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Acidity of Heat-Treated Nickel Sulfate

Since the discovery by Walling (*1*) of the surface acidity of solid metal sulfates, their acidic properties have been extensively studied. Tanabe *et al.* (*2,3*) showed that the acidity is produced only on heating and therefore concluded that the effect was not due to impurities. The structure of the acid site of nickel sulfate is postulated as a metastable configuration, lacking one ligand, intermediate between the monohydrate and anhydrous forms of the sulfate (*4*). Adsorption of water does not destroy the acidity but may convert it from a Lewis to a Brønsted type, by coordination to the nickel ion. As solvated nickel ion in aqueous solution has a low acidity, it is apparent that the type of coordinating ligand is critical in producing the acidity. In the case of the solid nickel sulfate, the configuration required is achieved by fixing the nickel ion in the solid matrix. Dissolution of the matrix in a solvent may, therefore, be expected to destroy the acidity by allowing replacement of the critical structure by the normal solvent cage. In this study we investigated the extraction of activated nickel sulfate by ethanol.

In the several papers on acidity of metal sulfates by Tanabe and co-workers there is no indication that the nickel sulfate samples were purified before activation. Accordingly samples of reagent grade nickel sulfate were activated by heating for several hours at a given temperature. The surface acidities were measured by titration with butylamine in benzene (*5*) with indicators, 4-phenylazo-1-naphthylamine, $pK = 4.0$, and *N*:*N*-dimethyl-*p*-phenylazoaniline, $pK = 3.3$. Table 1 gives the acidities (quantity of acid) for the various activation temperatures. The maximum acidity is produced by heat treatment at 350°C in agreement with the literature (*6*).

Further samples of the activated nickel sulfate were extracted over several days with aliquots of dry ethanol until the remaining solid showed no acidity on addition of indicator. It was found, however, that the ethanol extracts were now acidic. The acidities of the ethanol extracts are given in Table 1. The ethanol acidities vary with temperature in the same manner as the surface acidities. This result is surprising in view of the postulated model of the acidic site.

A check on the original unheated material showed that no acidic impurities were

TABLE 1
ACIDITIES OF SOLIDS AND ETHANOL EXTRACTS (mmol g^{-1})

Indicator, pK:		+4.0		+3.3	
Sample[a]	Activation temp (°C)	Solid	EtOH	Solid	EtOH
1	100	0.175	0.012	0.093	0.004
	350	0.286	0.067	0.196	0.037
	500	0.044	0.001	0.015	trace
2	350	0.050	0.030	—	—
3	350	0.063	0.002	—	—

[a] (1) Unpurified; (2) recrystallized; (3) extracted with ethanol then reactivated.

TABLE 2
ABSORPTION SPECTRA OF NICKEL ION

	Untreated $NiSO_4$–EtOH/H_2O	Activated $NiSO_4$–EtOH	$Ni^{2+}(H_2O)_6$[a]	$Ni^{2+}(EtOH)_6$[a]
$10^{-3}\bar{\nu}_1(cm^{-1})$	25.2	24.6	25.3	24.8
$10^{-3}\bar{\nu}_2(cm^{-1})$	13.7	13.3	13.8	13.4

[a] Imhof and Drago (7).

present if the sample was dissolved in water. An attempt was made, however, to purify the nickel sulfate by recrystallization six times from aqueous solution. Table 1 gives the acidities of the solid and of the ethanol extract of the recrystallized sample; both are reduced in magnitude but are still appreciable. Recrystallization does not, therefore, readily remove the source of acidity in the ethanol extracts.

Nevertheless it was found that the soluble acidity could be eliminated by extraction with ethanol. A fresh sample of nickel sulfate was activated at 350°C. The soluble acidity was extracted until the surface no longer changed indicator to the acid color. The sample was then reheated to 350°C and a portion was used to measure the surface acidity. Another portion was extracted with ethanol and the soluble acidity was determined. The results (see Table 1) show that the surface acidity is well developed but the soluble acidity is negligible. We conclude that nickel sulfate can form an acidic nickel species but, commonly, there is an impurity present which also becomes acidic under the same conditions.

Further evidence for the unique configuration of the nickel ion in the nickel acidic species, as postulated by Tanabe, was obtained from spectra of the ethanol extracts. After activation, the first ethanol extract was a yellow-green color and acidic. Further extracts were colorless and not acidic. If the solid was reactivated, the first extract was again yellow-green but, as shown above, was not acidic. The spectra of the yellow-green extracts showed two peaks which may be assigned to the nickel ion. These are listed in Table 2, together with the corresponding values for a nickel ion in an ethanol–water mixture. The values obtained by Imhof and Drago (*7*) for nickel hexa-ethanolate and hexa-aquo nickel are also given. It is seen that extraction of activated nickel sulfate by ethanol gives nickel hexa-ethanolate. Ethanol extracts of unheated or exhausted nickel sulfate gave no measurable spectra. The dissolution of the nickel ion in the ethanol is therefore associated with the acidic nickel entity and suggests a special configuration which facilitates solvation by ethanol. This ready formation of the nickel hexa-ethanolate contrasts with the more elaborate preparation method found necessary by Imhof and Drago for the bulk compound.

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