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SURFACE ACIDITY AND ACID STRENGTH OF NICKEL SULFATE

By

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Abstract

Acidity and acid strength of nickel sulfate heated at various temperatures ranging from 150 to 600°C were determined by the *n*-butylamine titration method. It has been found that the acidities at various acid strengths increase with increasing temperature of heat-treatment, attain to maxima around 350°C and then decrease and that acid sites having strong acid strength $H_0 \leq -3.0$ appear on the surface of the solid heated at temperatures from 150 to 464°C and those having mediate acid strength $H_0 = +4.0 \sim +3.3$ increase remarkably on heat-treatment at high temperatures beyond 464°C. From the observed acidic property and the kinetic data previously obtained for the depolymerization of paraldehyde catalyzed by solid nickel sulfate in benzene, it is shown that the acid sites having acid strength $H_0 \leq -3.0$ are catalytically active for the depolymerization.

Introduction

It has been reported previously that nickel sulfate showed fairly strong acidic property on the surface and that the acidity was changed remarkably by heat-treatment¹⁾. An attempt to use the solid acid instead of ordinary mineral acids as a heterogeneous catalyst of the acid-catalyzed depolymerization of paraldehyde in benzene was then made and it was found that the solid acid was catalytically active for the depolymerization and there was a parallel relation between the depolymerization rate constant and the acidity measured by using *p*-dimethylamino-azobenzene of $pK_a = +3.3$ as an indicator²⁾. Acid sites having *various acid strengths* may, however, exist on the surface of nickel sulfate. In order to test how the catalytic activity correlates with the acid strength of the catalyst as well as its acidity, the acidities at various acid strengths have been determined in the present work by employing many indicators having different pK_a 's ranging from +6.8 to -3.0.

A number of methods for determining acidity and acid strength of solid surfaces have been reported recently³⁾. Since, however, nickel sulfate has been

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used as an acid catalyst for a reaction in non-polar solvent, we employed the BENESI's method⁴⁾ which determines acidity together with acid strength of solid surface in non-polar solvent.

Experimental

Reagents and Materials: Roughly ground nickel sulfate ($\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, guaranteed reagent of Kanto Chemical Co., Tokyo) was heated in an electric furnace attached with a thermocouple for three hours at various temperatures ranging from 150 to 600°C and cooled in an evacuated desiccator before use. The 100~200 mesh powder was used for acidity measurement⁵⁾. The indicators used in the present study are as follows: an extra pure reagent grade neutral red (2-methyl-3-amino-6-dimethylaminophenazine), the product of the Kanto Chemical Co., Inc., with $pK_a = +6.8$,⁵⁾ an extra pure reagent grade methyl red (Kanto Chemical Co.), with $pK_a = +4.8$,⁶⁾ a guaranteed reagent grade benzene-azo- α -naphthylamine, the product of the Tokyo Chemical Industry Co., Ltd., with $pK_a = +4.0$,⁵⁾ a guaranteed reagent grade *p*-dimethylamino-azobenzene (Kanto Chemical Co.), with $pK_a = +3.3$,⁷⁾ a guaranteed reagent grade benzene-azodiphenylamine (Tokyo Chemical Industry Co.), with $pK_a = +1.5$ ⁵⁾ and dicinnamalacetone (1, 9-diphenyl-1, 3, 6, 8-nonatetraen-5-one), with $pK_a = -3.0$ ⁵⁾. Since neutral red was obtained in the form of the hydrochloride salt, it was converted to the neutral base by adding a slight excess of standard sodium hydroxide solution. Dicinnamalacetone was synthesized by the method of F. STRAUS⁸⁾ from cinnamic aldehyde and acetone and purified by recrystallization first from ethyl acetate, then from benzene and finally from alcohol. The crystal (m. p. 145°C) was stored in an evacuated sealed tube in a dark place, since it is unstable in air and in light. Benzene and *n*-butylamine used were a guaranteed reagent, the product of the Kanto Chemical Co. and an extra pure reagent, the product of Tokyo Chemical Industry Co. respectively.

Measurement of Acidity and Acid Strength: The acidity (the number of acid sites) having an acid strength H_0 equal to or lower than the pK_a value of the indicator used were determined by using the amine titration method developed by JOHNSON⁹⁾. In the present study, powdered samples of nickel sulfate suspended in benzene was titrated with a solution of 0.1 *N* *n*-butylamine in benzene, using an appropriate indicator described above. It was easy to observe the color changes of all indicators used, since the green color of nickel

*) Since the acidity at various acid strengths of solid nickel sulfate are diminished by moisture in air, dried solid was avoided to expose to air as practically as possible. By carrying out parallel test inside and outside a dry box, it was found that water adsorbed during grinding and sieving of dry sample had negligible effect on acidity and acid strength.

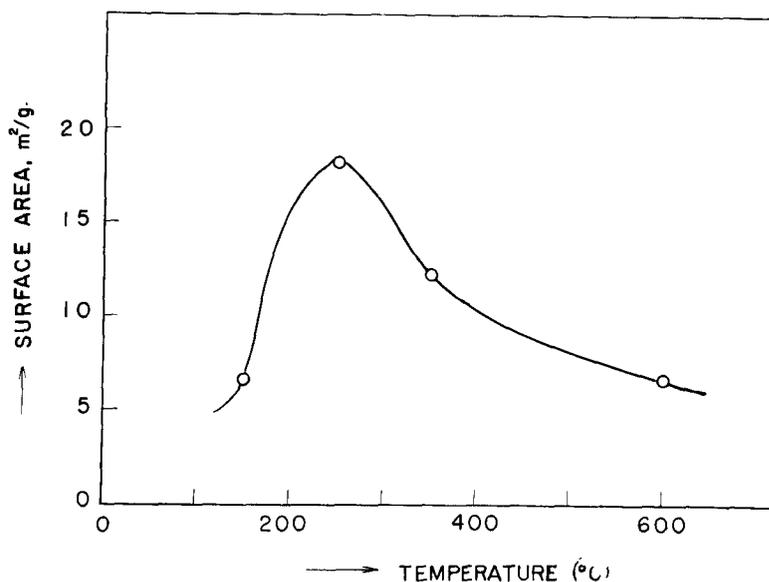


Fig. 1. Change of surface area of nickel sulfate on heat-treatment.

sulfate changed from green through light greenish yellow to light yellow on heat-treatment. As HOLM *et al.*¹⁰ pointed out, titrations required three hours or more even with the ground samples. The acidity is expressed in units of mmoles/m² calculated from the titer of 0.1 *N* *n*-butylamine required for unit surface area of solid nickel sulfate. Acid strength was determined according to BENESI⁵ or WALLING'S⁷ method by employing various indicators having different pK_a values mentioned above.

Determination of Surface Area: Surface area of heat-treated nickel sulfate were measured by the BRUNAUER-EMMETT-TELLER method¹¹ using nitrogen as an adsorbate. Surface area changes, as illustrated in Fig. 1, with increasing temperature of heat-treatment, the maximum surface area of 18.2 m²/g being observed on the sample heated at about 250°C.

Results and Discussion

The acidities (*n*-butylamine titers by definition) of nickel sulfate heat-treated at various temperatures are shown in Table 1. The second column shows the surface areas of nickel sulfate heat-treated at various temperatures which were taken from Fig. 1. Color change of nickel sulfate on heat-treatment is shown in the third column. In the next column are given *n*-butylamine titers (acidity) measured by using various indicators having different pK_a values. The acidities

TABLE 1. Acidity of Nickel Sulfate heat-treated at various Temperatures (mmoles/m²).

Temperature of Heat-treatment (°C)	Surface Area (m ² /g)	Color Change of NiSO ₄ on Heat-treatment	<i>n</i> -Butylamine Titrers, mmoles/m ²					
			Neutral red (<i>pK_a</i> = +6.8)	Methyl red (<i>pK_a</i> = +4.8)	Benzene-azo- α -naphthylamine (<i>pK_a</i> = +4.0)	<i>p</i> -dimethyl-amino-azobenzene (<i>pK_a</i> = +3.3)	Benzeneazo-diphenylamine (<i>pK_a</i> = +1.5)	Dicinnamal-acetone (<i>pK_a</i> = -3.0)
150	6.7	green	—	0.0046	0.0040	0.0034	0.0034	0
250	18.2	light green	0.0110	0.0054	0.0052	0.0046	0.0043	0.0016
325	13.4	light greenish yellow	—	0.0101	0.0103	0.0090	0.0088	0.0047
350	12.2	light greenish yellow	0.0189	0.0094	0.0103	0.0091	0.0088	0.0046
375	11.2	yellow	—	0.0101	0.0108	0.0096	0.0089	0.0049
400	10.4	yellow	—	0.0083	0.0084	0.0075	0.0069	0.0029
464	8.9	yellow	0.0202	0.0078	0.0075	0.0048	0.0047	0
600	6.6	light yellow	0.0091	0.0049	0.0033	<0.0006	<0.0006	0

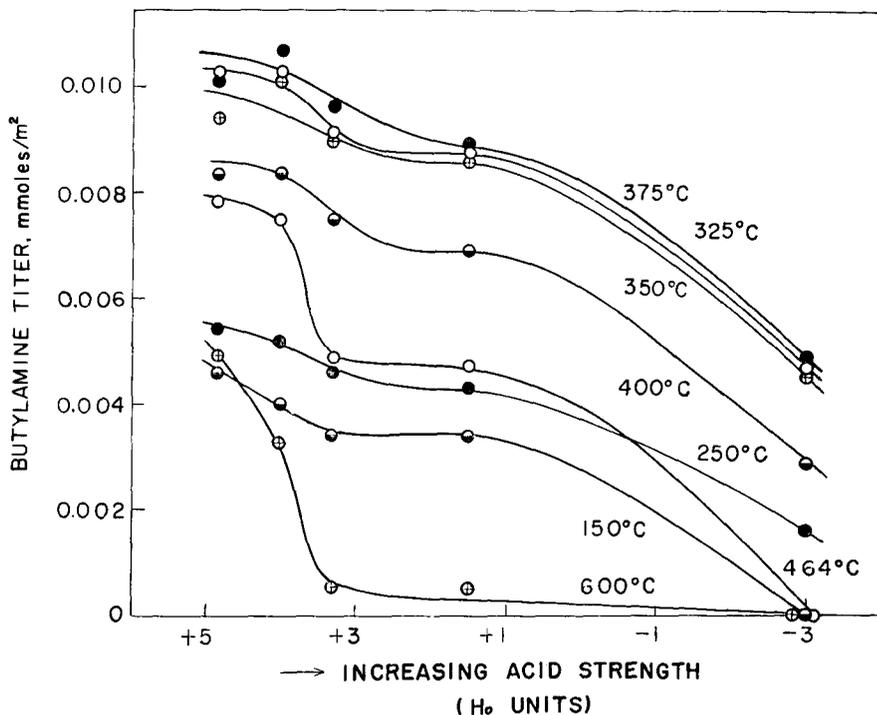


Fig. 2. Butylamine titer vs. acid strength for nickel sulfate heat-treated at various temperatures.

plotted against acid strength in Fig. 2 are cumulative; *i.e.*, they are measures of the number of acid sites (in mmoles/m²) having an acid strength H_0 equal to or lower than the pK_a value of the indicator used. It should be remembered that the acid strength of the surface increases, as H_0 decreases and approaches more negative values. The actual amount of surface acid in a given H_0 range is given by the difference between *n*-butylamine titers using the two indicators bracketing that H_0 range.

It is seen in Fig. 2 that the acid sites having acid strength stronger than $H_0 = -3.0$ appear on the surface of nickel sulfate heat-treated at temperatures between 150 and 464°C and those at mediate acid strength $H_0 = +4.0 \sim +3.3$ increase remarkably on heating at high temperatures beyond 464°C.

In Fig. 3 are plotted *n*-butylamine titers of nickel sulfate at various acid strengths against temperature of heat-treatment. The *n*-butylamine titers at any acid strengths increase with increasing temperature of heat-treatment, attain to maxima around 350°C and then decrease. As mentioned above, the color of nickel sulfate changes from green through light greenish yellow to light yellow

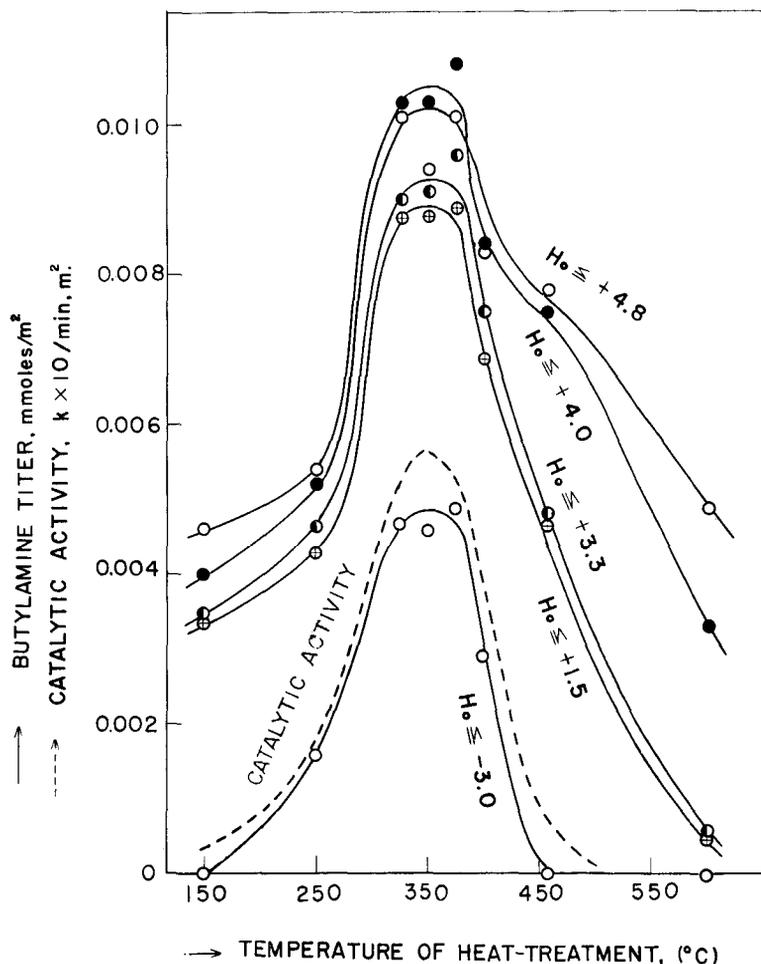


Fig. 3. Effect of heat-treatment on catalytic activity and acidic property of nickel sulfate.

with increasing temperature of heat-treatment. The temperature at which maxima of *n*-butylamine titers appear is in accord with that at which the color of nickel sulfate changes from light green to light greenish yellow.

WATANABE and one of the present authors²⁾ have previously observed that both the catalytic activity per gram of nickel sulfate catalyst for the depolymerization of paraldehyde in benzene and the acidity expressed in mmoles/g of nickel sulfate measured by using *p*-dimethylamino-azobenzene as an indicator show a maximum when the catalyst was heated at 350°C before use. The present investigation enables us to discuss more in detail how the catalytic

activity correlates with the acid strength as well as the acidity. The depolymerization rate constant per unit surface area of nickel sulfate plotted against temperature of heat-treatment is shown by broken line in Fig. 3. As seen in the figure, nickel sulfate heated at temperature below around 150 or above 450°C has a number of acid sites having acid strength weaker than $H_0 = +1.5$, but has no or little catalytic activity. Therefore, those relatively weak acid sites are considered to be catalytically inactive. The acid sites having acid strength stronger than $H_0 = -3.0$ which appear on heat-treatment at temperatures from around 150 to 450°C best correlate with catalytic activity and are catalytically active for the depolymerization reaction.

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