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THE ACIDITY OF SOLID SURFACES^{*)}

By

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Introduction

It is well known that silica-alumina, silica-magnesia and many clays such as kaolin, montmorillonite, fuller's earth *etc.* are solid acids¹⁾. In 1950, WALLING found that a few of metal oxides, sulfates and chlorides have also acidic property on the surfaces²⁾. In the present work we have attempted to examine by extending WALLING's indicator method whether many other inorganic chemicals show acidic property or not. The indicator method was extended by using methyl red dissolved in iso-octane and bromthymol blue in decalin, besides dimethyl yellow, as indicators.

Among forty chemicals examined in which metal oxides, sulfates, chlorides, carbonates, sulfides and cyanides are included, eleven chemicals were found to be strongly acidic, nine less acidic and a few slightly basic. It has been also found that the acidity of CaSO_4 , MnSO_4 , Al_2O_3 , TiO_2 , ZnS , HgCl_2 , *etc.* increased on heating in air or in vacuum, while that of SrSO_4 decreased. The acidity of AlCl_3 increased with increasing temperature of heating but decreased beyond 320°C . Change of acidity on heating has been quantitatively observed in the case of NiSO_4 by using amine titration method developed by JOHNSON³⁾. It has been found that the acidity of NiSO_4 shows a maximum near 350°C .

Experimental

Technique

In general, surface acidity was determined, according to WALLING's method²⁾, by placing about 2 ml. of the material to be tested in the form of powder in a 1×10 cm test-tube, adding 2 ml. of non-polar solvent (guaranteed reagent) containing about 0.2 mg. of indicator and shaking briefly. Adsorption, if it

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occurred at all, was rapid and the color difference between acid and base forms of the indicator striking.

Solvents and indicators

The solvent from which the indicator is adsorbed may also be adsorbed on, and alter, the acid properties of the surface. In order to minimize such effects, decalin, benzene, iso-octane and anisol were employed as medium for measurements. Indicators must be restricted to those which dissolve in the above solvents and satisfy several requirements mentioned by WALLING²⁾. Of the indicators listed in Table 1, those which are shown by open circles were found to satisfy the above requirements. Dimethyl yellow in iso-octane, methyl red in iso-octane and bromthymol blue in decalin were actually used in the

TABLE 1. Indicators and solvents.

| Indicators | Solvents | | | |
|--|------------|---------|--------|---------|
| | Iso-octane | Decalin | Anisol | Benzene |
| <i>o</i> -Nitro- <i>p</i> -Chloroaniline pKa = -0.91 colorless-Y | × | ○ | | |
| Cresol Red (C. R.) R 0.2~1.8 Y Y 7.2~8.8 R | × | × | × | × |
| Thymol Blue (T. B.) R 0.2~1.8 Y Y 8.0~9.6 B | × | × | × | × |
| <i>p</i> -Dimethylamino-azobenzene (Dimethyl Yellow) (D. Y.) pKa = 3.29 R 2.9~4.0 Y | ○ | × | × | |
| Bromphenol Blue (B. P. B.) Y 3.0~4.6 B | × | × | ? | |
| Bromcresol Green (B. C. G.) Y 3.8~5.4 B | × | × | ? | |
| Methyl Red (M. R.) R 4.2~6.3 Y | ○ | × | × | |
| Bromthymol Blue (B. T. B.) Y 6.0~7.6 B | × | ○ | ○ | |
| Arizarine Yellow GG (A. Y.) Y 10.0~12.0 O | × | ○ | ○ | |
| Alkali Blue (A. B.) V 9.4~14.0 P | × | × | × | |

Y = yellow, R = red, B = blue, O = orange, V = violet, P = pink.

present work. Dimethyl yellow in iso-octane is one of the indicators employed by WALLING and the indicator having highest value of pK_a in his case. Therefore, methyl red and bromthymol blue*¹⁾ seem to be useful for the detection of weaker acid or base.

Solid Samples

The materials given in Table 2 were selected from the stockroom and tested without further treatment. Those in Table 3 were heated in air or in vacuum, the detailed conditions being given in the last column of the Table. The heated materials were cooled and stored in desiccator before use.

Attempt to use fluorescein as indicator

The indicator method is obviously limited to white or light colored surfaces. WALLING suggested that it might be extended by the use of fluorescent indicator²⁾. We attempted to use fluorescent indicators for the acidity measurement of black or dark colored surfaces. Eosin, erythrosin B, fluorescein, salicylic acid, acridine, 2-naphthol 3,6-disulfonic acid, sodium 1-naphthol 2-sulfonate, 1-naphthol-4-sulfonic acid were employed as indicators and non-polar solvents as medium. There were, however, no indicators which satisfy the requirements mentioned above.

Quantitative measurement of acidity

Quantitative measurement of acidity has been made only in the case of NiSO₄ by using the amine titration method developed by JOHNSON³⁾. A 0.1~1 g of 120~250 mesh NiSO₄ has been dried for about 3 hours at desired temperature. It was placed in a 50 ml stoppered bottle and 5ml of dry benzene containing 0.2 mg of dimethyl yellow per 100 ml is added. The yellow dye reacts with the solid to form the red acidic form of the indicator. Then the base 0.1N *n*-butylamine in benzene, is added dropwise from a microburette. The neutralization is followed by noting the gradual disappearance of the red color of the solid particle. The end-point, which is quite sharp, is taken as the point at which all the red color disappears.

Results

As seen in Table 2, nine chemicals (SiO₂, ZnO, TiO₂, CeO₂, CaSO₄, MnSO₄, ZnS, PbCl₂, and HgCl₂) changed the color of methyl red from yellow to red, eleven chemicals (As₂O₃, Al₂(SO₄)₃, SrSO₄, CdSO₄, kaolin, FeCl₃·6H₂O, Cu₂Cl₂, SnCl₂·2H₂O, AlCl₃, CaCl₂ and SbCl₃) changed not only methyl red but also

*¹⁾ IKEBE, HARA and MITA used M. R. in benzene and B. T. B. in benzene-alcohol mixture for the acidity measurements of silica-alumina, though the solvent involving alcohol seems to be undesirable⁴⁾.

The Acidity of Solid Surfaces

TABLE 2. The acidity of various chemicals.

| Chemicals | Methyl Red in Iso-octane pH range (Y 6.3~4.2 R) | Dimethyl Yellow in Iso-octane pH range (Y 4.0~2.9 R) | Bromthymol Blue in Decalin pH range (Y 6.0~7.6 B) |
|---|--|---|--|
| 1. CaO | Y | Y | B |
| 2. MgO | Y | Y | X |
| 3. Cr ₂ O ₃ | — | ? | — |
| 4. NiO | — | X | X |
| 5. Al ₂ O ₃ | Y | Y | X |
| 6. SiO ₂ | light R | Y | Y |
| 7. ZnO | R | X | X |
| 8. TiO ₂ | R | X | X |
| 9. CeO ₂ | R | X | X |
| 10. As ₂ O ₃ | R | R | — |
| 11. K ₂ CO ₃ | Y | Y | B |
| 12. ZnCO ₃ | Y | Y | Y |
| 13. BaCO ₃ | ? | Y | Y |
| 14. BaSO ₄ | ? | Y | Y |
| 15. (NH ₄) ₂ SO ₄ | Y | Y | Y |
| 16. CaSO ₄ | R | Y | — |
| 17. MnSO ₄ | R | Y | Y |
| 18. Al ₂ (SO ₄) ₃ | R | R | — |
| 19. SrSO ₄ | R | R | — |
| 20. CdSO ₄ | R | R | — |
| 21. NiSO ₄ ·7H ₂ O | — | ? | — |
| 22. ZnS | R | X | — |
| 23. K ₂ CrO ₄ | ? | ? | ? |
| 24. KClO ₃ | ? | Y | ? |
| 25. Ba(NO ₃) ₂ | X | Y | ? |
| 26. CuCN | — | Y | — |
| 27. K ₄ Fe(CN) ₆ ·3H ₂ O | ? | ? | ? |
| 28. Kaolin | R | R | — |
| 29. NaCl | X | — | — |
| 30. BaCl ₂ ·2H ₂ O | ? | Y | Y |
| 31. NH ₄ Cl | X | Y | ? |
| 32. PbCl ₂ | R | Y | — |
| 33. HgCl ₂ | R | Y | — |
| 34. FeCl ₃ ·6H ₂ O | ? | R* | — |
| 35. Cu ₂ Cl ₂ | R | R | — |
| 36. SnCl ₂ ·2H ₂ O | R | R | ? |
| 37. AlCl ₃ | R | R | — |
| 38. CaCl ₂ | R | R | — |
| 39. SbCl ₃ | R | R | — |
| 40. CaF ₂ | ? | Y | Y |

X : No adsorption.

— : No measurement.

? : Not clear.

* : Compared with the color of the same chemical in iso-octane containing no indicator, because of the colored surface.

TABLE 3. Change of acidity on heating.

| Chemicals | M. R. | D. Y. | B. T. B. | Conditions |
|---|---------|-----------------------|----------|---|
| 2. MgO | — | — | ⊕ | 900~1000°C, 30 min |
| 4. NiO | — | ? | — | 300°C, 2 hr and 15 min |
| 5. Al ₂ O ₃ | ⊕ | ⊕ | — | " |
| 6. SiO ₂ | deep ⊕ | Y | — | " |
| 8. TiO ₂ | R | light ⊕ | — | " |
| 9. CeO ₂ | — | ⊕ | — | " |
| 14. BaSO ₄ | light ⊕ | Y | — | 300~380°C, 3 hr |
| 16. CaSO ₄ | R | ⊕ | — | " |
| 17. MnSO ₄ | R | ⊕ | — | 300°C, 1.5 hr |
| 18. Al ₂ (SO ₄) ₃ | R | R | — | " |
| 19. SrSO ₄ | light △ | △ | — | 300~380°C, 3 hr |
| 20. CdSO ₄ | R | R | — | 500°C, 3 hr |
| 21. NiSO ₄ | R | R | — | 350°C, 4 hr |
| 22. ZnS | R | ⊕ | — | 300°C, 2 hr and 15 min |
| 28. Kaolin | R | R | — | 300~380°C, 3 hr |
| 33. HgCl ₂ | R | light ⊕ | — | 180~200°C, 10 min in vacuum* |
| 36. SnCl ₂ | R | deeper ⊕ | — | 150~170°C, 12 min in vacuum |
| 37. AlCl ₃ { 37a 37b | R — | deeper ⊕ lighter △ | — — | 180°C, 9 min in vacuum 280~320°C, 4 min. in vacuum |
| 38. CaCl ₂ { 38a 38b | R — | R deeper ⊕ | — — | 150°C, 15 min in vacuum 180~270°C, 10 min in vacuum |
| 39. SbCl ₃ | R | R | — | 180°C, 10 min in vacuum |
| 40. CaF ₂ | Y | Y | Y | 300~380°C, 3 hr |

○ Increased acidity, △ Decreased acidity, * 10⁻⁶ mmHg.

dimethyl yellow from yellow to red respectively and two chemicals (CaO, K₂CO₃) changed bromthymol blue from yellow to blue. Of the above chemicals, TiO₂ and PbCl₂ were tested also by WALLING, but PbCl₂ did not adsorb the indicators employed by him, while TiO₂ adsorbed dimethyl yellow but did not react with it to form the red acidic form of the indicator. It is noted that methyl red was adsorbed on both of the chemicals and reacted with them to show red

color. In Table 2, "X" shows that the surface of the chemical showed neither the color of neutral base nor the conjugated acid of the indicator, namely that the indicator was not adsorbed on the chemical and "?" that the observation of the color of the indicator was not clear.

The results of change of acidity on heating are shown in Table 3, where numbers of chemicals of the Table correspond to those of Table 2 respectively. Open circles represent increased acidity and triangles decreased acidity. "Deeper R" in the third column in Table 3 represents that the red color of dimethyl yellow on the heated chemical is deeper than that on the untreated chemical of Table 2 and, in particular case of CaCl_2 , the red color of No. 38 b is deeper than that of No. 38 a. "Lighter R" in No. 37 means that the red color of No. 37 b is lighter than that of No. 37 a. The acidity of Al_2O_3 , SiO_2 , TiO_2 , CeO_2 , BaSO_4 , CaSO_4 , MnSO_4 , ZnS , HgCl_2 , CaCl_2 and SnCl_2 was increased by heating in air or in vacuum, while that of SrSO_4 decreased. MgO changed the color of bromthymol blue from yellow to blue when heated for half an hour at $900\sim 1000^\circ\text{C}$.

SHIBA and ECHIGOYA have reported that the acidity of alumina increased remarkably on heating and the catalytic activity of heated alumina coped with that of the well-known silica-alumina for the polymerization of ethylene⁵⁾. It is of interest to note that not only alumina but also many other oxides, sulfates and chlorides increased their acidity remarkably on heating.

The acidity of aluminum chloride was increased by heating in vacuum for 9 minutes at 180°C , but decreased when heated further for 4 minutes at $280\sim 320^\circ\text{C}$. There seems to be a parallelism between this observation and the fact that the catalytic activity of aluminum chloride for the polymerization of isobutene is low either when aluminum chloride contains water or when completely dehydrated but high when a small amount of water is present⁶⁾.

In order to examine that the observed acidity is not due to impurities of mineral acids such as sulfuric acid and hydrochloric acid, the following tests have been made. First, the material was immersed in 2 ml. of distilled water and the pH of the solution was measured. The pH was found to be near neutral in most of chemicals except chlorides and sulfates. Second, some of sulfates were heated with distilled water in porcelain crucible at 500°C and weighed. By repeating the above procedure until constant weight was obtained, they were purified. Cadmium sulfate *etc.* thus purified changed clearly dimethyl yellow to red. These observation and the fact that most of chemicals increased their acidity on heating seem to indicate that the color change of indicator is not due to impurities.

The acidity change of NiSO_4 on heating which was observed by use of

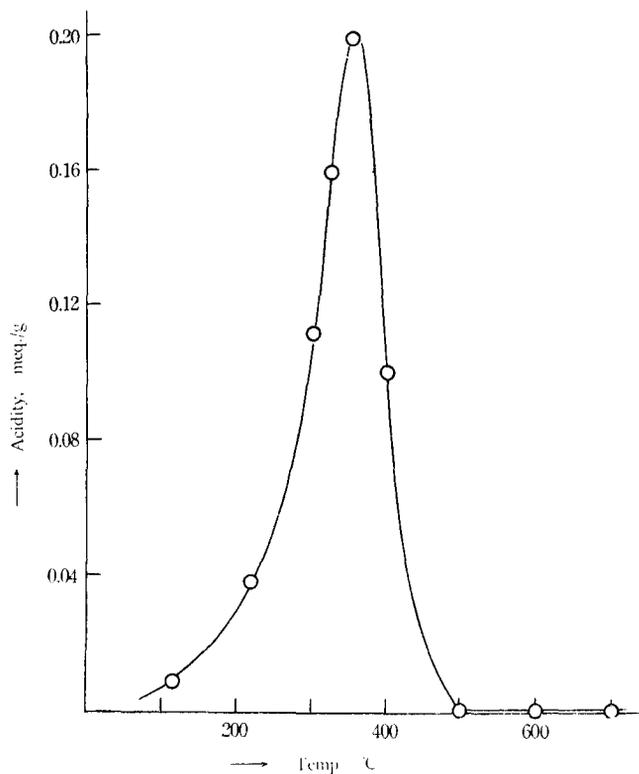


Fig. 1. Change of acidity on heating (NiSO_4)

TABLE 4. Acidity change of NiSO_4 on heating.

| Temperature heated °C | 0.1 N <i>n</i> -butylamine titre for 1 g of solid sample ml | Acidity by amine titration meq./g |
|--------------------------|--|---|
| 117 | 0.10 | 0.010 |
| 220 | 0.38 | 0.038 |
| 300 | 1.10 | 0.110 |
| 325 | 1.60 | 0.160 |
| 350 | 1.96 | 0.196 |
| 400 | 1.00 | 0.100 |
| 500 | 0.02 | 0.002 |
| 600 | <0.02 | <0.002 |
| 700 | <0.02 | <0.002 |

The Acidity of Solid Surfaces

the amine titration method is shown in Fig. 1, the detailed data being shown in Table 4. The acidity increased sharply with increase of temperature of heating, attained to a maximum near 350°C and then decreased. The acidity was almost lost when heated for 3 hours above 500°C. It was hard to recognize the red color of dimethyl yellow on the surface of NiSO₄ heated for 3 hours at 600°C or 700°C.

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