The NaF was determined by careful evaporation in platinum crucibles over a heat lamp followed by ignition at 750°. The weighing form was NaF.

## Discussion and Results

The results of the analyses of the solution and wet residues are given in Tables I and II and have been plotted in Fig. 1 and 2. At −15° at HF concentrations of less than 11%, all phases appear to be solids.

The solid phases existing in equilibrium with solution at both temperatures include NaF·HF, NaF·2HF, NaF·3HF and NaF·4HF. NaF exists in the 0° case and presumably at −15°. No solid phases containing water exist. The HF (wt. %) concentration limits for the solid phases at 0° are: NaF, 0 to 9.5%; NaF·HF, 10 to 57%; NaF·2HF, 55 to 58.5%; NaF·3HF, 58.5 to 62%; and NaF·4HF, 62 to 100%. In general, the solid phases containing HF are more stable at lower HF concentrations at −15° than they are at 0°. The solubility of NaF is in general somewhat lower at the lower temperature.

COLLEGE STATION, TEXAS

[CONTRIBUTION FROM THE RESEARCH LABORATORY, OLIN MATHIESON CHEMICAL CORPORATION]

# Change in the Ratio of Hydroxyl Groups Attached to Silicon and Aluminum Atoms in Silica–Alumina Catalysts upon Activation

BY H. G. WEISS, J. A. KNIGHT AND I. SHAPIRO

RECEIVED OCTOBER 18, 1958

A method for measuring the number of hydroxyl groups attached to silicon relative to those attached to aluminum atoms in silica–alumina catalysts is described. Essentially, the method consists of two steps: (a) exposing diborane to the catalyst in order to replace the proton of the hydroxyl group with boron atoms and (b) measuring the number of these boron atoms that can participate in boron exchange with labeled diborane. By this technique, it is found that initially hydroxyl groups are attached to both silicon and aluminum atoms; however, upon aging of the catalyst at temperatures below 400° hydroxyl groups, lost as water, must come predominantly from the silicon rather than the aluminum atoms. At temperatures above *ca.* 400° the ratio of hydroxyl groups attached to aluminum and silicon atoms goes through a maximum value.

The relation of bound water to the surface structure of silica gel, silica–alumina and aluminum oxide catalysts has been the subject of several investigations.[1-3] The influence of small amounts of water on the catalytic activity of alumina and silica–alumina also has been reported.[4-6] In this connection various methods[7,8] have been devised for measuring bound water content of catalysts; however, such methods (ignition, $D_2O$ or $D_2$ exchange, etc.) are satisfactory for bulk determinations but do not lend themselves readily to determination of the location of the bound water.

The nature of bound water (hydroxyl groups) in silica gel has previously been elucidated by a study of its reaction with diborane.[9] From the relative amount of diborane consumed to hydrogen generated, it was determined that the hydroxyl groups in silica gel lie principally on the surface of the solid, with the surface composition consisting of $Si-O-BH_2$ units. Similar results were indicated for reaction of diborane with silica–alumina.

The diborane-treated silica–alumina catalyst[10] exhibited a pronounced activity toward cyclization of acetylene to benzene, and from a detailed study of the cyclization reaction[11] there were indications that alumina provided the active sites in silica–alumina catalysts. That the borane counterpart is not the principal active site was indicated by the inactivity of diborane-treated silica gel; treated alumina gave only an initial reaction with acetylene. Further experiments with diborane now point to a way of distinguishing between hydroxyl groups located on silica and those on alumina sites.

In the exposure of silica gel and silica–alumina to diborane, hydrogen is liberated in the initial reaction. In experiments in which these two catalysts were activated at low temperatures (*ca.* 250°), the hydrogen-diborane ratio indicated no apparent differences in the nature of the borane-surface compound formed. However, with alumina and silica–alumina activated at higher temperatures (>400°) there was a decrease in the hydrogen–diborane ratio, thus precluding the possibility of only $M-OBH_2$ units forming. Boron-10 exchange experiments between gaseous diborane and the boron-surface compounds showed differences in the amount of exchangeable boron on the surface. Total boron exchange (100%) occurred in the borane–silica compound formed from diborane and silica gel. With alumina, however, only one-half (50%) of the attached boron atoms were capable of exchange. When exchange experiments were carried out in the silica–alumina–borane compound, the amount of boron participation varied between these limits. From the equilibrium exchange values, the ratio of hydroxyl groups on alumina to those on silica has been calculated. The results indicate that the hydroxyl groups in silica–alumina are on both aluminum and silicon atoms and that those attached to silica are more easily removed on heating.

Details of the exchange reactions between the diborane surface complexes and gaseous diborane are given.

---

(1) I. Shapiro and I. M. Kolthoff, THIS JOURNAL, **72**, 776 (1950).

(2) J. D. Danforth, *J. Phys. Chem.*, **61**, 1311 (1957).

(3) R. G. Haldeman and P. H. Emmett, THIS JOURNAL, **78**, 2917 (1956).

(4) S. G. Hindin and S. W. Weller, *J. Phys. Chem.*, **60**, 1501 (1956).

(5) S. W. Weller and S. G. Hindin, *ibid.*, **60**, 1506 (1956).

(6) R. G. Haldeman and P. H. Emmett, THIS JOURNAL, **78**, 2922 (1956).

(7) G. A. Mills and S. G. Hindin, *ibid.*, **72**, 5549 (1950).

(8) James K. Lee and Sol W. Weller, *Anal. Chem.*, **30**, 1057 (1958).

(9) I. Shapiro and H. G. Weiss, *J. Phys. Chem.*, **57**, 219 (1953).

(10) I. Shapiro and H. G. Weiss, THIS JOURNAL, **79**, 3294 (1957).

(11) H. G. Weiss and I. Shapiro, *ibid.*, **80**, 3195 (1958).

## Experimental

1. **Reagents: Diborane.**—Both the normal and $B^{10}$-enriched diborane used in these experiments were prepared by the lithium aluminum hydride–boron trifluoride etherate reaction[12] using the appropriate boron trifluoride etherate. Deuterodiborane ($B_2D_6$) was prepared using lithium aluminum deuteride and boron trifluoride etherate. Purification was accomplished by the usual high vacuum techniques prior to use. All materials were found spectroscopically pure by mass spectral analysis.

**Silica Gel** (I).—The silica gel used in these experiments has been described previously.[1,13] Samples were heated *in vacuo* at 250° prior to use.

**Alumina** (II).—Houdry high surface alumina was dried *in vacuo* at 450° prior to use.

0.3% **Platinum on Alumina** (III).—Baker and Company, Inc. $^1/_8$'' pellets were used. Treatment was identical with that used for catalyst II. In two runs this treatment was preceded by reduction with hydrogen gas at 100° for 90 minutes.

0.5% **Platinum on Alumina** (IV).—Houdry series A 200SR and Series A 100S pellets were used. Treatment was identical with that used for catalyst II.

**Silica–Alumina** (V).—Houdry synthetic type S-65 pellets containing 12% alumina, 86% silica were used. Samples were heated *in vacuo* to 250, 400 or 450° prior to use.

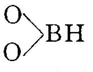
2. **Procedure.**—After the appropriate heat treatment of the catalyst (described above), a measured excess of diborane was transferred to a reactor (static system) by condensing at −196°. The reactor was then removed from the vacuum line, allowed to warm to room temperature and shaken intermittently for an additional ten minutes to ensure complete reaction. The entire procedure consumed *ca.* 20 minutes. (For silica gel and silica–alumina it was necessary to increase the contact time to 1–2 hr.) The reactor was again attached to the vacuum line and cooled to −196°. The bulk of the hydrogen was removed at this temperature and measured with a gas buret. After removal of most of the hydrogen, the reactor was again allowed to warm to room temperature. It was maintained at that temperature for at least 1 hr. in order to obtain complete removal (by Toepler pump) of all hydrogen and diborane which might have been adsorbed on the catalyst. Catalysts II, III and IV were heated to 65–70° while pumping off hydrogen. The diborane was separated from hydrogen by condensing at −196°, and the amounts of the two gases were then measured. Platinum was found to have no effect either on the initial reaction with diborane or on the exchange reactions reported here.

A measured amount of $B^{10}$-enriched diborane (96% $B^{10}$) was condensed into the reactor containing the diborane–catalyst complex formed in the above reaction. One minute before the start of the exchange reaction the reactor was rapidly warmed to room temperature with a heat gun. (For the 90° reaction, the reactor was then placed in an oil-bath maintained at 90° for the appropriate time.) The calculated total pressure at room temperature was *ca.* 184 mm. The reactor was shaken vigorously at intervals, although experiments showed that moderate to vigorous shaking was sufficient to give reproducible results.

After reaction, the reactor was quenched in a liquid nitrogen bath and replaced on the vacuum line where the diborane was removed and measured. In all experiments, except the long exposure exchanges with silica–alumina and silica gel, only trace quantities of diborane were lost during exchange. Calculations show that the diborane loss in the exchange on silica gel could not have appreciably changed the $B^{10}$ content of the residual diborane vapor. The residual diborane was analyzed mass spectroscopically with a Consolidated Model 21-103 mass spectrometer operating at an ionizing potential of 70 volts.

## Results and Discussion

**The Diborane–Silica Gel Reaction.**—A discussion of the initial reaction of diborane with silica gel (I) has been given previously.[9] In the experiments described here, diborane was allowed to react with silica gel at room temperature. The ratio of hydrogen generated to diborane consumed was three; the value is in agreement with that obtained previously.[9] Only HD was formed when deuterodiborane reacted with the silica.

The results of a series of exchange reactions between the borane–silica complex and $B^{10}$-enriched diborane indicate that complete participation of all borons occurred, *i.e.*, 100% exchange, after 20 hr. exposure time. The comparison is made between the actual $B^{10}$ content of the diborane after equilibrium had been reached and the calculated $B^{10}$ content assuming either all or one-half of the borons in the silica surface were involved. Actual values, of course, depend upon the amount of diborane initially consumed in the silica complex formation and the amount of $B^{10}$-enriched diborane used in the exchange experiment. For example, in one experiment the measured and calculated (100%) values were 82 and 81%, respectively. The fact that all boron on the silica is capable of exchange supports the previously postulated structure of the borane–silica surface of $SiOBH_2$ units. At room temperature the hydrogen–diborane ratio (*ca.* 3:1) indicates some of the surface borane may exist as  units[9]; the total exchange at room temperature shows that the borons in these units are exchangeable. A small number of boron atoms may be bonded completely to oxygen, and this may account for the small differences between experimental and calculated borane per cent. at 20 hr. reaction, since exchange would not be expected between diborane and a completely hydrolyzed borane unit.

**The Diborane–Alumina Reaction.**—The initial reaction which occurs when diborane is exposed to an alumina catalyst results in a loss of diborane and a build-up of hydrogen. The reaction is exothermic. Table I shows the diborane and hydrogen measurements for a number of runs at 25° on catalyst III. It can be seen that both diborane and hydrogen values are reproducible. For a large number of experiments with varying weights of catalyst (not tabulated) the average value for diborane consumed is six cc. (STP) per gram of catalyst, while the hydrogen to diborane ratio is unity. The amount of diborane reacting is in agreement with the water content of the alumina as determined by ignition. The reaction is the same for catalyst II, III or IV, while with catalyst III the quantity of diborane reacting was not changed by reducing the catalyst with hydrogen prior to exposure to diborane. At low temperature (−80°) only a slow reaction occurred. When the reaction mixture was warmed at a slow rate to room temperature, the final diborane and hydrogen values still closely approached the values reported above.

The reaction between diborane and the catalyst was rapid and essentially complete after a few minutes exposure at room temperature. Heating the borane–alumina complex to 65–70° for approximately 1 hr. liberated a trace quantity of hydrogen but no diborane. When deuterodiborane was passed over a sample of catalyst II and the product gases were then passed directly into the mass spectrometer, only HD was formed. Thus, half of the

---

(12) I. Shapiro, H. G. Weiss, M. Schmich, S. Skolnik and G. B. L. Smith, This Journal, **74**, 901 (1952).

(13) I. Shapiro and I. M. Kolthoff, *J. Phys. Chem.*, **52**, 1020 (1948).

TABLE I

REACTION OF DIBORANE WITH ALUMINA AT 25° (CATALYST III)

| Catalyst wt. (g.) | Diborane reacted cc. (STP) | Diborane consumed per g. catalyst (cc./g.) | Hydrogen evolved cc. (STP) | Ratio $H_2/B_2H_6$ |
|---|---|---|---|---|
| 0.5171 | 3.1 | 6.0 | 3.2 | 1.03 |
| .5125 | 3.1 | 5.9 | 3.0 | 0.97 |
| .5235 | 3.0 | 5.7 | 3.2 | 1.06 |
| .5040 | 2.9 | 5.8 | 2.9 | 1.00 |
| .5221 | 3.1 | 5.9 | 3.1 | 1.00 |

hydrogen evolved came from the catalyst and half from the diborane. This, along with the hydrogen-diborane data, implies a reaction of one molecule of diborane with each hydroxyl group in the alumina and suggest Al-O-$B_2H_5$ as the alumina-diborane surface complex. The structure of the catalyst-diborane complex is still being investigated. These diborane-treated catalysts exchanged boron atoms with diborane vapor at room temperature (25°). Curves showing the per cent. boron-10 in the gas phase against time of reaction at room temperature and at 90° are shown in Fig. 1. Curves obtained for catalysts II and IV differed only in the time required to reach equilibrium. Evidence that the value attained at room temperature is true equilibrium is given by the curve for exchange at 90°. It can be seen from these curves that equilibrium occurs at a $B^{10}$ value equivalent to exchange of half of the attached boron atoms. If the surface structure is truly represented as Al-O-$B_2H_5$, then 50% exchange would imply that only one of the two borons exchange. The structure of the surface-borane complexes alone do not appear to explain the differences in exchange on silica and alumina. The same (50%) equilibrium exchange values were obtained[14] for the exchange of pentaborane with the diborane-alumina adduct.

**Diborane-Silica-Alumina Reaction.**—Catalyst V dried at 250° and exposed to diborane at room temperature liberates hydrogen in the ratio of *ca.* 1.9 moles hydrogen per mole of diborane reacted. With increased drying temperature, however, the ratio of hydrogen to diborane decreases, giving an average of 1.3 at 400° and 1.2 at 450°. The reaction of silica-alumina with deuterodiborane again liberates only HD[15] (as was found with silica gel and alumina).

The hydrogen-diborane ratios obtained with the silica-alumina catalyst indicate reaction of diborane with hydroxyl groups attached to both silica and alumina. When room temperature exchange reactions similar to those described for silica gel and alumina are carried out with silica-alumina (dried at 400°), the exchange takes place at a rate intermediate between that for silica gel and that for alumina. The equilibrium value is also intermediate between the 50% boron exchange for alumina and the 100% boron exchange for silica gel. For silica-alumina dried at 250°, the rate of attainment of equilibrium is slower than for that dried at 400°, and the equilibrium value obtained is closer to that for complete boron exchange.

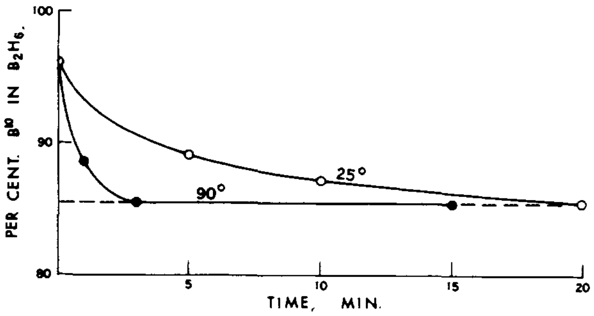


Fig. 1.—Diborane exchange on alumina (III) at 25 and 90°: ----, calculated equilibrium for 50% boron exchange.

**The Boron Number.**—The boron exchange on silica gel was found to be complete, while only half of the boron on the alumina was found to exchange. Assuming that the exchange reaction of silica-alumina is a composite of the silica gel and alumina reactions, equilibrium $B^{10}$ values can be calculated for various distributions of diborane on silicon and aluminum. Thus if complete exchange of boron occurred on the catalyst, the equilibrium value would represent total attachment of diborane to silicon, while if 50% exchange occurred, the equilibrium value would represent total attachment to aluminum. All equilibrium exchange values on silica-alumina must lie between these two values, and changes in equilibrium values must be directly proportional to the changes in per cent. diborane on the aluminum (or silicon). Using an arbitrary scale of zero to one for the amount of diborane on alumina, where zero represents complete exchange and one represents 50% exchange, then equilibrium values can be converted to numbers that represent the fraction of the total diborane on alumina. Since this value depends only upon the diborane in complex form and diborane in the vapor, it can readily be obtained for any catalyst sample regardless of weight of sample, water content, surface area, etc. This value is therefore defined as the "Boron Number" for silica-alumina. A typical calculation of the Boron Number is as follows: calculated equilibrium for complete exchange = 77.6, calculated equilibrium for 50% boron exchange = 85.5, experimental equilibrium value = 81.4, Boron Number ($B_n$) = (81.4 − 77.6)/(85.5 − 77.6) = 0.48. The change in Boron Number for Catalyst V for different heating temperatures is shown in Table II.

TABLE II

CHANGE IN % OF HYDROXYL GROUPS ON ALUMINUM IN SILICA-ALUMINA FOR VARIOUS HEATING TEMPERATURES AS CALCULATED FROM THE BORON NUMBER

| Temp. of activation, °C. | Boron number | % of total hydroxyls on aluminum |
|---|---|---|
| 250 | 0.21 | 15 |
| 325 | .29 | 21 |
|  | .42 | 32 |
| 400 | .48 | 38 |
|  | .53 | 43 |
| 500 (20 hr.) | .30 | 22 |
|  | .41 | 31 |

---

(14) H. G. Weiss, J. A. Knight and I. Shapiro, THIS JOURNAL, **81**, 1826 (1959).

(15) It was found that the HD formed in these experiments exhibited rapid self-exchange in the presence of alumina and silica-alumina as expected[5,16] but not in the presence of silica gel.

(16) V. C. F. Holm and R. W. Blue, *Ind. Eng. Chem.*, **43**, 501 (1951).

The Boron Number is a measure of the fraction of diborane on alumina in silica–alumina and can be used to calculate the fraction of total hydroxyl groups on alumina. To make this calculation it is necessary to know the exact value of the hydrogen to diborane ratio for reaction with hydroxyl groups attached to aluminum and silicon atoms in silica–alumina. Using the values obtained experimentally with the separate oxide gels, *i.e.*, 1:1 for alumina and 3:1 for silica, the fraction of hydroxyl groups on alumina can be calculated from the formula: $f(\mathrm{Al}) = B_n/[B_n + 1.5(1 - B_n)] = B_n/[1.5 - 0.5B_n]$, where $B_n$ is the Boron Number. Further work is indicated to determine whether the absolute values for fraction of hydroxyls on alumina shown in Table II are real. However, relative to one another the changes are significant. It can be seen from Table II that the OH sites on silica–alumina are associated with both silicon and aluminum atoms when the catalyst has been heated at 250°. The hydroxyl ratios also show that heating to higher temperatures tends to eliminate the silica hydroxyl groups at a faster rate than those associated with the alumina. The fact that the Boron Number and Hydroxyl Ratio drops on long-time heating at 500° indicates that water is now being eliminated from the aluminum or that hydroxyls may be transferring from aluminum to silicon atoms. In addition to the change in Boron Number, the above conclusions are supported by the following corroborating evidence: (1) the hydrogen–diborane ratios decrease with increasing drying temperatures until they approach the limiting ratio (1:1) of alumina and, (2) the exchange reactions for catalyst dried at low temperatures exhibit the slow rate characteristic of silica, while for samples heated to higher temperatures this rate of exchange increases (as in alumina).

Other exchange studies, involving diborane–catalyst adducts, are currently being studied and will be reported separately. The utility of the concept of Boron Number for studies on silica–alumina has been demonstrated for this particular work on activation temperatures. The possibility that Boron Number and catalyst activity may be related is also being examined.

Pasadena, Cal.

---

[Contribution from the Research Laboratory, Olin Mathieson Chemical Corporation]

# Boron Exchange between Diborane and Pentaborane-9 in the Presence of Alumina Catalysts

By H. G. Weiss, J. A. Knight and I. Shapiro

Received October 29, 1958

Boron exchange between diborane and pentaborane occurs in the presence of $\gamma$-alumina at 90°; no such exchange takes place under comparable conditions in the absence of the catalyst. The role of the alumina has been elucidated by use of isotopic techniques. The alumina provide sites for the formation of a diborane–catalyst complex, which is capable of exchanging boron atoms with either diborane or pentaborane-9. The exchange of the catalyst complex with pentaborane-9 is slower than with diborane.

Mixtures of isotopically different diboranes are known to reach equilibrium distributions quickly at room temperature.[1] This exchange, of course, arises from the rapid equilibrium between diborane and borane, *viz.*, $B_2H_6 \rightleftarrows BH_3$. Of the exchange reactions reported between diborane and higher molecular weight boron hydrides only the unstable hydrides,[2] $B_4H_{10}$ and $B_5H_{11}$, have shown boron participation. The boron exchange of diborane with these molecules has been explained[2] on the basis of fragmentation of the $B_4H_{10}$ or $B_5H_{11}$ molecules. The stability of pentaborane-9 and decaborane (relative to $B_4H_{10}$ and $B_5H_{11}$) is such that boron exchange with diborane should be considerably less than in the case of $B_4H_{10}$ or $B_5H_{11}$. In fact, it was found that there was no boron exchange between diborane and pentaborane-9[3,4] at 80° or between diborane and decaborane[5] at 100°, although there was hydrogen exchange under these conditions. The tendency of the stable boron hydrides to resist boron exchange even at high temperatures is illustrated in the self exchange of pentaborane[6] at 250° (vapor phase); in this case no boron exchange was observed even though considerable decomposition had occurred.

In our Laboratory, boron exchange was observed between pentaborane-9 and $B^{10}$-enriched diborane on exposure to a chrome–alumina catalyst at 90°. Similar results were obtained under the same conditions on platinum–alumina and on $\gamma$-alumina. The reactions discussed here were carried out using platinum on alumina. Pentaborane-9 was found to exchange with diborane through a mechanism involving a catalyst–diborane complex, which also exchanged with diborane vapor. Relative rates of the two exchange reactions are such that diborane (vapor) was essentially in equilibrium with the complex at all times.

## Experimental

1. **Reagents.** **0.3% Platinum on Alumina Catalyst.**—Baker and Co., Inc., 1/8″ pellets were dried *in vacuo* at 450° prior to use.

**Diborane.**—$B^{10}$-enriched diborane was prepared by reaction of lithium aluminum hydride with $B^{10}$-enriched boron trifluoride etherate.[7]

---

[1] P. C. Maybury and W. S. Koski, *J. Chem. Phys.*, **21**, 742 (1953).

[2] W. S. Koski, Résumés of Communications, 16*th* Internat. Cong. Pure and Appl. Chem. (Paris), 1957.

[3] W. S. Koski and J. J. Kaufman, *J. Chem. Phys.*, **24**, 221 (1956).

[4] J. J. Kaufman and W. S. Koski, *ibid.*, **24**, 403 (1956).

[5] J. J. Kaufman and W. S. Koski, This Journal, **78**, 5774 (1956).

[6] I. Shapiro and B. Keilin, *ibid.*, **77**, 2663 (1955).

[7] I. Shapiro, H. G. Weiss, M. Schmich, S. Skolnik and G. B. L Smith, *ibid.*, **74**, 901 (1952).