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Studies on Solid Catalysts with a Basic Character I.

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The acidic and basic properties of catalysts obtained by saturation of silica gel with various amounts of NaOH were investigated. The investigations were carried out on catalysts dried at 120°C and roasted at 1000°C.

The strength of the superficial base was determined semiquantitatively from the adsorption of acidic indicators from nonpolar solutions. It was established that catalysts with small amounts of sodium have acidic properties and after application of larger amounts of sodium show basic properties.

The superficial basicity was determined by titration with sulfuric acid in an aqueous medium and by titration with perchloric acid in anhydrous acetic acid.

Attempts were also made to determine the superficial acidity of the same catalysts by titration with Na ethoxide in anhydrous picoline.

The investigations showed that on the surface of the investigated catalysts, beside centers of a basic character, there exist centers of an acidic character. Moreover it was established that roasted catalysts loose their acidic character, probably as a result of splitting off of OH groups, their basicity remaining unchanged.

The catalytic activity of the surfaces of solids is generally attributed to active centers. The centers constituting the source of protons or electron acceptors are acids according to Brønsted's or Lewis's theory. Those which exhibit basic properties in Brønsted's sense, bind protons; the adjoining of protons is conditioned by the presence of a free electron pair.

The problem of surfaces of an acidic character has lately been the object of numerous works (*1–5*), however, in the literature no investigations concerning surface basicity have been found. In the present paper the basicity of the surface was studied using silica gel saturated with various quantities of sodium hydroxide as a model surface.

On the basis of investigations on the activity of the surface and taking into consideration the basicity as defined by Brønsted (*2*), the surface was examined from the point of view of its affinity to the proton. The basicity of the surface can be defined as the ability to convert an adsorbed neutral acid to its conjugate base by means of proton exchange. On the basis of this definition and of Walling's (*6*) paper, the strength of the surface base was determined by utilizing the adsorption of indicators of the character of electrically neutral acids from monopolar solutions, which, delivering the proton to the surface, change to the basic form with simultaneous change of color.

The equation for indicators of the character of electrically neutral acids is:

$$AH \rightleftharpoons A^- + H^+$$

In this case the strength of the base on the surface can be measured by the function of Hammett and Deyrup (*7*) in relation to the indicator with acidic properties:

$$H'_0 = pK + \log (C_{A^-}/C_{AH})$$

where C_{AH} is the concentration of the acidic form of the indicator and C_A is the concentrations of the basic form of the indicator.

Seven catalysts, prepared by saturating the silica gel with various quantities of sodium hydroxide, have been examined. The investigations comprised:

(1) the semiquantitative determination of the base strength by the indicator method in polar solutions;
(2) titration of the suspension in water with H_2SO_4 solution;
(3) measurement of the Brønsted basicity by means of potentiometric titration of the catalyst suspension in anhydrous acetic acid with perchloric acid solution in anhydrous acetic acid;
(4) measurement of the protonic acidity by means of potentiometric titration of the catalyst suspension in picoline with a solution of Na ethoxide in benzene.

EXPERIMENTAL

Seven catalysts with a varying Na content (Table 1) were tested. Their catalytic activity in the condensation reaction has been described elsewhere (*8–10*).

The silica gel used had the following properties:

Content of alkali metals	
Sodium	0.0053%
Potassium	0.0024%
Bulk density	0.268 g/cu cm
Specific surface area	147 sq meter/g
Pore volume	1.58 cu cm/g
Mean pore radius	21.5μ

Experiments were made with catalysts dried at 120° for 24 hr under vacuum (20 mm Hg) and catalysts dried at 1000° for 12 hr. The total water content was determined as the loss in weight during drying from 120° to 1000°.

TABLE 1
COMPOSITION OF CATALYSTS

No.	Na content (mole/100 g Si gel)	Total H_2O content (mole/100 g Si gel)
1	0.00031	0.105
2	0.014	0.126
3	0.025	0.138
4	0.036	0.148
5	0.081	0.176
6	0.125	0.244
7	0.187	0.284

The measurements were accomplished by the visual method. The change of color begins to be perceivable in the adsorbed indicator layer when about 10% of the second form is present, i.e. when the ratio of the basic form, A^-, to the acidic form, AH, amounts to:

$$C_{A^-}/C_{AH} = 0.1/0.9 \cong 0.1$$

Further increase of the color intensity is imperceptible to the eye; it can only be seen when 90% of the basic form is already present, i.e.:

$$C_{A^-}/C_{AH} = 0.9/0.1 = 10$$

Substituting these values into Hammett's equation:

$$H'_c = \mathrm{pK} + \log (C_{A^-}/C_{AH})$$

TABLE 2
DESIGNATION OF STRENGTH OF THE SURFACE BASE AND INDICATORS USED FOR MEASUREMENT

Indicator	pH	pK	Color	
			Acid	Base
Thymol blue	1.8–2.8	2.5	red	yellow
Bromophenol blue	3.0–4.6	3.8	yellow	blue-violet
"Congo" red	3.0–5.2	4.1	rose	blue
Alizarin sodium sulfonate	3.7–5.2	4.5	yellow	violet
Methyl red	4.4–6.2	5.2	red	yellow
Bromocresol purple	5.2–6.8	6.0	yellow	purple
Bromothymol blue	6.2–7.6	7.1	yellow	blue
Phenolphthalein	8.5–10.0	9.3	colorless	red

we see that the first change of color begins at the moment when:

$$H'_0 = \mathrm{pK} - 1$$

and the next takes place when:

$$H'_0 = \mathrm{pK} + 1$$

We assume that the intermediate color appears when 50% of the second form of the indicator is formed. Then:

$$C_{\mathrm{A^-}}/C_{\mathrm{AH}} = 1$$

and function

$$H_0 = \mathrm{pK}$$

According to this assumption the approximate value which characterizes the base strength on the surface is the pK value of the adsorbed indicator at which the intermediate color appears. The results are presented in Fig. 1.

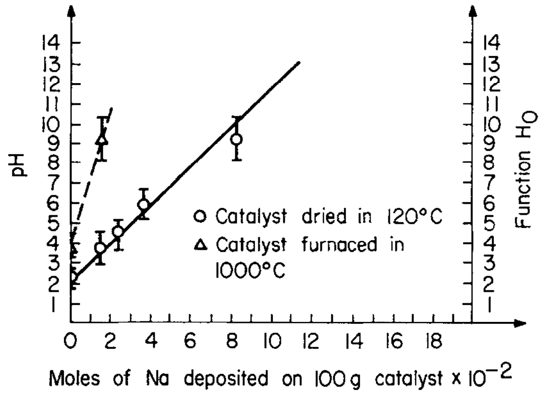

FIG. 1. pH values and Hammett function, H_0, estimated by means of adsorption on acid indicators from the nonpolar solvent medium vs. moles of Na in 100 g of silica gel catalyst.

Determination of Basicity in Water Suspension

The catalyst was thoroughly ground in a mortar and 0.5 g samples were weighed out. Four samples were taken of each catalyst: two were dried at 120°C and two roasted at 1000°C. The weighed sample was placed in a conical flask with 150 ml of distilled water and the mixture maintained in a state of mild boiling for half an hour, whereupon the samples were left to stand until the next day. Then 10 ml of 0.1 N H_2SO_4 were poured in, the mixture was brought to a boil and 1 ml of phenolphthalein solution was added. The excess of H_2SO_4 was titrated with NaOH solution until the first change of color of the indicator appeared. The results of measurement expressed as the quantity of gram-atoms of sodium/100 g of the catalyst are presented in Fig. 2 as a function of the Na quantity impregnated on the silica gel.

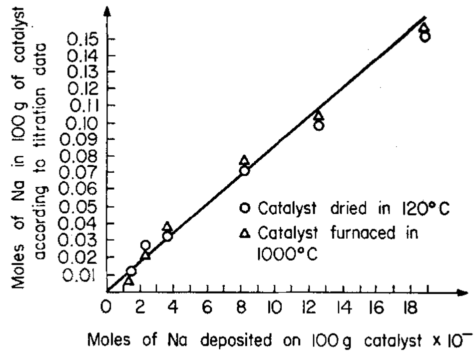

FIG. 2. Quantity of Na found by titration in water vs. quantity of Na impregnated on silica gel.

Measurement of the Brønsted's Basicity in an Anhydrous Acetic Acid Medium

The sample (ca. 1 g) of the catalyst was dried once more, directly before the measurement, at 120°C for 1 hr and 150 ml of anhydrous CH_3COOH was added. In the beaker a small stirrer and two electrodes

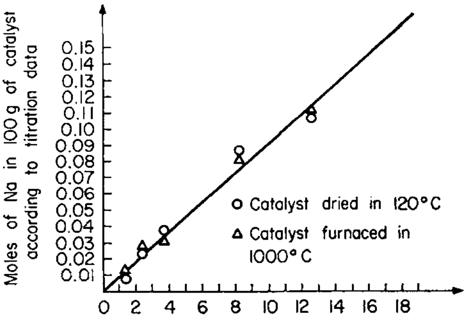

FIG. 3. Quantity of Na found by potentiometric titration in 100% acetic acid vs. quantity of Na impregnated on silica gel.

were placed—one of glass and the other of silver chloride—connected to the potentiometer: the suspension was titrated under stirring with 0.1 *N* perchloric acid solution in acetic acid. The equivalence point was determined from the change of potential. The results are expressed as the quantity of gram-atoms of sodium/100 g catalyst and are shown in Fig. 3 as a function of the Na quantity impregnated on silica gel.

Determination of the Protonic Acidity

A sample of the catalyst was dried once more, directly before measurement, at 120°C for 1 hr and placed in a beaker to which 150 ml of anhydrous picoline was added. The suspension was titrated with a 0.1 *N* solution of Na ethoxide in benzene, using the same electrodes as in the previous experiment. The results expressed as the quantity of gram-equivalents of protons/100 g of catalyst are presented in Fig. 4 as a function of the Na quantity impregnated on silica gel.

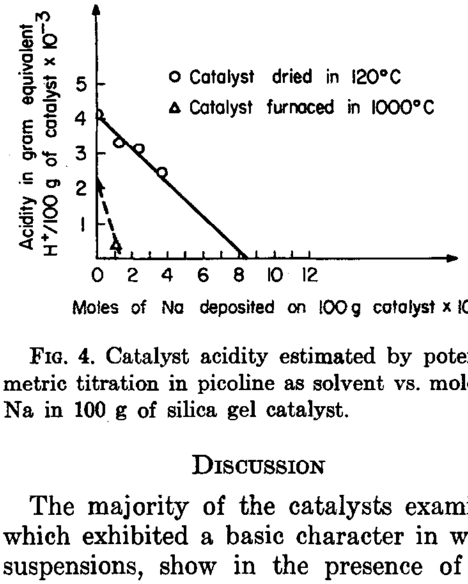

FIG. 4. Catalyst acidity estimated by potentiometric titration in picoline as solvent vs. moles of Na in 100 g of silica gel catalyst.

DISCUSSION

The majority of the catalysts examined which exhibited a basic character in water suspensions, show in the presence of the same indicators, in nonpolar solvents, acidic properties. In Fig. 1 is plotted the pK value equal to Hammett's function in dependence on the quantity of sodium impregnated on the silica gel.

It is obvious that in water partial hydrolysis of the —ONa groups to —OH and NaOH takes place on the surface, giving an alkaline reaction and a change of color of the indicators corresponding to the basic form. In the nonpolar solvents the mechanism of this process is different and consists in the capacity of the surface to detach a proton from the acid indicator. If the strength of the surface acting on the proton is small, the color does not change, as the acidic form of the indicator prevails. In the case of a strong action of the surface on the proton the basic form of the indicator predominates and a change of color occurs; the intermediate state is characterized by an intermediate color.

The result of our investigations suggests that the surfaces of the catalysts examined have both basic and acidic centers which interact: the acidic ones weaken the strength of the basic ones and vice versa. On the grounds of the aforementioned assumption the strength of the surface bases of the catalysts examined determined by means of indicator adsorption from nonopolar solutions represents the resultant value.

As foreseen, titration of a water suspension of the catalyst with sulfuric acid proved Arrhenius basicity (Fig. 2) which is due to the presence of OH^- ions formed in the solution owing to hydrolysis of the Si–ONa compound (salt of weak acid and strong base) to Si–OH and NaOH.

Potentiometric titration of the catalyst suspension in anhydrous acetic acid with perchloric acid gave almost identical results as the titration in water suspension, although the interaction is different: it consists in the exchange of a proton, characteristic of the basicity defined by Brønsted (Fig. 3).

The results of titration in anhydrous acetic acid have confirmed our supposition that the basicity of the catalysts examined is closely linked with the presence of sodium atoms on the surface.

In view of Bronsted's theory claiming that substances which are weak acids in water will undergo extensive protolytic reactions with basic solvents, we undertook determination of the acidic centers on the catalyst surfaces by titrating the catalyst suspension in anhydrous picoline with Na ethoxide. The results of titration are presented in Fig. 4.

The comparison of results of titrations in acetic acid and picoline permits us to advance the hypothesis that, on the surface of the examined catalysts, acidic and basic centers are simultaneously present.

This phenmenon may be explained as follows: It is known that there are hydroxylic groups on the surface of the silica gel; saturation of the silica gel with NaOH solution changes the —OH groups into —ONa groups, whereas systems in which all hydroxylic groups have not been exchanged for —ONa groups, possess acidic centers (—OH) along with basic ones (—ONa).

The results of titration in picoline seem to indicate a gradual decrease of the number of —OH groups until their complete disappearance. This point, found by way of extrapolation, corresponds to a content of ca. 0.09 gram-equivalent Na/100 g of the catalyst. This result is approximately in conformity with the calculated quantity of NaOH necessary for neutralizing all —OH groups on the surface. The calculation was made on the basis of measurement of the specific surface area of the silica gel examined and of the knowledge of the surface area occupied by one —OH group. Catalysts containing more than 0.09 gram-equivalents Na/100 g of gel do not exhibit any acidic properties.

The presence of both acidic and basic centers on the surface of some of the catalysts examined is confirmed by the results of the same experiments performed with catalysts dried at 120°C or roasted at 1000°C. The results are presented in Figs. 1–4. The roasted catalysts show no change of basicity as compared with the dried ones, however, their acidity diminishes considerably after this treatment. Besides the sodium-free gel, only one catalyst, that with the lowest Na content on the surface, exhibited some weak acidic properties. This fact may be explained by the reduced quantity of —OH groups on the catalyst surface involving a loss of acidic properties.

We have so far not found in the available literature any conception of amphoteric ability such as that advanced here. It would seem that this conception might explain some of the phenomena of the catalytic action of the surfaces, especially as far as reactions of ionic character are concerned.

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