalyst water content on deuterium distribution are clearly demonstrated by the data of this figure. In general, the average deuteration per molecule for a given evacuation temperature increases with the total water content of the catalyst.

It should be mentioned that different catalyst portions subjected to the same pretreatment gave average deuterations in agreement within 0.5 deuterium atom per isobutane molecule reacting.

The exchange data may be expressed in another useful form, *i.e.*, as the rate of formation of isobutane species which contain one or more deuterium atoms. This quantity, k_I, having units millimoles per hour per mm. per gram of catalyst

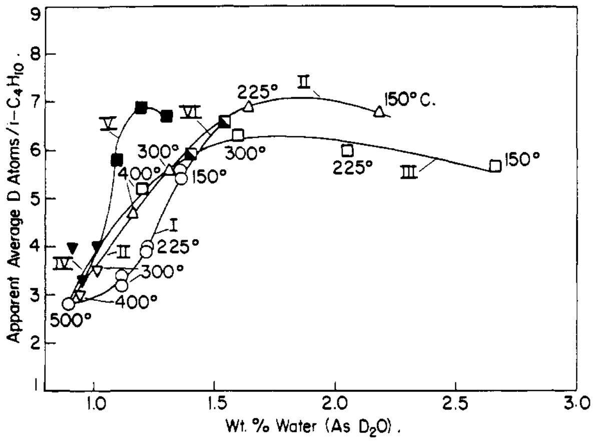

Fig. 4.—Apparent average number of deuterium atoms per molecule of exchanged isobutane as a function of the water content and pretreatment of the catalyst: ○, curve I; △, curve II; □, curve III; ▽, ▼, curve IV; ■, curve V; ◪, curve VI. For open symbols, catalyst was evacuated at the indicated temperatures; for solid symbols, water vapor was added at 150° to a catalyst previously evacuated at 500° (see text).

is readily calculated from the k_H and A' data. These results are given in Fig. 5.

Exchange experiments at 150° were made also over the base-exchanged silica–aluminas, the silica gel and the activated alumina. Observations were made on each sample after standard pretreatment, *i.e.*, after cooling the sample from 500° to 150° in 20 mm. of water vapor and evacuating it for 1 hr. at that temperature. Observations were also made on the base-exchanged silica–aluminas after they had been evacuated at 500° and had 0.13 weight % D_2O added back and fixedly adsorbed on them at 150°. These results are compared in Table I with the average values for the non-base-exchanged silica–alumina.

TABLE I

EXCHANGE RESULTS AT 150° ON VARIOUS CATALYSTS

	Exchange rate, $10^4 \times k_H$ Standard treatment	Fixed adsorption
Silica–alumina (SA)	10.0	10.0
Potassium silica–alumina (KSA)	0.2	0.0
Barium silica–alumina (BSA)	0.8	1.6
Alumina (A)	0.2	...
Silica (S)	0.0	...

These results indicate that the acid sites of the catalyst are necessary for hydrogen exchange, since the reaction is strongly poisoned by metal ions placed on the catalyst by base exchange. Further, the component oxides are inert for hydrogen exchange; it seems evident that a combination of these substances is required to produce the acid sites and the hydrogen exchange sites.

Discussion

As a basis for discussing the results of the present paper, it is convenient to itemize the individual observations that appear to be significant and useful in helping to elucidate the surface structure of the silica–alumina catalysts and the nature of the active sites on which hydrocarbons react. The pertinent points from the present and preceding paper are as follows.

(1) Evacuation of a deuterated silica–alumina cracking catalyst at 500° left 0.79% water on the catalyst; similar evacuation of catalysts into which by base-exchange 0.58 and 0.46 meq. of K^+ or Ba^{++} had been incorporated left 0.64 and 0.73% water, respectively (Table III of reference 5).

(2) The rate of exchange of the hydrogen of i-C_4H_{10} at 150° with the deuterium content of a deuterated cracking catalyst is very low when the catalyst was evacuated at 500° immediately prior to a run (Fig. 1 or 5).

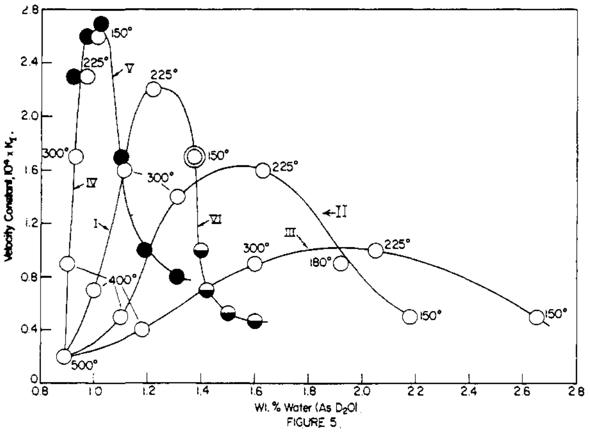

Fig. 5.—Composite data for the rate of exchange of i-C_4H_{10} molecules with a deuterated silica–alumina cracking catalyst at 150° as a function of the % D_2O present. Symbols have same meaning as in Fig. 1. k_1 is expressed as millimoles of i-C_4H_{10} picking up one or more deuterium atoms per hour per mm. of i-C_4H_{10} per gram of catalyst.

(3) Adding back to a catalyst evacuated at 500° small quantities of water at temperature T and then evacuating the sample for an hour at this same temperature T leaves small but finite quantities of added water on Al_2O_3, on Al_2O_3–SiO_2 catalysts and even on Al_2O_3–SiO_2 catalysts containing K^+ or Ba^{++}, but does not cause an increase in the water content of SiO_2 gel, when T is 110°; this "fixed adsorption" amounts to about 0.2% by weight on silica–alumina cracking catalysts with or without K^+ and Ba^{++} ions and to 0.54% on activated alumina (Fig. 4, 5 and 6, reference 5).

(4) The "fixed adsorption" (as defined in item 3 above) for T = 150° causes a 13- to 20-fold increase in the rate of exchange of isobutane with a deuterated catalyst (Fig. 1 or 5, curve IV). However, small additions of added water do not give appreciable activity to activated alumina or silica gel and only a slight activity (2 to 16% as much as for a regular silica–alumina catalyst) to a cracking catalyst containing 0.57 meq. K or 0.46 meq. of Ba per gram (see Table I).

(5) The adding back of more than about 0.13% water to a catalyst evacuated previously at 500° causes an abrupt drop in the exchange activity of the catalyst for i-C_4H_{10}. This amounts to a 50% drop in values of k_1 for the first extra 0.1% water added back in excess of that required to reach peak activity (curve V, Fig. 5).

(6) Evacuating the silica–alumina catalyst at 500°, cooling it in 20 mm. of water vapor to 150° and then evacuating it for an hour at this temperature gives a catalyst of relatively high activity as judged by k_I values (curve I, Fig. 5). However, evaucation at about 225° enhances the activity. Evacuation at temperatures higher than 225° lowers the activity as also does the addition of small amounts of added water (curve VI, Fig. 1 and 5).

(7) Exposing a cracking catalyst after evacuation at 500° to 20 mm. of water vapor while it is cooled to 30° and then holding the catalyst at 70% relative humidity (curve II, Fig. 1 or 5) or 100% relative humidity (curve III, Fig. 1 and 5) for several hours puts the catalyst in such a condition that evacuation for 1 hr. at 150° yields relatively small values of k_1 whereas evacuation at about 225° yields optimum activity. Evacuation at temperatures higher than 225° lowers the k_I values. It is evident that the large amount of "body water" picked up by the catalyst at 70 to 100% relative humidity lowers the activity of a catalyst for exchange somewhat, but it is not nearly as poisonous per unit amount of water as the small amounts added in excess of the optimum to catalysts not exposed to water below 150° after evacuation at 500° (curve V and VI, Fig. 1 and 5).

(8) The average number of deuterium atoms picked up per molecule of isobutane reacting is in the 5.5 to 7.0 range for samples having D_2O contents equal to or greater than 1.4%. On curves IV and V, this range of exchange is reached as soon as the added D_2O is sufficient to cause the values of k_I to start to decrease with added D_2O. This occurs at about 1.1% D_2O for curve V.

(9) Examination of curves in Fig. 1 shows that to a close approximation the total amount of deuterium transferred to the isobutane during a run depends primarily on the temperature of final evacuation of the catalyst sample regardless of the prior history or absolute amount of water vapor in the sample. Thus, evacuation at 225° yields approximately the same activity for the samples containing 0.9, 1.2, 1.6 and 2.1% water, respectively, as shown on curves IV, I, II and III. This constant value of k_H is apparently due to a compensating effect by which excess added water causes a decrease in the *number* of isobutane molecules picking up at least one deuterium atom (see curves IV, I, II and III, Fig. 5) but causes an increase in the average number of deuterium atoms going in to each isobutane undergoing any exchange.

With these facts before us, we can now make a few comments as to deductions that can be drawn as to the nature of the active points on the silica–alumina catalysts and the details of the exchange mechanism. As to the nature of the active points on this silica–alumina catalyst, we believe that the data from the present paper combined with other published work show that 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. The very sharp rise in curve IV, Fig. 1 and 5, and similar results by Hindin, Mills and Oblad[3,4,8] and Hansford and co-workers[5] establish this point. One might at first be inclined to feel that this sharp rise in activity results from a more plentiful supply of surrounding –OD groups or from a trigger action facilitating the transfer of deuterium to the adsorbed molecule.[3,4] The fact that small quantities of "added back water" also increases rates of isomerization or cracking[8] of hydrocarbons by a factor of about 20 argues against this explanation. To us, it seems impossible to avoid the conclusion that at least a small portion of the added water is actually utilized in creating active sites for the adsorption of i-C_4H_{10} or other saturated hydrocarbons. We feel, therefore, that the evidence is rather strong against the suggestion of Milliken, Mills and Oblad[9] to the effect that saturated hydrocarbons can react with a silica–alumina site to form a carbonium ion by passing a hydride ion onto a Lewis acid site on a cracking catalyst (see equation 2, reference 9).

If, as pointed out above, we conclude that isobutane will be chemisorbed only on sites that have water present as H^+ ions or at least as potential H^+ ions,[10] we are naturally led to inquire as to how we may estimate the residual protons or potential protons on a silica–alumina catalyst evacuated at 500°. The summary in Table II seems useful in placing the various data in proper perspective.

Items a to f in Table II make it clear that all of the aluminum in a cracking catalyst containing 10% Al_2O_3 and about 90% SiO_2 cannot be coördinated with one proton per aluminum ion on a catalyst evacuated at 500°. There are only $^1/_4$ enough protons if each water yields 1 proton and $^1/_2$ enough if each water yields 2 protons.

Item g in Table II emphasizes that adding about 0.05% D_2O back to a catalyst evacuated at 500° is equivalent to adding 0.03 meq. of H^+ if each molecule furnishes 1 H^+ on the catalyst. This would mean that prior to the addition of the 0.05% water, the proton concentration would have been $^1/_{20}$th of 0.03 or 0.0015 meq. per gram, assuming k_I is proportional to the proton concentration. However, as pointed out in item 4 above, the "fixed adsorption" of water at 100° is 0.21 ± 0.02% on the catalysts with 0.57 meq. of K^+ or 0.46 meq. of Ba^{++} incorporated by base exchange as well as on the unexchanged catalyst. Hence, 0.02% H_2O or 0.01 mmole of water per gram is the maximum amount of the added water that can be going on active sites to form protons. This is only $^1/_3$ of the amount of added back water required to increase the rate of exchange, isomerization or cracking about 20-fold. If we assume, as a safer figure, that 10% of the added back water goes to form protons, item i shows a figure of 0.00015 meq. of H^+ per gram as the calculated initial H^+ concentration. If one isobutane can be chemisorbed on each of these, one would obtain a figure of 0.00015 mmole or 0.0033 cc. per gram. The figure in item k for the observed chemisorption is

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

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

(10) M. W. Tamale, *ibid.*, **8**, 270 (1950).

TABLE II

FACTS AND CALCULATIONS RELATIVE TO ACID SITES ON A TYPICAL SILICA–ALUMINA CRACKING CATALYST CONTAINING 10% Al_2O_3 AND 90% SiO_2

(a)	Mmoles of SiO_2	15.0[b]	
(b)	Mmoles of Al_2O_3	1	
(c)	Milliatoms of Al	2	
(d)	Mmoles of water after evacuation at 500°	0.5	(0.89%)
(e)	Milliatoms of H or H^+ if *one* of two hydrogens in H_2O is ionic	0.5[a]	
(f)	Mmoles of added back H_2O needed for 10- to 50-fold increase in rate of exchange,[3,4] rate of isomerization[8] and rate of cracking[7] satd. hydrocarbons	0.03	(0.05%)
(g)	Milliequivalents of H^+ from added back water	0.03	
(h)	Meq. of H^+ ions calcd. to have been present initially if 0.03 meq. causes a 20-fold rate increase	0.0015	
(i)	"Fixedly adsorbed water" at 110° is 0.21 ± 0.02% on silica–alumina with and without 0.57 meq. K^+ or 0.46 meq. Ba^{++}. This 0.02% uncertainty means less than 0.01 mmole of "added back" water goes to form Brönsted H^+ ions. Hence, all "added back" water required for a 20-fold rate increase cannot form H^+ ions on active sites. If we assume 10% of the "added back" water goes to form H^+ ions, then mmoles of added H_2O forming one H^+ each on active sites	0.003	
(j)	Meq. of H^+ calcd. to be present before added back water	0.00015	
(k)	Approximate chemisorption of i-C_4H_{10} at 150°, mmoles	0.0001 (0.002 cc.)	
(m)	Mmoles of quinoline per g. for complete poisoning[10]	0.01	
(n)	Mmoles of 1-C_4H_8 chemisorbed or held as polymer at −78°	1.0	
(o)	Mmoles of 1-C_4H_8 left after evacuation at 100° (Original catalyst was evacuated at 750° before adding butene at 25° and pumping at 100°)	0.15	

[a] This is also about the usual figure obtained as an estimate of surface activity made by base-exchange experiments. [b] All figures in this column are on a per gram basis.

approximate, the true value probably being within a factor of ten of the one shown. This figure is, however, the right order of magnitude to agree with this estimate (item j) of proton concentration on a catalyst evacuated at 500°.

Item m is an upper limit to the amount of strong poison required[11] to block cracking at 500°. Probably a much smaller amount would be required at 150°.

The olefin sorption values in items (n) and (o) may represent surface polymerization rather than true chemisorption.[12] The figure in item (n) is twice as great as the maximum proton figure as listed in item (e). The olefin may therefore quite clearly utilize most of the water content during its chemisorption and may perhaps form carbonium ions as postulated by Oblad and co-workers.[9]

It is not too difficult to see how small quantities of added water can activate Lewis sites for the chemisorption of hydrocarbons. It is more difficult to see how small extra quantities of water added back to a catalyst previously pumped at or above 500° can have a poisoning effect not only on the exchange (curves V and VI, Fig. 1 and 5) but on the isomerization and cracking of saturated hydrocarbons[8] at 150°. Perhaps, the extra water tends to form H_3O^+ ions in place of H^+ ions. There simply is no definite proof yet as to the nature of the poisoning action.

One of the most amazing features of the exchange experiments[2–4,7] is the relatively large number of deuterium atoms picked up by each isobutane that undergoes any exchange. As pointed out in item 7 above and illustrated in Fig. 4, this usually amounts to six or seven deuterium atoms per molecule. With a solid catalyst, a complete exchange of all but the tertiary hydrogen is made difficult by the relative scarcity of D atoms on the surface. Thus, as pointed out by Hindin, Mills and Oblad,[4] a catalyst containing 1% D_2O has one deuterium atom per 50 Å.^{2} of surface even if all the water is surface water. To pick up seven deuterium atoms an i-C_4H_{10} molecule must, therefore, use the D atoms from at least 350 Å.^{2} surface area. Actually, if statistical equilibrium is reached between the hydrogen atoms of an isobutane molecule and the deuterium atoms in a deuterated catalyst, then for an average of seven deuteriums per isobutane, a total of about 30 deuterium atoms would have to equilibrate with each isobutane molecule. These 30 deuterium atoms would cover an area of 1000 to 1500 Å.^{2} Presumably, the deuterium (as D^+, OD radicals or D_2O molecules) must diffuse from such an area on an average during the time of attachment of an isobutane molecule to an active site. This does not seem unreasonable in view of the rapid equilibration of water vapor with the entire deuterium content of the catalyst.[5]

Finally, it should be pointed out that no very clear explanation exists as to the mechanism by which "body water" in the catalysts (curves II and III, Fig. 1 and 5) slows down the exchange. It seems likely that this extra water may, by hydrating the silica gel and possibly some of the alumina, discourage the formation of the silica–alumina Lewis sites which, in the presence of the right amount of water, are transformed into acid sites active in the exchange reaction,[2–4] isomerization and in cracking[2,8,13] of saturated hydrocarbons.

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[11] G. H. Mills, E. R. Boedeker and A. G. Oblad, THIS JOURNAL, **72**, 1554 (1950).

[12] Thesis by R. C. Zabor, University of Pittsburgh, 1952.

[13] R. C. Hansford, "Advances in Catalysis," Vol. IV, Academic Press, Inc., New York, N. Y., 1952, p. 1.