132. *The Hydrogenation of Simple Sulphur Compounds. Part I. Nickel Subsulphide as a Catalyst.*

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Nickel subsulphide, Ni_3S_2, is a catalyst for the hydrogenation of the simple sulphur compounds which are present in small amounts in purified coal gas. The formation of this sulphide from metallic nickel, by way of the normal sulphide, has been investigated and the adsorption on it of carbon disulphide, carbon oxysulphide, methylthiol, sulphur dioxide, and hydrogen has been measured up to 350°.

IN the hydrogenation of carbon disulphide, Evans and Stanier (*Proc. Roy. Soc.*, 1924, *A*, **105**, 626) showed that nickel subsulphide, Ni_3S_2, was a useful catalyst at temperatures about 420°. Renewed attention has recently been directed to the hydrogenation of carbon disulphide, carbon oxysulphide, methylthiol, and sulphur dioxide by the discovery (Hutchison, *Inst. Gas Eng.*, 1937, Publication 175, p. 8) that sulphur compounds more volatile than carbon disulphide are present in purified coal gas, and that nickel catalysts can be prepared which are active for their decomposition at temperatures from 150° upwards (Griffith, *ibid.*, p. 45).

The reactions occurring during the formation of the active catalyst and the adsorption of the reactants on it have been surveyed and are now summarised; more detailed studies of the individual hydrogenation reactions will be described in subsequent communications.

EXPERIMENTAL.

Nickel hydroxide was prepared by precipitation from nickel chloride solution with sodium hydroxide, and washed completely free from chloride. Carbon disulphide was of A.R. quality; carbon oxysulphide was prepared by the interaction of ammonium thiocyanate and sulphuric acid (Moser, " Die Reindarstellung von Gasen," 1920, p. 120), condensed by acetone–solid carbon dioxide, and finally purified by fractionation to b. p. —48°; methylthiol was obtained by mild hydrogenation of carbon disulphide with a deficiency of hydrogen, followed by fractionation to b. p. 6°. These distillations were carried out by Gooderham's method (*J. Soc. Chem. Ind.*, 1937, **56**, 32T). Sulphur dioxide was obtained from the liquid. All reagents and gases were dried when necessary by means of calcium chloride and phosphoric oxide; electrolytic hydrogen was purified by treatment with chromous chloride solution and drying.

The Action of Carbon Disulphide and Sulphur Dioxide on Nickel.—Nickel hydroxide was formed into small pellets about 0·15″ in diameter and 0·25″ long by the method of Griffith and Hill (*Trans. Faraday Soc.*, 1937, **33**, 405), and was reduced in a stream of hydrogen at 350° for 2 hours. The product was highly pyrophoric and was therefore never exposed to air.

The metallic nickel so obtained was converted into the sulphide by the action of carbon disulphide vapour carried in nitrogen for 3 hours at 350° (100 c.c./min. of nitrogen, with carbon disulphide at about 250 mm. pressure), or similarly carried by hydrogen. The products obtained by treatment of the reduced nickel with sulphur dioxide and with mixtures of sulphur dioxide and hydrogen were also examined, and the analyses of the different products are shown in Table I.

TABLE I.

Source of material.	Ni, %.	S, %.	C, %.	O, %.
Ni + CS_2 + N_2 at 350°	60·2	35·0	4·8	—
Calc. for NiS + $\frac{1}{2}$C	60·6	33·2	6·2	—
Ni + CS_2 + H_2 at 350°	60·2	37·5	2·2	—
,, excess H_2	—	—	0·7	—
,, subsequently reduced	67·2	26·0	6·8	—
Calc. for Ni_3S_2 + $1\frac{1}{2}$C	68·2	24·8	7·0	—
Ni + SO_2 at 350°	72·5	12·5	—	15·0
Calc. for 2NiO + NiS	73·3	13·3	—	13·4
Ni + SO_2 + H_2 at 350°	63·2	27·1	—	9·7
Ni + coal gas, 21 days at 250°	72·5	24·4	3·1	—

In practice, for the treatment of coal gas, the catalyst was prepared by reduction of nickel hydroxide at 350°; after contact with coal gas for several weeks it was found to be chiefly in the form of nickel subsulphide, as shown by the analysis included above. Methods of preparation of nickel sulphide involving precipitation from aqueous solution were not adopted in view of the results of Middleton and Ward (J., 1935, 1459), who showed that the isolation of pure products by such means was extremely difficult.

Attempts were made to measure the rate of reaction of carbon disulphide with evacuated metallic nickel, with the results given in Table II, but these figures are only very approximate owing to the large evolution of heat. At low temperatures, for instance, a definite acceleration of the reaction could be detected after a period of a few seconds, which must be attributed to a rise in temperature of the solid. When carbon disulphide was admitted to a small quantity of reduced nickel packed round a thermocouple at 20°, a rapid rise in temperature to 200° was observed, which ceased on cutting off the supply of carbon disulphide.

The results in Table I show that nickel decomposes carbon disulphide with the formation of nickel sulphide and carbon and that when hydrogen is present the formation of carbon is reduced, practically none being deposited with excess of hydrogen. The carbon once formed, however, does not react with hydrogen subsequently brought into contact with it at 350°, although decomposition of nickel sulphide occurs under these conditions, as described below.

In contact with sulphur dioxide, nickel is converted into a mixture of oxide and sulphide as found by Neogi and Adhicary (*Z. anorg. Chem.*, 1910, **69**, 209), but when hydrogen is also present, the oxide is reduced, while the sulphur content is only diminished towards that required by formation of the subsulphide.

TABLE II.

Velocity of reaction of carbon disulphide with nickel at 200°.

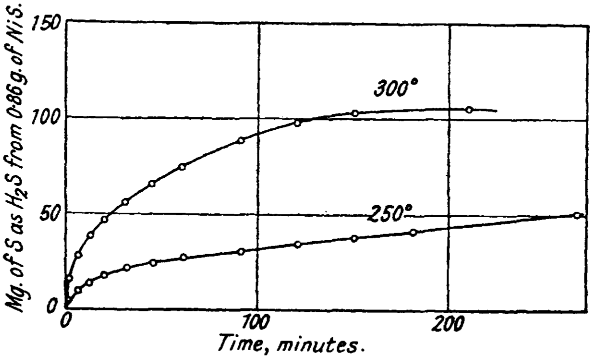
Time (secs.)	15	25	35	45	60	75	90	2220
CS_2 vapour taken up, c.c./g. of Ni	107·5	116	118	125	126	133	134	141

The Action of Hydrogen on Nickel Sulphide.—Although Evans and Stanier showed that reduction of nickel sulphide to Ni_3S_2 took place at 420°, it appeared desirable to measure the rate of reaction of hydrogen with the sulphide produced under the present conditions. The mixture of carbon and sulphide resulting from the action of carbon disulphide on nickel, as shown above, was therefore heated in a hard-glass tube at 350° for 20 hours in nitrogen to remove adsorbed carbon disulphide, and then treated with pure dry hydrogen (100 c.c./min.)

at 250° and 300°, the rate of hydrogen sulphide formation being determined. The results obtained are shown in Fig. 1 and it is clear that the subsulphide Ni_3S_2 is formed, and is produced rather more quickly at 300° by this method than was previously found by Evans and Stanier (*loc. cit.*) at 420°. The action of hydrogen on Ni_3S_2 at 300° is very slow.

Specimens of Ni_3S_2 used in adsorption measurements were prepared by reduction of NiS in hydrogen at 300° for 3 hours; the progress of the reduction was checked by determination of hydrogen sulphide in the exit gas. The solid was cooled in pure nitrogen to room temperature.

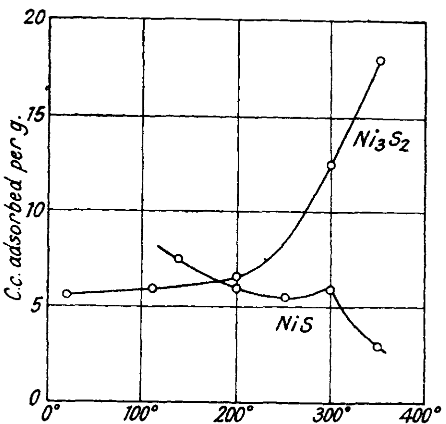
FIG. 1.



Rate of decomposition of NiS *by hydrogen. The formation of* Ni_3S_2 *requires the removal of* 102 *mg. from* 0·86 *g. of* NiS.

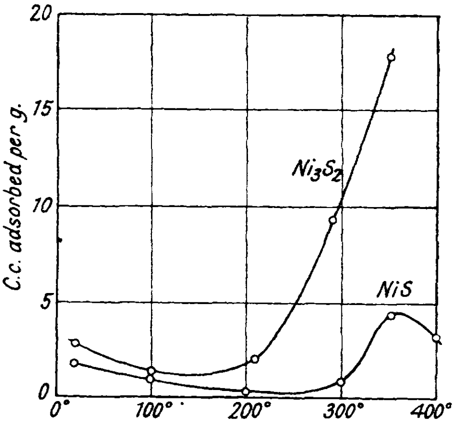
Adsorption on Nickel Subsulphide.—Griffith, Hill, and Plant's apparatus (*Trans. Faraday Soc.*, 1937, **33**, 1419) was used for measurement of adsorption. The weight of sulphide used was about 0·2 g., and it was exhausted to below 0·001 mm. pressure for at least 8 hours at 350°. Every sample was then cleaned by admission of a little hydrogen at 350°, followed by renewed evacuation. A fresh specimen, from a single preparation, was taken for each reagent investigated. Measurements were generally carried out at temperatures rising from 20° to 350°, and where the results showed any interest, the determinations were repeated after evacuation. Velocity measurements were also carried out in certain cases.

FIG. 2.



Isobars at 65—70 *mm. pressure for adsorption of* CS_2 *on nickel sulphides.*

FIG. 3.



Isobars at 65—70 *mm. for adsorption of* SO_2 *on nickel sulphides.*

In Figs. 2 and 3 are shown isobars for the adsorption of carbon disulphide and sulphur dioxide on Ni_3S_2 and, for comparison, also on NiS; in Table III are given the results obtained with hydrogen, carbon oxysulphide, and methylthiol.

TABLE III.

C.c. of gas adsorbed per g. of Ni_3S_2.

Temp.:	20°.	100°.	150°.	200°.	250°.	300°.	350°.
Hydrogen	0·29	0·49	—	0·61	—	0·59	1·08
CH_3·SH	2·06	0·76	0·36	0·17	0·32	0·08	0·0
COS	0·94	0·15	—	0·02	—	0·0	—

From the adsorption measurements, the information summarised below has been obtained:

Carbon disulphide. On nickel sulphide adsorption is extensive and reversible, having measurable velocities throughout the temperature range explored and also showing van der Waals adsorption at the lower temperatures. On the subsulphide extensive adsorption also occurs, but a slow reaction takes place, and repeated adsorptions after evacuation approach the lower values given by the normal sulphide. Examples of the changes are given by the velocity measurements of Table IV. Isobars obtained when the adsorption is irreversible are characterised by an unbroken rise with temperature, so that the inflexion generally shown by activated adsorption is absent.

TABLE IV.

Velocity of CS_2 *adsorption on* Ni_3S_2.

Time	Adsorption, c.c. of CS_2 vapour per g. of Ni_3S_2.			
(mins.)	200°.	200° (repeated).	300°.	300° (repeated).
1	2·8	0·7	2·4	0·1
25	4·7	2·0	5·2	1·3
50	5·4	2·6	6·1	1·9
100	6·4	3·2	7·3	2·5
150	7·0	3·9	8·2	3·1

Hydrogen. Although the amounts involved are very much smaller than the quantity of carbon disulphide taken up, it is evident that activated adsorption begins between 100° and 200° on Ni_3S_2. The behaviour of NiS towards hydrogen is, of course, obscured by the formation of hydrogen sulphide at about 200—250°.

Sulphur dioxide. This gas is adsorbed normally by NiS, showing activated adsorption at 300° upwards; with the lower sulphide there is clear evidence for activated adsorption beginning about 200°, but the results are then complicated by slow decomposition of the solid and the adsorption is only partly reversible.

Methylthiol. Van der Waals adsorption predominates at temperatures below 200°, but activated adsorption sets in above this point. The amounts involved are small compared with those of carbon disulphide.

Carbon oxysulphide. Only very small adsorption could be detected at any temperature and there is no evidence for an activated type.

Effect of Carbon on Adsorption.—Measurements carried out on specimens of nickel sulphide prepared from carbon disulphide severally in the presence and in the absence of hydrogen showed that any carbon deposited at this stage was almost entirely without effect on the adsorption of carbon disulphide. A slight increase in the amount taken up at the lower temperatures was detectable when carbon was present, but this difference disappeared as the temperature rose.

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