# BASICITY AND ACIDITY OF SOLID SURFACES*)

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(Received November 13, 1963)


## Abstract

A method has been developed for the determination of the basicity of solid surfaces which consists of the titration of the solid suspended in benzene with benzoic acid, using bromthymol blue as the indicator. Surface basicity of MgO and CaO was determined by this method to be 0.033 and 0.007 mmoles/g respectively and the basicity of these solids found to be changed remarkably by heat-treatment. MgO showed a maximum basicity of 0.069 mmoles/g when treated at 500°C before the basicity measurements and the basicity of CaO treated at 650°C was found to be ten times as large as that of untreated one. No reliable data were obtained for the basicity of $K_2CO_3$, $Na_2CO_3$ and $Na_2CO_3 \cdot 10H_2O$ due to the strong hydrolyses. ZnO and ZnS which were reported to be solid bases by KRILOV *et al.* and NISHIMURA showed no basic property in this method. ZnO showed a slight acidity of 0.004 mmoles/g at acid strength $H_0 \leqq +6.8$, and *ca.* 0.010 mmoles/g at the same acid strength when heated in air or in vacuum. High acidity was observed for ZnS, *i.e.*, 0.773 mmoles/g at $H_0 \leqq +6.8$, 0.355 mmoles/g at $H_0 \leqq +4.8$ and 0.092 mmoles/g at $H_0 \leqq +4.0$. The acidity changed on heat-treatment and maximum acidities 2.77-1.45 mmoles/g at acid strength range, $+3.3 < H_0 \leqq +6.8$, were obtained when treated at 300°C.


## Introduction

A number of methods for determining acidity and acid strength of solid surfaces have been reported recently[1] and extensively used for the study concerning the correlation between catalytic activity and acidic property of solid catalyst. Very little work, however, has been made on basic property of solid surfaces. Only two methods for measuring basicity have been reported: i) method to observe the color change of bromthymol blue adsorbed on solid suspended in decalin[2] or in benzene[3] and ii) ,method to measure the amount of phenol vapor adsorbed on solid[4]. Basic property of MgO, CaO, $K_2CO_3$, ZnO, ZnS *etc.* has been measured by these methods. However, both the methods are not satisfactory, since method i) is quite qualitative and in method ii) phenol is very weak acid. Recently a method for the determination of the basicity of slag obtained during steel-making which consists of the titration of the slag

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*) Presented at the 13th Discussion Meeting on Catalysis, Sapporo, September 24, 1963.

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with $10^{-6}$ $N$ benzoic acid, using bromthymol blue as the indicator has been reported[5]. By developing this method we have attempted to measure the basicity of the solids which were reported once before to be basic and observed the change of the basicity on heat-treatment.

## Experimental

**Materials and Reagents**: Guaranteed reagents of MgO, CaO and $K_2CO_3$ (products of Kanto Chemical Co.) and of $Na_2CO_3$, $Na_2CO_3 \cdot 10H_2O$ and ZnO (products of Wako Pure Chemical Industries, Ltd.) and an extra pure reagent of ZnS (product of Kanto Chemical Co.) were employed. Powdered sample collected between 100 and 200 mesh sieves from each sealed new reagent bottle was used for basicity or acidity measurement. The sample was avoided to expose to moisture as practically as possible. In the case of MgO, CaO, ZnO, ZnS and $SiO_2 \cdot Al_2O_3$, roughly ground solids were heated in air or in vacuum ($10^{-5}$ mmHg) for 3 or 4 hours at various temperatures ranging from 300 to 700°C and allowed to cool in an evacuated desiccator before use. The 100–200 mesh powder was used for basicity or acidity measurement. About 3 minutes were required for grinding and sieving of sample, but moisture adsorbed on or reacted with these samples during the above procedures had negligible effect on basicity or acidity. $SiO_2 \cdot Al_2O_3$ was prepared by the method described by HARA *et al.*[6]

Bromthymol blue (B. T. B.) used as the indicator for basicity measurement was a guaranteed reagent of Kanto Chemical Co. The Hammett indicators used for acidity measurement are the same preparations as those described in our previous paper[7] and decrease in basicity from neutral red (N. R., $pK = +6.8$), through methyl red (M. R., $pK = +4.8$), phenylazo-$\alpha$-naphthylamine (P. N. A., $pK = +4.0$) and *p*-dimethylamino-azobenzene (D. Y., $pK = +3.3$) to benzeneazo-diphenylamine (B. D. A., $pK = +1.5$). Benzene (Kanto Chemical Co., guaranteed reagent) and benzoic acid (E. Merck, guaranteed reagent) were used without further purification.

**Measurement of Basicity and Acidity**: One half of one gram of the 100–200 mesh sample was put into a 100 ml Erlenmeyer flask with a ground glass stopper containing 20 ml of benzene and 1 ml of indicator solution (128 mg of B. T. B. in 100 ml of benzene) was added. If sample has basic property, the yellow dye reacts with the solid to show the green color of the indicator. Then the 0.1 $N$ benzoic acid in benzene was added dropwise from microburette. The neutralization was followed by noting the gradual disappearance of the green color of the solid particle. The end-point was taken as the point at which all the green color disappeared. Titration required about 15 minutes. The basicity is expressed in units of mmoles/g calculated from the titre of 0.1 $N$ benzoic acid required for the amount of solid sample.

Benzoic acid ($pK = +4.17$) having low volatility appeared satisfactory as the titrating acid. Phenol cannot be used in this case because its $pK(9.98)$ is greater than the $pK(7.10)$ of B. T. B.

Surface acidity and acid strength were measured similarly as in the previous work[7].

## Results and Discussion

1) **Basicity of Solids without Heat-treatment.** The results are shown in Table 1, where the third column gives pH*) of aqueous solution saturated with the

TABLE 1. Basicity of solids without heat-treatment

| Solid samples | Basicity mmoles/g | pH of aq. soln. saturated with solids |
|---|---|---|
| MgO | 0.033 | 10.8 |
| CaO | 0.007 | 12.4 |
| $K_2CO_3$ | 0.067 | $>13$ |
| $Na_2CO_3$ | not clear | $>13$ |
| $Na_2CO_3 \cdot 10\,H_2O$ | not clear | $>13$ |
| ZnO | 0 | 6.9 |
| ZnS | 0 | 5.0 |

solids. As seen in the Table, all solids except ZnO and ZnS hydrolyze and the aqueous solutions show basicity. Therefore, the basicity of basic materials formed by hydrolyses may be included in the observed basicity given in the second column, though sample and solvent were prevented from entering of moisture as practically as possible as mentioned in the foregoing section. Reliable data cannot be obtained for $Na_2CO_3$, $Na_2CO_3 \cdot 10\,H_2O$ and $K_2CO_3$, since these materials show strong basicity due to hydrolyzed products. It was difficult in the cases of $Na_2CO_3$ and $Na_2CO_3 \cdot 10\,H_2O$ to determine the end-point of titration, since the green color of B. T. B. adsorbed on the solids changes to yellow by the addition of benzoic acid, but the yellow changes again gradually to green in several minutes.

MgO and CaO showed the basicity of 0.033 and 0.007 mmoles/g respectively. These values seem considerably reliable on the following grounds. The amounts of the hydroxides of magnesium and calcium formed by hydrolyses are calculated

*) Measured by pH meter (Horiba Model M3).

to be $4.3 \times 10^{-4}$ and $1.8 \times 10^{-2}$ mmoles per ml of water from the observed pH given in Table 1, by taking the value $0.7 \times 10^{-14}$ as the dissociation constant of water at 20°C. Therefore, if one assumes that the observed basicity is all due to the hydroxide, 76.8 and 0.4 ml of water should be required for the formation of the hydroxides of respective amounts. In the present experimental condition, however, the amount of water included in sample and benzene as solvent is far less than the above figures. In this sense, data for dried samples given in Table 3 are furthermore reliable.

ZnO and even heated ZnO showed no basic property (see also Table 3). However, it is reported by KRILOV and FOKINA that considerable amount of phenol vapor was adsorbed on ZnO[4]. This seems to indicate that extremely weak basic sites are included in the observed basicity according to his method, since $pK$ of phenol is much greater than that of B. T. B. NISHIMURA has reported that ZnO without heat-treatment adsorbs B. T. B. to give green color[3], but his observation was not reproduced.

2) **Acidity of ZnO and ZnS.** ZnO and ZnS are reported to show both basic and acidic property but both solids showed no basic property in the present work as shown in Table 1. Since there are no quantitative data for acidic property of the solids, we have measured their acidity and acid strength.

TABLE 2. Acidity and acid strength of ZnO and ZnS

| Solid samples | Acidity (mmoles/g) | | | |
|---|---|---|---|---|
| | N. R. ($pK=+6.8$) | M. R. ($pK=+4.8$) | P. N. A. ($pK=+4.0$) | D. Y. ($pK=+3.3$) |
| ZnO | 0.004 | 0 | — | — |
| ZnS | 0.773 | 0.355 | 0.092 | 0 |

As shown in Table 2, ZnO showed 0.004 mmoles/g acidity at the acid strength $H_0 \leqq +6.8$ and no acidity at $H_0 \leqq +4.8$, *i.e.*, the acid strength of ZnO is weak and its acidity small. High acidity 0.773 at $H_0 \leqq +6.8$, 0.355 at $H_0 \leqq +4.8$ and 0.092 at $H_0 \leqq 4.0$ was found in ZnS. Since, however, ZnS did not change the basic color of D. Y., its acid strength is smaller than that of $NiSO_4$[7] or $SiO_2 \cdot Al_2O_3$[8]. $NiSO_4$ which is soluble in water loses its acidic property and catalytic activity in aqueous solution and $SiO_2 \cdot Al_2O_3$ shows little catalytic activity in aqueous solution. Since ZnS is insoluble in water, its application as acid catalyst in aqueous solution is expected.

3) **Basicity of Heat-treated Solids.** As shown in Table 3, MgO shows the maximum basicity 0.069 mmoles/g on heat-treatment at 500°C. The basicity of CaO heat-treated at 650°C was found to be almost ten times larger than that

TABLE 3. Basicity of heat-treated solids

| Solid samples | Temperature of heat-treatment (°C) | Time of heat-treatment (hr.) | Basicity (mmoles/g) |
|---|---|---|---|
| MgO | 300 | 3 | 0.036 |
| | 500 | 3 | 0.069 |
| | 700 | 3 | 0.051 |
| CaO | 650 | 3 | 0.073 |
| ZnO | 300 | 3 | 0 |
| | 400, in vacuum | 3 | 0 |
| $SiO_2 \cdot Al_2O_3$ | 500 | 4 | — |

of untreated one (see Table 1). Neither ZnO heated in air at 300°C nor in vacuum at 400°C showed basic property. In the case of $SiO_2 \cdot Al_2O_3$, the surface adsorbs B. T. B. to show bloodish red. This is considered due to the occurrence of any reaction other than acid-base transfer of B. T. B. Therefore the determination of basicity for $SiO_2 \cdot Al_2O_3$ by this method is difficult.

MgO and CaO react with water, if it presents, to form respective hydroxides as described in section 1), but the hydroxides change to their oxides on heat-treatment (*e.g.*, temperature of change to oxide is 580°C in the case of $Ca(OH)_2$). Since, therefore, the heated oxides do not contain their hydroxides, the results given in Table 3 give actually the basicity of the oxides. Another evidence for this is provided by the fact that the basicity of heated oxides which were allowed to stand in air for 5 minutes or one and a half hour were almost the same within the limit of the experimental error. The basicity of MgO is 0.86 mmoles/g at 25°C according to KRILOV's method. That this value is larger than the maximum value we obtained is considered due to the difference of $pK$ of adsorbents as mentioned in the foregoing section.

4) **Acidity of Heat-treated ZnO and ZnS.** As shown in Table 4, the acidity of heated ZnO was found to be three times as large as that of untreated one (see Table 2). There was found no difference in acidity between ZnO heated

TABLE 4. Acidity of heat-treated ZnO

| Temperature of heat-treatment (°C) | Time of heat-treatment (hr.) | Acidity (N. R.) (mmoles/g) |
|---|---|---|
| 300 | 3 | 0.010 |
| 500 | 3 | 0.010 |
| 400, in vacuum | 3 | 0.009 |

TABLE 5. Acidity and acid strength of heat-treated ZnS

| Temperature of heat-treatment (°C) | Acidity (mmoles/g) | | | | |
|---|---|---|---|---|---|
| | N. R. ($pK=+6.8$) | M. R. ($pK=+4.8$) | P. N. A. ($pK=+4.0$) | D. Y. ($pK=+3.3$) | B. D. A. ($pK=+1.5$) |
| 300[1)] | 2.77 | 2.54 | 1.45 | 0 | — |
| 400[2)] | *) | 1.08 | 0.460 | 0 | — |
| 500[3)] | 1.78 | 1.21 | 0.738 | 0.313 | 0 |
| 650[4)] | 0.060 | 0.058 | 0.010 | 0 | — |

1) The color of solid surface changes from pale yellow to slightly pinkish yellow on heat-treatment. 2) Slight brown. 3) Slightly brownish yellow. 4) Light yellow.
*) Difficult to observe the color change of N. R. for this sample.

in air and that heated in vacuum, though it is known that the semiconductivity of ZnO is changed by heating in air or in vacuum[9)]. The acidity of ZnS was changed by heat-treatment as shown in Table 5. Maximum acidities 2.77 at $H_0 \leqq +6.8$, 2.54 at $H_0 \leqq +4.8$ and 1.45 at $H_0 \leqq +4.0$ were obtained for ZnS treated at 300°C. It is interesting to note that no acid sites having $H_0 \leqq +3.3$ appear on ZnS treated at 300, 400 or 650°C, but the acid sites do appear when treated at 500°C.

**Acknowledgments**

We wish to express our thanks to Prof. HORIUTI and to Dr. M. KATAYAMA for their comments on the present work.

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