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(Note)

ACIDITY MEASUREMENT OF NICKEL SULFATE BY DTA AND TGA METHOD

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A number of methods have been presented for the measurement of surface acidity.[1] The differential thermal analysis (DTA) was applied to differenciate between acid strengths by BREMER and STEINBERG.[2] By observing the DTA diagram of SiO_2–MgO catalysts coated with pyridine, they estimated the relative acid strengths of the catalysts heat-treated at various temperatures. Recently, SHIRASAKI *et. al.*[3] have measured the acid amount together with the acid strength of SiO_2–Al_2O_3 by analyzing the diagram of DTA and thermogravimetric analysis

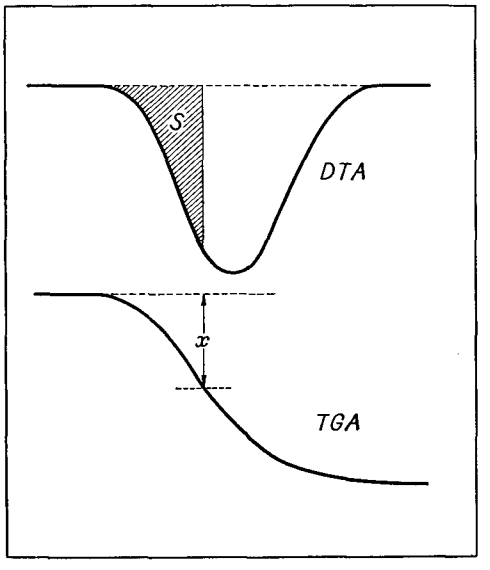

Fig. 1. A model of DTA and TGA diagram.

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(TGA) of the catalyst on which organic bases had been adsorbed. Their method makes it possible to estimate continuously acid amounts at various acid strengths of even colored samples and the experiment is speedy and simple. In the present work, the acidic property of solid nickel sulfate which was fully studied previously[4] was measured by employing the latter method and the observed values were compared with those measured by indicator method.

The principle of DTA and TGA method[2] is as follows. A typical DTA and TGA diagram of a solid on wich an organic base had been adsorbed is shown in Fig. 1. The amount x of the base retained on the solid is obtained from the TGA curve and the corresponding amount of heat absorbed from the area S defined by the DTA curve. From the curve of S against x, dS/dx can be calculated. Plotting x against dS/dx gives the acid amonts at various acid strengths (or the heat required for the desorption of the base).

Experimental

A heptahydrate of nickel sulfate was calcined at 350 or 600°C and the 100~200 mesh powders were immersed in pyridine or *n*-butylamine and then dried at 110°C for 15 hours. The DTA and TGA diagram was recorded at a heating rate of 5°C/min by using Shimadzu Differential Thermal Balance (MTG-11 type).

Results and Discussions

The DTA and TGA diagrams of nickel sulfates calcined at 350 or 600°C on which pyridine or *n*-butylamine was adsorbed are shown in Figs. 2 and 3. It is seen in Fig. 2 that pyridine adsorbed on the sulfate calcined at 350°C begins to be desorbed at 300°C, the maximum endothermic peak being observed at 365°C, while no heat of absorption due to pyridine desorption is found for the sulfate calcined at 600°C, but a small exothermic peak which is probably due to the burning of pyridine appears at 365°C. Since the acid sites of the sulfate calcined at 350°C are stronger than those calcined at 600°C as shown in Table 1,[4] pyridine

TABLE 1. Acidity of Nickel Sulfate*)

Temp. of Calcination °C	Surface Area m^2/g	Acid Amounts, mmol/g					
		$pK_a=6.8$	$pK_a=4.8$	$pK_a=4.0$	$pK_a=3.3$	$pK_a=1.5$	$pK_a=-3.0$
350	12.2	0.230	0.115	0.126	0.111	0.107	0.0561
600	6.6	0.0601	0.033	0.022	0	0	0

*) Taken from ref. 4. Measured by *n*-butylamine titration method using various indicators of different pK_a's.

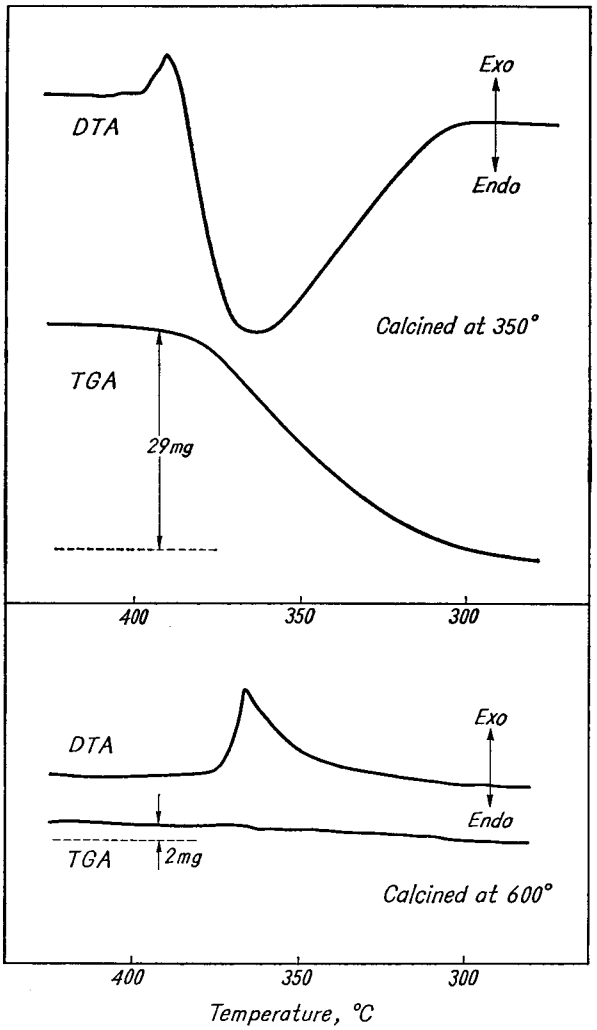

Fig. 2. DTA and TGA diagram of $NiSO_4$ calcined at 350 or 600°C on which pyridine was adsorbed. Sample weight: 300 mg.

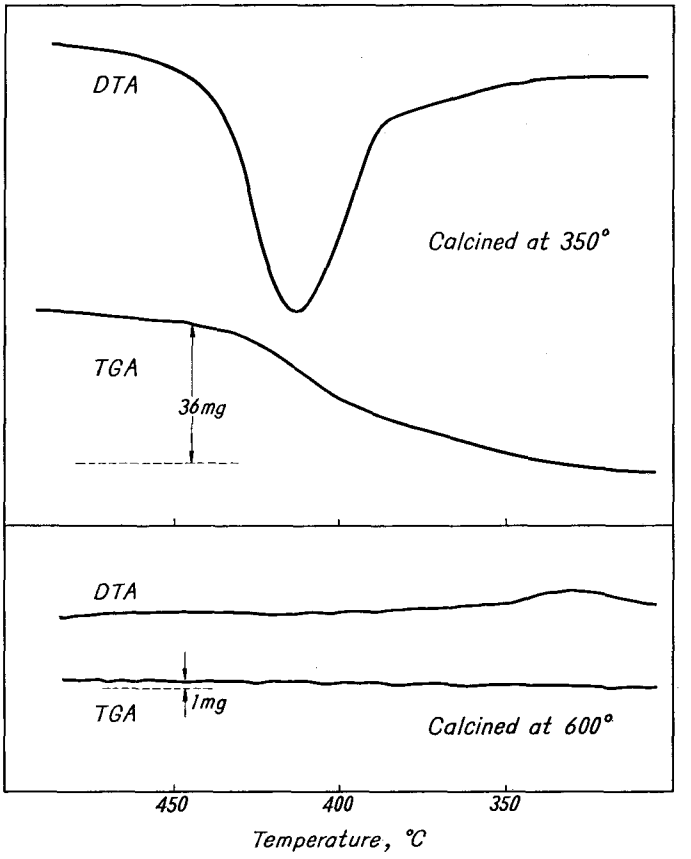

Fig. 3. DTA and TGA diagram of $NiSO_4$ calcined at 350 or 600°C on which *n*-butylamine was adsorbed. Sample weight: 300 mg.

adsorbed on stronger acid sites is desorbed at relatively high temperature, but that on weaker sites or physically adsorbed pyridine at low temperature, 9 mg of pyridine being desorbed up to 300°C. The pyridine adsorbed on stronger acid sites of the sulfate burns also at higher temperature.

In the case of *n*-butylamine-covered sample, the desorption peak appears at 415°C, a higher temperature than that in the pyridine-covered sample (see Figs. 2 and 3). This is due to that the pK_a value (10.62) of *n*-butylamine is higher than that (5.17) of pyridine. The sulfate calcined at 600°C which has only weak acid sites does not much adsorb even a stronger base, *n*-butylamine, a small amount of the base being weakly adsorbed.

Since the endothermic peak in Fig. 2 consists of the peaks due to pyridine

desorption and water dehydration, we obtained the peak of only pyridine desorption by reducing the peak of only water dehydration given in Fig. 4 from the peak in Fig. 2. The result is shown in Fig. 5, where the weight loss

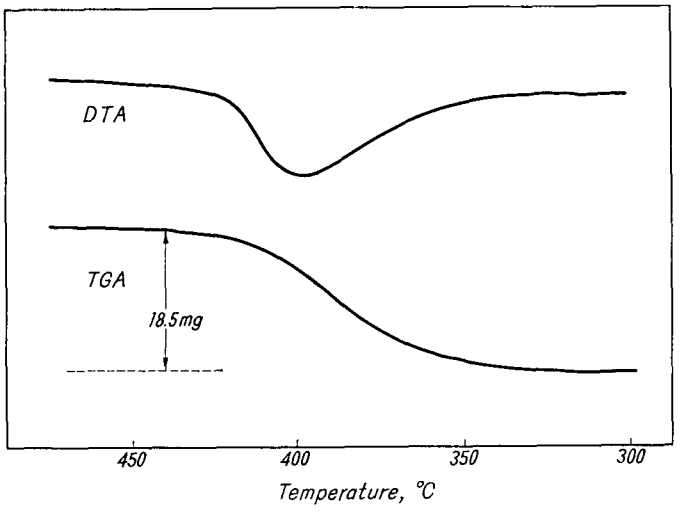

Fig. 4. DTA and TGA diagram of $NiSO_4$ calcined at 350°C. Sample weight: 300 mg.

due to only pyridine desorption which was obtained similarly from TGA curves in Figs. 2 and 4 is also given. The curve of S against x (Fig. 6) is obtained from Fig. 5. The dS/dx calculated from the tangent of the curve was now plotted against x (mmo/g) in Fig. 7. The acid sites whose amount is less than 0.1 mmol/g have relatively high acid strength, dS/dx (the heat required for the desorption of pyridine). This result is in fairly good agreement with the result obtained by the amine titration method given in Table 1. Noting that the acid amount in a given H_0 range is given by the difference between the acid amounts using the two indicators bracketing that H_0 range, the acid strength of the sites less than 0.1 mmol/g corresponds to $H_0 \leqq +1.5$. The acid strength of SiO_2–Al_2O_3 is known to be much higher than that of $NiSO_4$ calcined at 350°C according to the indicator method. The acid strength, dS/dx ($cm^2 \cdot g/mmol$), measured by DTA and TGA method using pyridine was 6.5,[3] whose value is much higher than that (0.4) of $NiSO_4$. The total acid amount of $NiSO_4$ calcined at 350°C is 0.23 mmol/g according to the amine titration method (see Table, 1), but the total amount of the sites corresponding to the desorption of pyridine is 0.87 mmol/g according to the present method (Fig. 7). This large value probably includes the sites on which pyridine was physically adsorbed. The amout

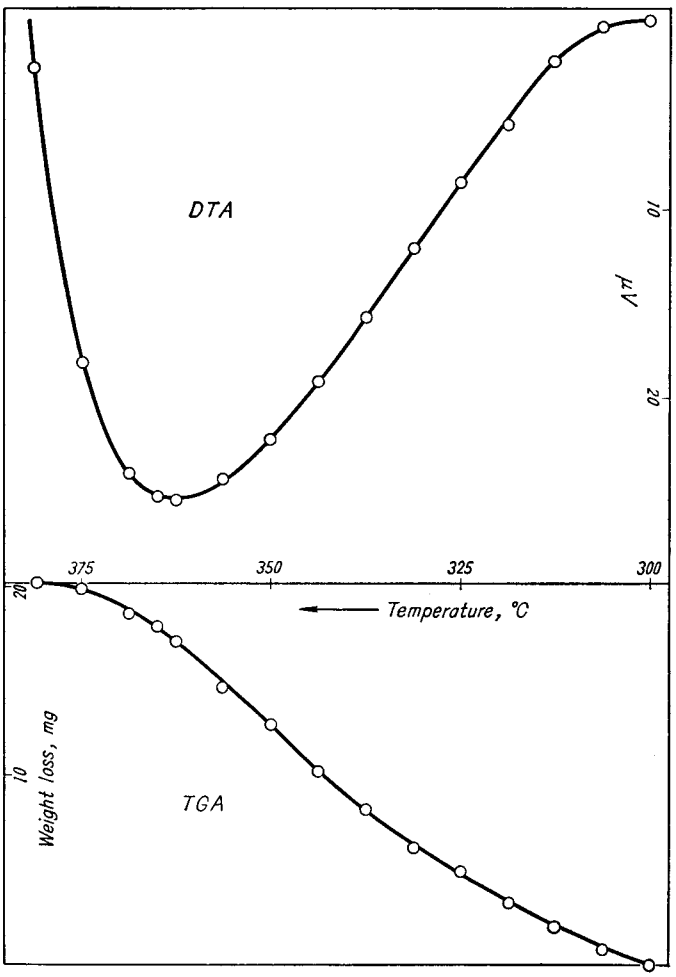

Fig. 5. Corrected DTA and TGA curves of $NiSO_4$ calcined at 350°C and covered by pyridine.

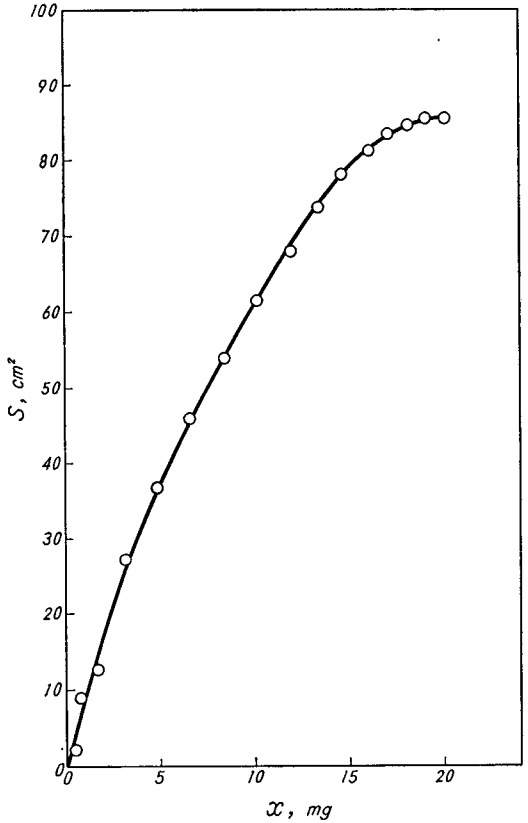

Fig. 6. Curve of S, area defined by DTA against x.

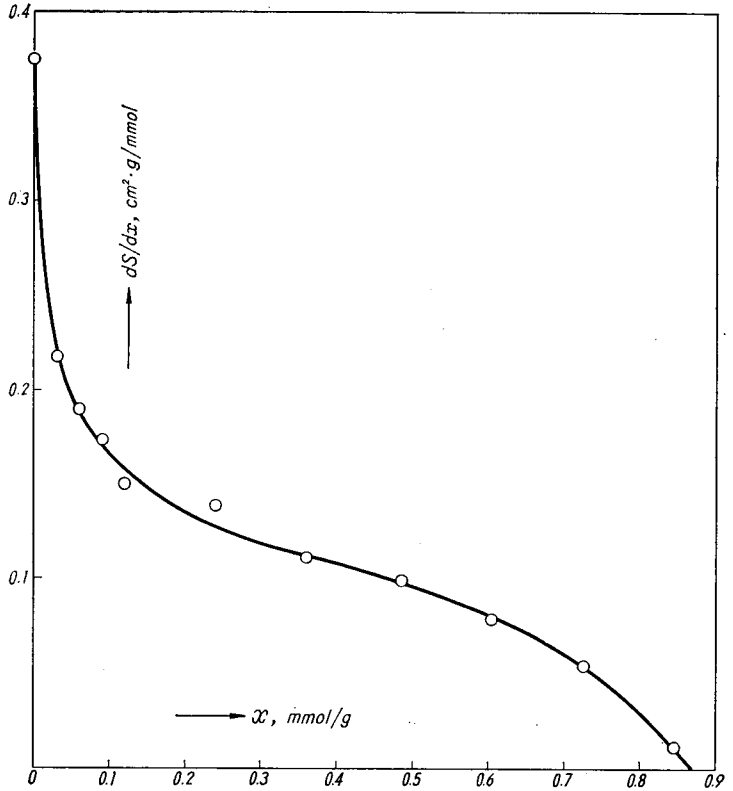

Fig. 7. Relative desorption heat of pyridine *vs.* amount of sites on $NiSO_4$ calcined at 350°C.

of sites which physically adsorb pyridine and the desorption heat on such sites may be obtained ey using the sample poisoned with stronger base, as suggested by SHIRASAKI *et al.*[3] In the case of *n*-butylamine-covered nickel sulfate, the curve of S against x was concave upwards in contrast with the case of pyridine-covered sulfate, though the case can be hardly interpreted.

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