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# Brönsted and Lewis Acidity of Solid Nickel Sulfate

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The distribution of Brönsted and Lewis acidities of nickel sulfates heat-treated at various temperatures in air or in a vacuum has been determined by observing the infrared spectra of pyridine adsorbed on the sulfates in the range 1300—1600 cm$^{-1}$. It has been found that the Brönsted acidity increases with the rise of temperature of heat treatment in air, attains a maximum value at 250°C and then decreases, while the maximum of the Lewis acidity appears at a higher temperature (about 400°C), the sum of both acidities giving the total acidity measured by *n*-butylamine titration method. An experiment in a vacuum showed that Lewis acid is converted into Brönsted acid by the addition of water. The structural nature and the catalytic activity of the Brönsted and Lewis acid sites on nickel sulfate are discussed.

Solid nickel sulfate shows remarkable acidic property on being subjected to heat treatment[1] and is used as a new type of effective catalysts in a number of acid-catalyzed reactions.[2] It was found that the total acidity[3] (Brönsted plus Lewis acidity) of the sulfate heat-treated at various temperatures measured by *n*-butylamine titration method correlates well with the catalytic activity of the depolymerization of paraldehyde,[1] polymerization of propylene[4] and aldehydes,[5] hydration of propylene,[6] exchange reaction of chlorine between benzyl chloride and hydrogen chloride,[7] *etc.* However, no good correlation was found for the isomerization of α-pinene[8] and the hydrolysis of methylene chloride.[9] This was tentatively interpreted as due to the fact that isomerization depends on Brönsted acidity and hydrolysis on Lewis acidity,[2] on the basis of the structural study of acid sites.[10] However, since we have no experimental evidence for each type of acid site, we have attempted to measure Brönsted and Lewis acidities separately, by employing the infrared spectroscopic method[11] of pyridine adsorbed on the solid acid catalyst. The results are discussed in connection with the nature and the activity of acid sites of nickel sulfate catalyst.

## Experimental

Infrared spectra of adsorbed pyridine were measured for nickel sulfate heat-treated in air or in a vacuum *in situ* cell. Heptahydrate of nickel sulfate was heat-treated in a glass

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[3] Acidity is defined as an acid amount in the present paper.

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[8] R. Ohnishi, T. Takeshita, and K. Tanabe, *Shokubai* (Tokyo), **7**, 306 (1965).

[9] T. Yamaguchi and K. Tanabe, Fourth International Congress on Catalysis, Moscow, 1968, Preprint of the Paper, No. 80.

[10] T. Takeshita, R. Ohnishi., T. Matsui, and K. Tanabe, *J. Phys. Chem.*, **69**, 4077 (1965).

[11] E. P. Parry, *J. Catalysis*, **2**, 371 (1963).

tube at various temperatures in the range 200—500°C for 3 hr in air and the glass tube was sealed off. Immediately after the tube was opened, it was connected to vacuum apparatus and evacuated to $10^{-6}$ mmHg for 30 min at room temperature and then pyridine (about 2 mmHg) was introduced and adsorbed for 10 min. After removing excess pyridine by evacuating for 30 min at room temperature, 5 mg of the sample was mixed with 200 mg of KBr powder and pressed into a tablet 12 mm in diameter by means of a pressure approximately 3000 kg/cm$^2$. The spectrum range in the 1300—1700 cm$^{-1}$ was observed with an infrared spectrophotometer (Hitachi EPI-2).

In an *in situ* cell experiment, nickel sulfate mounted on silica gel (35 wt% as anhydride) was used. The sample discs were placed in the cell and heat-treated at various temperatures in a vacuum for 3 hr. After cooling to room temperature, pyridine (about 2 mmHg) was introduced and adsorbed for 15 min. After evacuation for 30 min at 50°C and further evacuation for 30 min at 100°C, the spectra were recorded on a Hitachi EPI-G2 double beam grating spectrophotometer. In some experiments, the effect of water on the spectrum of chemisorbed pyridine was examined to see whether Lewis acid can be converted into a Brönsted one. Weight loss of heptahydrate of nickel sulfate by dehydration in air or in a vacuum with the rise of temperature of heat treatment was also measured by weighing the samples treated for 3 hr at various temperatures.

Pyridine was purified by dehydration over molecular sieve 4A and by distillation in a vacuum. Heptahydrate of nickel sulfate was a guaranteed reagent of Kanto Chemical Co. Tokyo. Silica gel used was prepared by the hydrolysis of ethylorthosilicate, which had little acidity on the surface.

## Results and Discussion

The spectra of pyridine adsorbed on nickel sulfate heat-treated at various temperatures in air are shown in Fig. 1, where two main absorption bands (1520 and 1425 cm$^{-1}$) are observed. Since the band of higher frequency disappears when the sample was heat-treated at 350°C, while the band of lower frequency still remains even by heat treatment at 450°C, both the bands seem to be those of different species of adsorbed pyridine. It is known that the band of coordinately bonded pyridine appears at 1445—1460 cm$^{-1}$ on the surface of η-alumina,11) silica-alumina,11,12) and cation exchanged zeolites,13–15) while the band of pyridinium ion or salts at 1530—1540 cm$^{-1}$ on silica-alumina,11,12) cation exchanged zeolites13–15) or in various pyridine complexes.16) Therefore, the band near 1520 cm$^{-1}$ in Fig. 1 has been assigned to the band due to pyridinium ion and that at 1425 cm$^{-1}$ due to coordinately bonded pyridine. Since the acid strength of the sulfate is lower than those of the solid acids mentioned above,2) and it is known that the band of pyridine adsorbed on weaker acid site appears at lower frequency,15) it seems likely that the species responsible for the bands at 1520 and 1425 cm$^{-1}$ were adsorbed on much weaker Brönsted and Lewis acids respectively. Thus, the bands at 1520 and 1425 cm$^{-1}$ in Fig. 1 can be respectively taken as those corresponding to Brönsted and Lewis acid. Figure 2 shows the changes in intensities of these two bands with change of temperature of heat treatment. It is seen that Brönsted acidity shows its maximum when the sample was heat-treated at 250°C, whereas Lewis acidity attains its maximum at about 400°C.

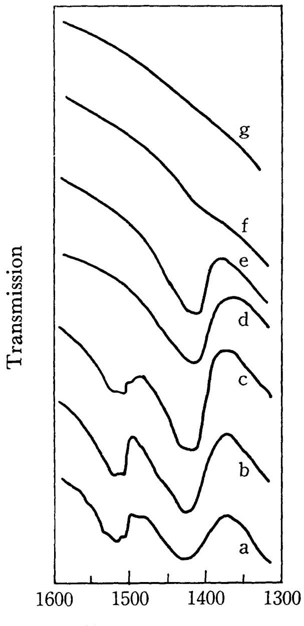

Fig. 1. Infrared spectra of pyridine on nickel sulfates heat-treated at various temperatures in air.
a : 200°C, b : 250°C, c : 300°C, d : 350°C, e : 400°C, f : 450°C, g : 500°C

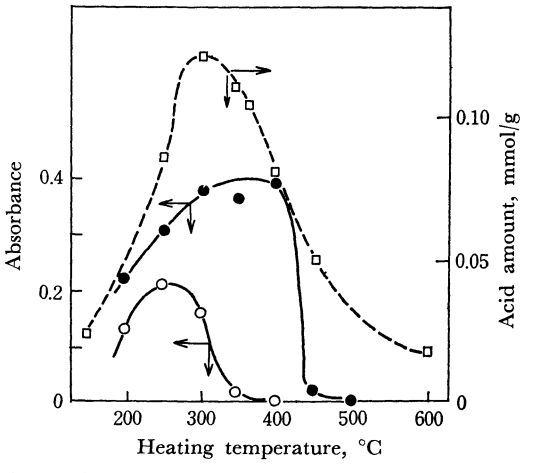

Fig. 2. Variation of absorbances at 1425 cm$^{-1}$ (●) and at 1520 cm$^{-1}$ (○) with heating temperature. Dotted line shows acid amount at acid strength $H_0 \leq 3.3$ measured by *n*-butylamine titration1).

The spectra of pyridine adsorbed on nickel sulfate heat-treated in a vacuum are shown in Fig. 3. The shape of the bands differs somewhat from that ob-

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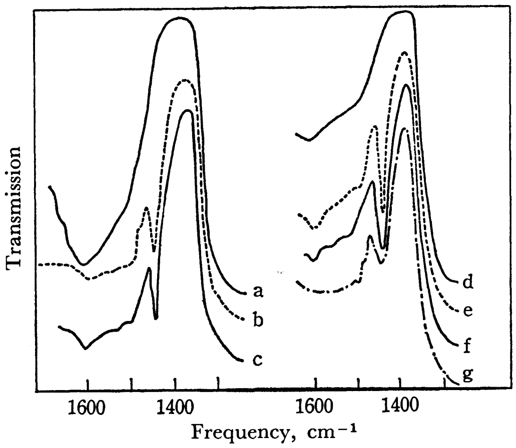

Fig. 3. Infrared spectra of pyridine on silica supported nickel sulfates heat-treated in a vacuum.

- a ; background spectrum of silica supported nickel sulfate heat-treated at 150°C for 3 hr
- b ; a+pyridine and evacuated at 50°C for 30 min
- c ; further evacuation of b at 100°C for 30 min
- d ; background spectrum of silica supported nickel sulfate heat-treated at 200°C for 3 hr
- e ; d+pyridine and evacuated at 50°C for 30 min
- f ; further evacuation of e at 100°C for 30 min
- g ; f+water vapor of about 2 mmHg and evacuated at room temperature for 30 min

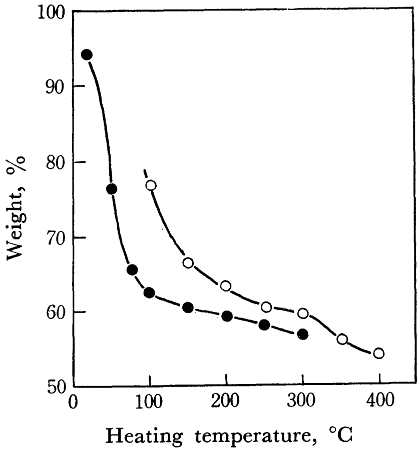

Fig. 4. Weight loss of nickel sulfate as a result of dehydration by heating in a vacuum (●) and in air (○).
Weight % of anhydrous sulfate is calculated to be 55.1%, by taking weight % of the heptahydrate as 100%.

served for the samples heat-treated in air, though both spectra are essentially the same. The difference is considered due to the fact that the absorption bands of pyridine[11)] adsorbed on silica which was used as a carrier in a vacuum experiment are superposed near 1600 cm$^{-1}$ and 1440 cm$^{-1}$. Thus, the bands at 1490—1550 cm$^{-1}$ become broader and those at 1440 cm$^{-1}$ become sharper in the case of vacuum experiment (Fig. 3). The bands at 1490—1550 cm$^{-1}$ for the samples heat-treated at 150°C seem to be large compared with those at 200°C (compare b and c with e and f in Fig. 3; the relative strength of the absorption at 1490—1540 cm$^{-1}$ to that at 1440 cm$^{-1}$ is larger for the samples heat-treated at 150°C than for those at 200°C). This indicates that Brönsted acidity decreases with the rise of temperature of heat treatment from 150 to 200°C in a vacuum. Dehydration curves in air and in a vacuum shown in Fig. 4 reveal that the temperature of heat treatment required for a definite extent of dehydration is about 100°C lower in a vacuum than in air. Thus, Brönsted acidity is expected to show its maximum value when heat-treated at about 150°C in a vacuum. The addition of water resulted in a decrease in the intensities of the 1440 cm$^{-1}$ band and in a slight increase in the intensities of the 1490—1550 cm$^{-1}$ band (Fig. 3, curves f and g). This indicates that Lewis acid is converted into Brönsted acid to some extent by the addition of water.

We shall now give some explanation on the Brönsted and Lewis acidity curves in Fig. 2, by taking into account the structural nature of acid sites of nickel sulfate. According to our studies with infrared, X-ray, electron spin resonance, *etc.*,[10)] the acid center of nickel sulfate is considered to be an empty orbital on the nickel ion which appears in an incompletely dehydrated, metastable transition structure. Intermediate configuration is formed between the monohydrate and anhydrous form. The vacant orbital, and the resulting affinity for an electron pair, explains the Lewis acid nature of nickel sulfate. The Brönsted acidity arises from two sources. One is the water coordinated directly with a nickel ion. The nickel ion tends to attract the oxygen atom, thus setting a hydrogen ion free. The other is the surface water acidified by the inductive effect of neighboring cationic Lewis acid centers. Thus, Brönsted acid appears when the vacant orbital of nickel ion is formed by dehydration and its acidity increases with the rise of dehydration temperature. However, since the amount of hydrated water decreases as the temperature of heat treatment is increased, the Brönsted acidity begins to decrease at 250°C (Fig. 2). The Lewis acidity also increases with the rise of dehydration temperature, but does not decrease until the metastable structure having the vacant orbital collapses and changes to a stable structure at 450°C. Therefore, the maximum of Brönsted acidity appears at a lower temperature (250°C) and that of Lewis acidity at a higher temperature (400°C). The sum of both acidity curves gives the total acidity which was measured by *n*-butylamine titration method[1)] (Fig. 2).

We reported that the rate maxima of the isomerization of α-pinene to camphene[8)] and the formation of formaldehyde by the hydrolysis of methylene chloride[9)] with nickel sulfates heat-treated in air at various temperatures were observed respectively at 250°C and 400°C, which do not coincide with the maximum of total acidity measured by *n*-butylamine titration method. The rate maxima coincide respectively with the maxima of Brönsted and Lewis acidity observed in the present experiment, and the activity curves for isomerization and hydrolysis plotted against the temperature of heat treatment of nickel sulfate correlate well with Brönsted and Lewis acidity curves shown in Fig. 2. This confirms our conclusions[2,9)] that the isomerization of α-pinene is catalyzed by Brönsted acid, and the hydrolysis of methylene chloride by Lewis acid.