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Hydroxyl Groups on Silica, Alumina, and Silica-Alumina Catalysts

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In order to characterize the surface hydroxyls on silica, alumina, and silica-alumina catalysts, several kinds of organometallic compounds were used. Experiments were carried out with a closed system under normal nitrogen atmosphere and the volume of ethane produced was measured. For the silica-alumina catalyst, the results obtained with all the reagents were the same and were comparable to the amount of hydroxyl group measured by another method. For alumina and silica, the results obtained with ethyllithium, ethylmagnesium bromide, and triethylaluminum were also the same. The amounts obtained with diethylaluminum chloride and ethylaluminum dichloride were smaller. It seems that the hydroxyl groups on silica-alumina are different from those on alumina or silica, which are composed of two or more kinds of hydroxyl groups. Alkali-poisoned, ion-exchanged, or catalysts supported on other materials were also examined.

INTRODUCTION

Since silica, alumina, and silica-alumina have been widely employed as catalysts or as catalyst supports, a considerable amount of research has been devoted to elucidating the nature of their properties and functions. In general, these catalysts have been regarded as acid-type catalysts, and there are various methods by which the acidity is measured. For example, this can be done by determining the amount of ammonia or amine adsorbed in the vapor phase (*1*, *2*) or the ion-exchange capacity in aqueous solution (*3*, *4*), or by making *n*-butylamine titration in nonaqueous solution (*5–7*). The strength is determined from the correlation between the amount of ammonia or pyridine adsorbed in the vapor phase and the temperature employed, or by a series of titrations in nonaqueous solution using various indicators.

On the other hand, many authors have studied how these acid properties arise and how the acidities are correlated to catalytic activities and selectivities. Millikan *et al.* (*8*) found that there is a proportional correlation between the activity for the cracking of cumene and the acidity of silica-alumina. Tamele (*9*) reported that the activity for the polymerization of propylene was proportional to the acidity of silica-alumina, but the activity for the cracking of cumene was not proportional to the acidity. Holm *et al.* (*10*, *11*) studied the activities for various types of reactions, i.e., the cracking of *n*-octane, the polymerization of propylene, the isomerization of *o*-xylene, and the hydrogen transfer between decalin and isobutene, with a series of silica-alumina compositions. We also reported (*12*, *13*) that the activities for the cracking of cumene, the polymerization of propylene and 1-butene, and the double-bond migration of 1-butene were closely correlated with the Brönsted acidity and that the activity for the cracking of isobutane was proportional to Lewis acidity.

It is reasonable to consider that Brönsted acid is related to a part of the surface hydroxyl groups on a catalyst. There are various techniques for determining the surface hydroxyl, i.e., by infrared spectra (*14–19*), by the diborane technique (*20–22*), by exchanging the hydrogen atom of the surface hydroxyl group with deuterium or heavy water (*19, 23–25*), and by using alkyllithium or alkylmagnesium bromide (*26*).

The first method requires an infrared spectrophotometer and an adequate apparatus which is made of infrared-transparent materials and which can be used at high temperature under high vacuum. Moreover, it is well known that silica or alumina have two or more bands attributed to the surface hydroxyl groups and that the hydroxyl group connected with Brönsted acids in silica-alumina can not be detected by infrared spectroscopy. In some cases of catalysts supported on other materials, it is supposed that the bands are shifted to a higher or longer region and are so broadened as to become difficult to detect or evaluate with the kind of the material supported. Therefore, it seems to be hard to assign and estimate all hydroxyl groups of catalysts.

The second method gives an error owing to autoevaluation of hydrogen from the reaction between the boron compounds used and those produced. In addition, the assumption that the hydrogen–diborane ratio changes from 2 to 1 with the distance between two hydroxyl groups still leaves some question.

The third method requires a mass spectrometer and the procedure is troublesome. Under these circumstances the fourth method using organometallic compounds appears attractive since it can be very easily carried out without any instrument.

The basis of this chemical technique (*27, 28*) is the reaction of an organometallic reagent with the surface hydroxyl groups on a catalyst. Recently, an enormous number of organometallic compounds have been synthesized and among those there are many reagents which react with the compounds containing active hydrogen to produce hydrogen or hydrocarbons. It is well known that the stronger the ionic character of the carbon–metal bonds, the more the reactivity increases (*29–31*). If various types of hydroxyl groups were present on the surface of a catalyst, different results would be obtained depending on the organometallic compounds used. From the results obtained, one should be able to determine the site on which alkali or the material added is deposited, and whether the material added reacts with the surface hydroxyl groups or not. In this way it is possible to evaluate acidity of the catalysts. The following experiments were carried out.

EXPERIMENTAL

Catalysts. Silica was prepared by hydrolysis of redistilled ethyl orthosilicate with aqueous ammonia, filtered, dried at 120°C, and then calcined at 550°C for 2 hr. Alumina was also prepared by hydrolysis of redistilled aluminum isopropoxide in isopropyl alcohol with distilled water, washed, filtered, dried at 120°C and then calcined at 500°C for 2 hr. Coprecipitated silica-aluminas with various compositions were prepared by hydrolysis of the isopropyl alcohol solution containing ethyl orthosilicate and aluminum isopropoxide with distilled water, washing, filtering, drying at 120°C, and then calcining at 550°C for 2 hr. The cogelated silica-alumina with 85% silica content was prepared as reported previously (*12*). Then, Na-poisoned silica was prepared by allowing 1 g of the above silica to stand in an aqueous solution containing 0.032 g of sodium carbonate, filtering, drying at 120°C, and then calcining at 500°C for 2 hr. Na-Poisoned alumina was also prepared by the same procedure as silica. Na-Poisoned silica-aluminas were prepared by ion-exchanging the coprecipitated silica-alumina (SiO_2:Al_2O_3 = 80:20 and 20:80) with aqueous sodium formate solution, filtering, drying at 120°C, and then calcining at 550°C for 2 hr. Alumina-boria catalyst was prepared by letting 1 g of the alumina stand overnight in the aqueous solution containing 0.104 g of boric acid, evaporating, and then calcining at 550°C for 2 hr. Molybdenum-alumina catalysts were prepared by the usual method from γ alumina (Nihon Keikinzoku K. K.) and ammonium molybdate. The surface area of all catalysts were measured by the BET method using nitrogen.

Reagents. Ethylmagnesium bromide was prepared by mixing 23.8 g of ethyl bromide with 5.8 g of magnesium ribbon in 80 ml of di-*n*-butyl ether at 30–40°C. Ethyllithium (*32*) was prepared by adding 29.4 g of ethyl bromide in 50 ml of ethyl ether to 3.5 g of lithium wire in 20 ml of ethyl ether, the ether was distilled *in vacuo,* and then 50 ml of di-*n*-butyl ether was added thereto. Triethylborane (*33*) was prepared by reacting triethylborate with triethylaluminum, and then redistillation before use. Triethylaluminum, diethylaluminum chloride, and ethylaluminum dichloride were commercial products from Ethyl Corporation, used without further purification. In order to decrease the error resulting from the vapor pressure of a solvent, decalin was used as a solvent except in cases where ethyllithium and ethylmagnesium bromide were used. In both cases the solutions obtained synthetically were used as soon as possible after preparation. The concentration of reagents was 0.5 or 1.3 mole/liter and all the experiments were carried out under nitrogen atmosphere. Nitrogen was purified by deoxygenation using reduced copper on Kieselguhr at 170–200°C and dried using silica gel and phosphorous pentoxide.

Apparatus and procedure. Figure 1 is a schematic drawing of the apparatus employed in this study. The reactor A was made of Pyrex glass and the volume was about 20 ml. The total volume of the system was about 150 ml. The capacities of the burets C and C′ were 10 and 30 ml, respectively. About 0.2 g of the catalyst calcined at 550°C was placed in reactor A and then the reactor was slowly heated to 450°C by a tubular electric furnace under nitrogen atmosphere.

After carefully lowering the pressure to 10^{-2}–10^{-3} mm Hg, the reactor was heated

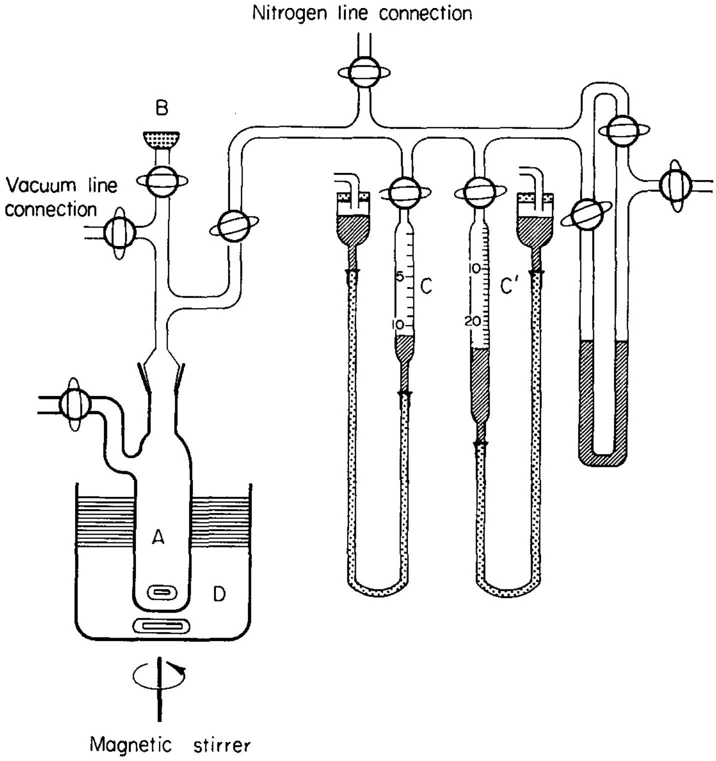

FIG. 1. Apparatus: A, reactor; B, serum cap for addition of organometallic compound; C,C′, gas buret; D, thermostat.

for 2 hr under this pressure. By removing the furnace, the reactor was cooled to room temperature and then nitrogen was allowed into the system up to atmospheric pressure. The reactor was removed from the system while passing nitrogen gas into the reactor and a magnetic stirrer was put into the reactor. Then a thermostat was put in place and set up at the desired temperature and the pressure in the system was corrected to atmospheric pressure. After the system was isolated by operating glass cocks, 1.0 or 1.5 ml of the above solution which contained about four or five equivalents of organometallic compound to one of surface hydroxyl groups was poured into the reactor through the serum cap B with an injection syringe provided with a long stainless steel capillary tube whose end was able to reach the reactor bottom. The volume of evolved gas was measured by the buret C or C′ as a function of the reaction time. From the volume obtained, the volume of the solution used and the error resulting from the vapor pressure of the solvents was corrected. The error arising from changes of room temperature was also corrected for by a correction chart obtained beforehand. In ethyllithium runs, a blank test was carried out immediately after each experiment, because the reagent reacts with di-*n*-butyl ether to produce ethane and 1-butene (*34*, *35*). The gas evolved was determined by gas chromatography.

RESULTS AND DISCUSSION

Reactions between organometallic compounds and the hydroxyl groups of catalysts fundamentally proceed as shown in Fig. 2. The rapid ethane evolution takes place from the reaction of the surface hydroxyl groups with the reagents, and then the hydroxyl groups in the pores react slowly, with diffusion of the reagents. It requires 2 hr to determine the hydroxyl content of catalysts (*5*, *7*).

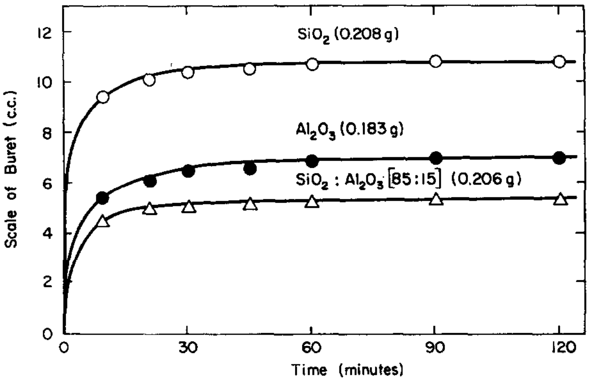

FIG. 2. Volume of ethane evolved against reaction time at 30°C.

The results obtained on silica-aluminas with triethylaluminum at various temperatures are shown in Table 1. It is clear that the total volume of ethane evolved was constant at 0°, 30°, and 60°C. From the experiments carried out with various amounts of triethylaluminum, it has also been found that only one ethyl group among the three ethyl groups reacted with the surface hydroxyl groups.

TABLE 1
EFFECT OF REACTION TEMPERATURE ON THE VOLUME OF ETHANE EVOLVED FROM TRIETHYLALUMINUM

Reaction temp. (°C)	C_2H_6 evolved [ml/g (NTP)]	Equiv./m² $\times 10^6$	OH/cm² $\times 10^{-14}$
0°	18.9	8.45	1.49
30°	17.9	7.95	1.40
60°	18.2	8.12	1.43

The results obtained with alumina,

TABLE 2

Hydroxyl Groups on Silica, Alumina, and Silica-Alumina Calculated from the Volume of Ethane Evolved

Organometallic compound	Cogelated silica-alumina (85:15), 343 m²/g			Silica, 807 m²/g			Alumina, 249 m²/g		
	C_2H_6 [ml/g (NTP)]	equiv./m² $\times 10^6$	OH/cm² $\times 10^{-14}$	C_2H_6 [ml/g (NTP)]	equiv./m² $\times 10^6$	OH/cm² $\times 10^{-14}$	C_2H_6 [ml/g (NTP)]	equiv./m² $\times 10^6$	OH/cm² $\times 10^{-14}$
C_2H_5Li	—	—	—	33.8	1.87	1.13	25.1	4.50	2.70
C_2H_5MgBr	15.7	2.04	1.23	34.7	1.92	1.16	25.6	4.59	2.76
$(C_2H_5)_3Al$	17.9	2.33	1.40	39.0	2.16	1.30	26.2	4.70	2.82
$(C_2H_5)_2AlCl$	16.1	2.10	1.26	24.9	1.38	0.83	15.4	2.76	1.66
$(C_2H_5)AlCl_2$	16.8	2.18	1.32	11.0	0.61	0.37	7.25	1.30	0.78
$(C_2H_5)_3B$	0	—	—	0	—	—	0	—	—

silica, and silica-alumina with various organometallic compounds at 30°C are shown in Table 2.

Silica-alumina reacted with all the organometallic compounds to produce the same volume of ethane per gram within experimental error. Silica and alumina also produced the same volume of ethane with ethyllithium, ethylmagnesium bromide, and triethylaluminum, but with diethylaluminum chloride and ethylaluminum dichloride, both gave only a smaller volume of ethane than with the other three organometallic compounds.

The results obtained from the reactions of a series of coprecipitated silica-aluminas with triethylaluminum and ethylaluminum dichloride are shown in Table 3 and Fig. 3.

Silica and alumina gave different volumes of ethane from the reactions with triethylaluminum and ethylaluminum dichloride, respectively. These facts show that silica or alumina have at least two different types of hydroxyl groups.

In a series of coprecipitated silica-aluminas, the composition which produced the largest volume of ethane with ethylaluminum dichloride was at 80:20, both per gram and per cm². In comparing the results shown in Table 3, it has been found that two silica-aluminas (silica: alumina = 60:40 and 80:20) gave the same volume of ethane from the reactions with both reagents, but silica-aluminas with low silica content (silica:alumina = 20:80 and 40:60) gave a different volume of ethane like alumina or silica, respectively.

It is well known that silica-alumina has Brönsted acid and Lewis acid sites. The total acidity of the cogelated silica-aluminas which was produced by the same procedure as the silica-alumina (85:15) in Table 2 was $1\text{–}2 \times 10^{-6}$ equiv./m² (*12*). The value for the coprecipitated silica-alumina (80:20) in Table 3 was 0.36×10^{-6} equiv./m². On comparing the results in Tables 2 and 3 with the acidities for those catalysts, it is clear that the total acidity

TABLE 3

Hydroxyl Groups on a Series of Coprecipitated Silica-Aluminas Calculated from the Volume of Ethane Evolved

Catalyst		$(C_2H_5)_3Al$			$C_2H_5AlCl_2$			
SiO_2: Al_2O_3 (wt %)	Surface area (m²/g)	Volume of gas evolved [ml/g (NTP)]	equiv./m² $\times 10^6$	OH/cm² $\times 10^{-14}$	Volume of gas evolved [ml/g (NTP)]	equiv./m² $\times 10^6$	OH/cm² $\times 10^{-14}$	$\frac{C_2H_5AlCl_2}{(C_2H_5)_3Al}$
100:0	807	39.0	2.16	1.30	11.0	0.61	0.37	0.29
80:20	277	13.4	2.16	1.30	13.1	2.11	1.27	0.98
60:40	331	11.2	1.51	0.91	11.8	1.59	0.96	1.06
40:60	330	11.8	1.60	0.96	8.5	1.15	0.69	0.72
20:80	313	17.5	2.50	1.50	7.6	1.08	0.65	0.43
0:100	249	26.2	4.70	2.82	7.25	1.30	0.78	0.28

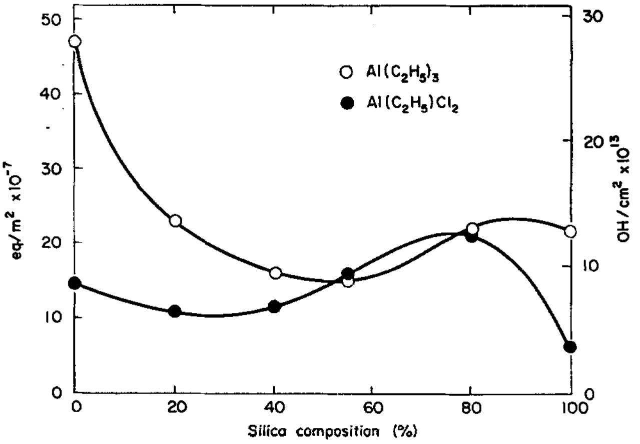

FIG. 3. Relation between surface hydroxyl groups and silica-alumina composition.

is 10–50% of surface hydroxyl groups with the assumption of the correctness of the acidity. Even if the total acidity is all due to Brönsted acid, it is clear that different types of hydroxyl groups [(III), (IV) in Fig. 4] than the hydroxyl group of a Brönsted acid [(I) or (II) in Fig. 4] are also present on the surface of silica-aluminas with high silica content; the same results were obtained with triethylaluminum and with ethylaluminum dichloride. In silica-aluminas with low silica content in which considerable differences arise between results obtained with triethylaluminum and with ethylaluminum dichloride, it is obvious that still other types of hydroxyl groups exist on the surface. In conclusion, there are two or more types of hydroxyl groups on the surface of silica-alumina catalysts.

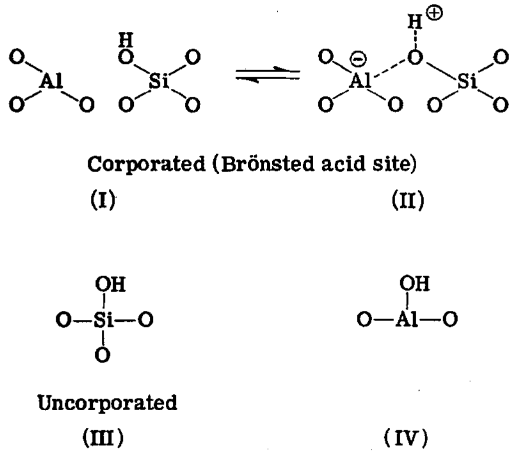

FIG. 4. Hydroxyl group on silica-alumina: (I) and (II), Brönsted acid site; (III) and (IV), other Free hydroxyl groups.

It is well known that the cracking activity for silica-alumina catalysts is due to the strong Brönsted acid and that the distribution of acid strength is in the stronger range, $pK_a = -8.3$, of a Hammet indicator. On the other hand, it was reported that trialkylboranes are hydrolyzed with a mineral acid like hydrogen bromide (*36*) under reflux and more readily hydrolyzed with a carboxylic acid (*37*, *38*) like acetic acid.

$$(n\text{-}C_4H_9)_3B + HBr \rightarrow (n\text{-}C_4H_9)_2BBr + n\text{-}C_4H_{10}$$

$$(n\text{-}C_4H_9)_2BBr + H_2O \rightarrow (n\text{-}C_4H_9)_2BOH + HBr$$

$$(C_2H_5)_3B + CH_3COOH \rightarrow (C_2H_5)_2BOCOCH_3 + C_2H_6$$

If triethylborane reacts with the Brönsted acid on silica-alumina, diethylboron silicate and ethane would be obtainable. But triethylborane did not react with silica-alumina at 30° and 98°C. This fact is of interest from the concept of Brönsted acid, and it is clear that the Brönsted acid on silica-alumina is no usual Brönsted acid. The reason might be considered as follows:

A Brönsted acid containing trigonal aluminum is considered to be Lewis acid (V) or Lewis base (VII), as shown in Fig.

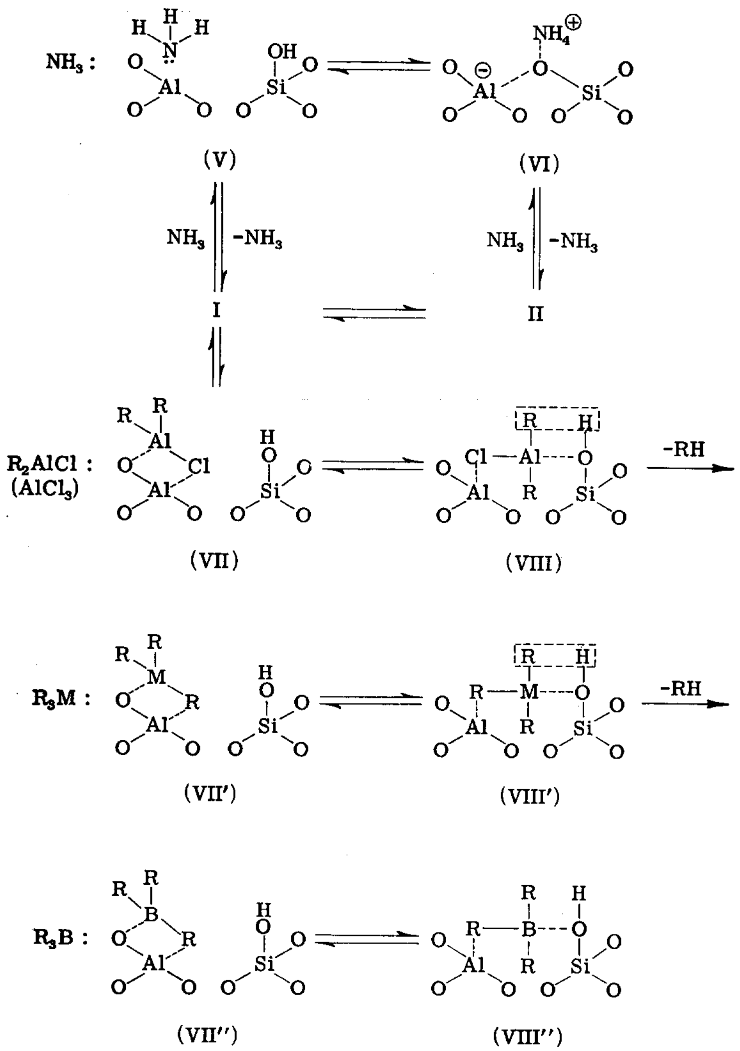

FIG. 5. Coordinate complexes of Brönsted site with ammonia and organometallic compounds.

5, because of its ability to become tetrahedrally coordinated due to its electron-accepting property. When an organometallic compound is added to silica-aluminas the reagent coordinates with (I) or (II) to produce (VII), (VII′), or (VII″). For triethylborane, the hydroxyl groups of (VII″) are too inactive to react with the adjacent B–R group or with another triethylborane molecule. Therefore, triethylborane can not react with the proton of Brönsted acid on silica-aluminas.

From Table 2, it can be concluded that the numbers of surface hydroxyl groups are as follows: cogelated silica-alumina (85:15), 1.4 × 10^{14} OH/cm^2; silica, 1.3 × 10^{14} OH/cm^2; alumina, 2.8 × 10^{14} OH/cm^2, respectively. Hall *et al.* (*39*) determined by a deuterium exchange technique that silica-alumina, silica, and alumina evacuated at 550°C have 1.4 × 10^{14} OH/cm^2, 2.5 × 10^{14} OH/cm^2, and 2.4 × 10^{14} OH/cm^2, respectively. The results are very consistent in spite of the difference in preparation and pretreatment. Therefore, it is obvious that to determine the number of surface hydroxyl groups on solid catalysts, the procedure using organometallic compounds like ethyllithium, ethylmagnesium bromide, and triethylaluminum is a suitable method and that among the three reagents, triethylaluminum is the most convenient, because this compound is commercially obtainable and gives no evolution of hydrocarbon, unlike ethyllithium (*34, 35*).

$$C_2H_5Li + C_4H_9OC_4H_9 \rightarrow C_3H_7CHLiOC_4H_9 + C_2H_6$$

$$C_3H_7CHLiOC_4H_9 \rightarrow CH_2{=}CHC_2H_5 + LiOC_4H_9$$

The results obtained from Na-poisoned and ion-exchanged catalysts and catalysts supported on other materials are shown in Table 4. The concentration of hydroxyl groups on Na-poisoned silica was 2.91 × 10^{-6} equiv./m^2 and the surface area was 148 m^2/g. Therefore, it is clear that the decrease of hydroxyl groups per gram is caused by the decrease of surface area and that the hydroxyl groups per unit area actually increase from 1.3 × 10^{14} to 1.7 × 10^{14}/cm^2 by poisoning. The proton of silanol groups is acidic like silicic acid, and therefore, alkali reacts with the silanol group or the Si–O–Si bond to produce SiONa or SiONa and SiOH. On calcining in the presence of excess water, the surface area greatly decreases. In alumina, the number of hydroxyl groups did not change on poisoning with sodium carbonate. The activity and selectivity for isobutane cracking greatly changed on poisoning alumina with sodium carbonate (*40*). These facts show that alkali adsorbs at active sites or reacts with some hydroxyl groups or Al–O–Al bonds to produce AlONa or AlONa and AlOH, and that during calcining in the presence of excess water the same amount of hydroxyl groups is produced again.

TABLE 4

HYDROXYL GROUPS ON NA-POISONED CATALYSTS AND CATALYSTS SUPPORTED ON OTHER MATERIALS

		$(C_2H_5)_3Al$			$C_2H_5AlCl_2$			
Catalyst	Surface area (m^2/g)	C_2H_6 (evolved) [cc/g (NTP)]	equiv./m^2 10^6	OH/cm^2 10^{-14}	C_2H_6 (evolved) [cc/g (NTP)]	equiv./m^2 10^6	OH/cm^2 10^{-14}	$\frac{C_2H_5AlCl_2}{(C_2H_5)_3Al}$
SiO_2	807	39.0	2.2	1.3	11.0	0.61	0.37	0.28
Na-poisoned	148	9.46	2.91	1.71	—	—	—	—
Al_2O_3	248	23.3	4.18	2.53	6.60	1.18	0.71	0.28
NH_3 adsorbed	—	23.4	4.26	2.58	—	—	—	—
Na-poisoned	—	23.1	4.14	2.50	7.02	1.26	0.76	0.304
Al_2O_3—B_2O_3	272	12.8	2.30	1.39	6.32	1.13	0.68	0.494
γ-Al_2O_3	142	16.5	5.20	3.12	—	—	—	—
15% MoO_3	140	15.0	4.80	2.88	—	—	—	—

Alumina was treated with ammonia at 450°C under 10^{-2}–10^{-3} mm Hg and then the hydroxyl groups were measured by the usual procedure with triethylaluminum at 30°C. As shown in Table 4, the value per gram was not changed. This fact shows that in treating alumina with ammonia at 450°C, the dehydration reaction between surface hydroxyl groups and ammonia was not carried out.

In the case of B_2O_3-supported alumina, the amount of hydroxyl groups which can react with triethylaluminum decreased considerably, but the amount of hydroxyl groups which can react with ethylaluminum dichloride was not changed. These results show that the surface hydroxyl groups on alumina react with boric acid during calcination and that the hydroxyl groups with weak reactivity react with boric acid. In the case of MoO_3-supported alumina, the hydroxyl groups numbered 4.8 × 10^{-6} equiv./m^2, namely, 2.88 × 10^{14} OH/cm^2. It is clear that taking into consideration the MoO_3 added, the hydroxyl groups do not react with ammonium molybdate during calcination.

The results obtained from two ion-exchanged silica-aluminas are shown in Table 5. In these catalysts, the amount of sur-

TABLE 5
HYDROXYL GROUPS ON ION-EXCHANGED SILICA-ALUMINA

	Unexchanged			Exchanged			
SiO_2:Al_2O_3	C_2H_6 (evolved) [cc/g (NTP)]	equiv./m² $\times 10^6$	OH/cm² $\times 10^{-14}$	C_2H_6 (evolved) [cc/g (NTP)]	equiv./m² $\times 10^6$	OH/cm² $\times 10^{-14}$	Difference equiv./m² $\times 10^6$
80:20	13.4	2.16	1.30	11.8	1.90	1.15	0.26
20:80	17.5	2.34	1.41	14.3	2.03	1.23	0.31

face hydroxyl groups decreased from 2.16×10^{-6} and 2.34×10^{-6} equiv./m² to 1.90×10^{-6} and 2.03×10^{-6} equiv./m², respectively. The acidities of these catalysts were determined by the Benesi method to be 0.36×10^{-6} and 0.54×10^{-6} equiv./m². From these results, it seems that the difference of the amount of surface hydroxyl groups produced before and after ion-exchanging is concerned with the Brönsted acidities of the catalysts and with the question whether the ion exchange is carried out perfectly or not. The Brönsted acidity has generally been calculated by subtracting the Lewis acidity obtained by Leftin's method (*41*) from the total acidity obtained by the Benesi method (*7*). The Lewis acidity obtained by this procedure is ambiguous. Therefore, it is preferable to determine Brönsted acidity independently and to calculate the Lewis acidity by subtracting the Brönsted acidity obtained from the total acidity. If ion exchange can be carried out in the solvent containing no active hydrogen, it seems to be possible for the Brönsted acidity to be independently determined without the destruction of catalyst surface. We are studying further details on this point.

CONCLUSIONS

The determination of the number of surface hydroxyl groups on oxide- and acid-type catalysts and on catalysts supported on other materials was carried out by measuring the volume of ethane produced from the reaction with several kinds of organometallic compounds. From the results, the following facts were discovered: (1) In silica-alumina with high silica content, the volume of ethane was constant, but in silica-alumina with low silica content, silica or alumina, the volume was changed with the kind of reagents used. (2) In order to determine the total surface hydroxyl groups, triethylaluminum is most convenient, since this compound is very reactive and gives no evolution of hydrocarbon, unlike ethyllithium. (3) Triethylborane can not react with silica-alumina containing a strong Brönsted acid. It is concluded that the Brönsted acid of silica-alumina is different from the usual Brönsted acid and the reason has been discussed. (4) In catalysts supported on other materials it is possible to determine whether the material added reacts with the surface hydroxyl groups of a carrier or not. (5) There is some possibility of determining the amount of Brönsted acid from the difference of the number of surface hydroxyl groups before and after ion-exchanging.

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