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Chemisorption of Hydrogen Sulfide on a Supported Nickel Catalyst

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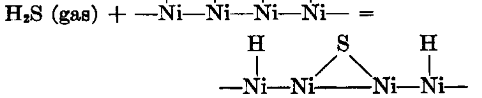
The chemisorption of hydrogen sulfide on some nickel catalysts has been studied in the temperature range 550–645°C. The sulfur uptake is a function of the ratio p_{H_2S}/p_{H_2}. A saturation layer has been observed at ratios above 5×10^{-6}, approximately, and at ratios above 10^{-3} bulk sulfide (Ni_3S_2) was formed. The sulfur content of the saturation layer is correlated with the nickel area determined by volumetric measurements of hydrogen chemisorption at −72°C. The mechanism of the chemisorption of hydrogen sulfide is discussed.

INTRODUCTION

Hydrogen sulfide is known to poison nickel catalysts, the hydrogen sulfide being retained on the catalysts.

The poisoning of a nickel catalyst may occur even when the concentration of hydrogen sulfide ought not to cause formation of a bulk compound of sulfur and nickel. As an example, it appears from Rosenqvist's investigation of the thermodynamics of nickel sulfide phases (*1*) that formation of bulk-phase sulfide at temperatures around 500°–700°C requires a p_{H_2S}/p_{H_2} ratio of the order of 10^{-3}. This ratio is about 100–1000 times above what would normally cause poisoning at those temperatures. Therefore, *a priori*, hydrogen sulfide may be assumed to be retained by a chemisorption process.

Literature on the chemisorption of hydrogen sulfide on nickel is very scanty. Den Besten and Selwood (*2*) have found by magnetochemical measurements on nickel catalysts in the temperature range 0° to 115°C that hydrogen sulfide is dissociatively chemisorbed, forming four chemisorptive bonds with the nickel surface. The following mechanism is suggested:


$$\mathrm{H_2S\ (gas)} + -\overset{|}{\mathrm{Ni}}-\overset{|}{\mathrm{Ni}}-\overset{|}{\mathrm{Ni}}-\overset{|}{\mathrm{Ni}}- = -\overset{\overset{\mathrm{H}}{|}}{\mathrm{Ni}}-\mathrm{Ni}\overset{\mathrm{S}}{\diagup\diagdown}\mathrm{Ni}-\overset{\overset{\mathrm{H}}{|}}{\mathrm{Ni}}- \tag{1}$$

At high coverage the dissociated hydrogen will gradually be desorbed as the sulfur atoms take its place. Thus it would be reasonable to believe that all hydrogen originating from the chemisorbed hydrogen sulfide might be desorbed as molecular hydrogen. This is, however, not the case, as only about two-thirds of the hydrogen can be removed from a surface saturated with hydrogen sulfide—even by evacuation at 400°C. Measurements by Kemball *et al.* (*3*) and by Muller and Gibert (*4*) have supported Selwood's observation concerning the dissociative chemisorption. However, from their measurements on nickel films in the temperature range −80° to 0°C, Kemball *et al.* suggest that each molecule of hydrogen sulfide occupies three nickel atoms and that the breakdown of the molecule as an intermediate stage may involve an HS radical occupying one site and blocking a second with an H atom on the third site.

The results of Muller and Gibert, who repeated the study of Den Besten and Selwood, show identical rates of hydrogen sulfide chemisorption and hydrogen desorption, when the surface has been completely covered with dissociated hydrogen sulfide. This, too, is hardly in accordance with the simple mechanism including four nickel atoms.

All the studies mentioned above have

been performed at low temperatures, but there seem to be no publications on chemisorption of hydrogen sulfide at higher temperatures. The present work is part of a study of chemisorption of hydrogen sulfide on supported nickel at temperatures above 400°C. The study of the saturation layer has been performed by correlating the sulfur content of the saturated catalyst with the nickel area measured by hydrogen chemisorption.

METHODS

1. *Catalysts*

In order to avoid sintering effects, four catalysts called A, B, C, and D, which were made for high-temperature employment, were used for the experiments. The catalysts contained about 10 wt % Ni and were supported on different carriers consisting of magnesium aluminum spinel. Catalyst A contained a few percent of potassium, which may be of no importance to this investigation. The sulfur content of the catalysts prior to chemisorption has been determined to 5 − 20 wt ppm.

2. *Hydrogen Sulfide Chemisorption*

Apparatus. The measurements of the chemisorption of hydrogen sulfide were performed at atmospheric pressure by passing until equilibrium was established a mixture of hydrogen sulfide, hydrogen and, in some experiments, argon over the catalyst, which was placed in a tubular reactor.

A hydrogen flow, purified in a copper oven, was passed through a hydrogen sulfide generator with a constant production of hydrogen sulfide per unit of time. The partial pressure of the hydrogen sulfide was changed by varying the hydrogen flow. It was also possible to send hydrogen and argon, free from hydrogen sulfide, to the reactor. The hydrogen and argon flows were adjusted by needle valves and were meassured with flow meters. Sampling for analysis could be made before and after the reactor.

The hydrogen sulfide generator was based on hydrolysis in an acidic solution of thioacetamide to acetamide and hydrogen sulfide. Swift and Butler (*5*) have determined the kinetics of this hydrolysis in the temperature range of 60–90°C to be of first order with respect to the concentrations of both hydrogen ions and thioacetamide. The hydrolysis has been successfully used at 25°C as a hydrogen sulfide generator in the range of 0.01–100 mg S/hr.

The apparatus was made mainly of glass, apart from the reactor, which was made of 18.8 stainless steel. It is true that this made the reactor adsorb hydrogen sulfide, but this feature appeared to be of no influence on the investigation. The reactor (internal diameter 15 mm) was placed in an electrically heated oven, and the temperature in the catalyst layer was regulated with a thyristor controller.

Analytical. The gas was analyzed for hydrogen sulfide by passing it for a certain period through a bubble flask containing an acidic solution of cadmium acetate, and the collected sulfur was then determined colorimetrically by the methylene blue reaction. By means of the flow of hydrogen sulfide thus determined and the hydrogen flow measured by the flow meters, the molar ratio H_2S/H_2 was calculated.

The sulfur content of the catalysts was determined by driving off hydrogen sulfide with hydroiodic acid in an apparatus described by Gustavson (*6*). The hydrogen sulfide was then analyzed as mentioned above. This method has a relative standard deviation of about 2%, and the results were in accordance with those obtained from radiochemical analysis.

Chemisorption conditions. After reduction of the catalyst for 1 hr in dry hydrogen at 850°C the chemisorption of hydrogen sulfide was performed by passing a hydrogen sulfide containing hydrogen flow over the catalyst at 550°C (in some experiments 645°C). After having passed to the catalyst the amount of sulfur that was expected to be retained by it, the hydrogen sulfide flow was measured before and after the reactor. Then, normally, these flows were close to each other, but the reactor was given at least twice the amount of sulfur that was expected to be retained before closing the experiment. In some experiments a number of catalyst types were treated simultaneously.

3. Nickel Area and Hydrogen Chemisorption

Principle. Chemisorption of hydrogen and carbon monoxide has been used for determination of nickel areas; still, owing to the fact that carbon monoxide may be bound to the surface in different ways (*7*) and because there is also a risk of formation of nickel carbonyl (*8*), it seems reasonable to prefer hydrogen, which is assumed to be bound in a well-defined way.

However, the hydrogen-nickel system is also complicated, as a fast chemisorption is followed by slow, activated effects. This feature has resulted in a great many different conceptions (*7, 9, 10*), which are not to be discussed here. Maybe this uncertainty is the reason for the existence of several different procedures for determination of the nickel area of catalysts by means of chemisorption of hydrogen (*11–15*).

The method used in the present case is based upon the assumption that the hydrogen uptake observed by Beeck (*16*) resulting from the fast chemisorption on unoriented nickel films at $-196°C$ and $p_{H_2} = 0.1$ mm Hg, reflects a coverage with one hydrogen atom per nickel atom of the surface. However, in order to avoid physical adsorption on the carrier, the temperature had to be increased to $-72°C$, which could be done without any influence from the activated hydrogen uptake.

Knor and Ponec (*17*) have criticized the BET measurements (among which were those with krypton) that were the basis of the results of Beeck and Ritchie (*16*). Beeck as well as Knor and Ponec found that about 0.8 mole of krypton per mole of hydrogen is adsorbed on a randomly oriented nickel film. However, Beeck used a calculated value of the area of a krypton molecule (14.6 Å^2) whereas it appears reasonable to use an experimental value (21 Å^2), as was done by Knor and Ponec. The latter value results in an area of a hydrogen site on the nickel surface of 8.9 Å^2, whereas Beeck used 6.18 Å^2. From crystallographic considerations an equal distribution of (100), (110), and (111) planes in the surface yields a mean area of a nickel site of 6.5 Å^2.

However, not the area but rather the adsorbed amounts of hydrogen are of interest for the present work.

Apparatus and procedure. An ordinary apparatus for determination of BET areas was used. The sample container was a quartz flask equipped with a tube at the bottom so that hydrogen could flow through the catalyst layer. During reduction and evacuation, the flask was surrounded by an electrically heated oven. The evacuation was carried out by means of an oil diffusion pump. The hydrogen was purified in a copper oven, and a gold foil trap was used to protect the sample against mercury vapor. After some few measurements, a palladium alloy diffusion cell was also used for purification but, apparently, this had no influence on the results.

The measurements were mainly performed under the following conditions:

Amount of catalyst: 10–20 g.

Reduction: 2 hr at 850°C in a stream of dry hydrogen (2 moles/hr).

Evacuation: 850°C until $p < 10^{-4}$ mm Hg.

Chemisorption: $-72°C$ (freezing mixture of ethanol and solid CO_2). First measuring point was read after a period of half an hour, whereas the following three to four points were read at intervals of 10 min.

When the adsorbed hydrogen volume is plotted against the hydrogen pressure, one gets an isotherm appearing as a straight line with a slightly positive slope. The first point will normally be located on the ordinate axis. The intersection of the straight line with the ordinate axis is taken as a measure for a monolayer of hydrogen on the nickel surface corresponding to the volume adsorbed at low pressure ($\sim$0.1 mm Hg).

RESULTS

1. Chemisorption of Hydrogen Sulfide

Preliminary experiments indicated that the chemisorption of hydrogen sulfide is re-

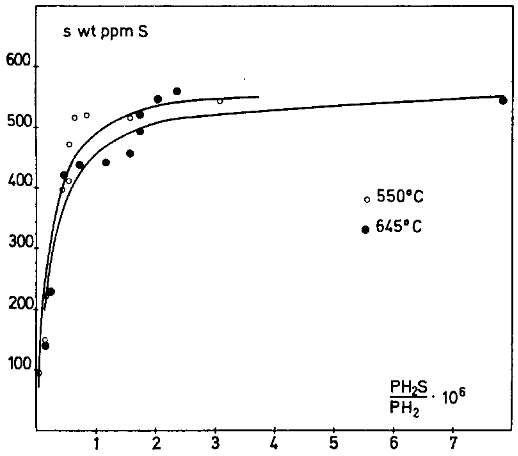


FIG. 1. H_2S chemisorption. Isotherms at 550°C and 645°C, Catalyst A. Estimated Langmuir isotherms are shown.

versible and that the sulfur uptake depends on p_{H_2S} as well as on p_{H_2}. Results from experiments at 550° and 645°C performed with different values of p_{H_2S} and p_{H_2} are shown in Fig. 1 and Table 1. From Fig. 1 it appears that the amount of sulfur retained by the catalyst (called s) may be considered a function of the ratio p_{H_2S}/p_{H_2} (called r) and, furthermore, that a saturation layer is obtained at a ratio above $2–5 \times 10^{-6}$. Equal amounts of sulfur per unit area are taken up at the two temperatures.

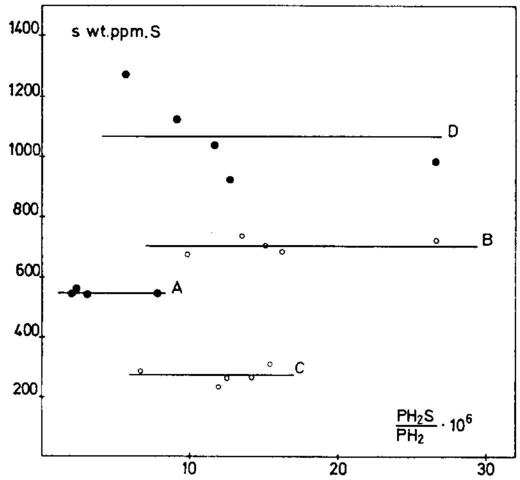


FIG. 2. H_2S chemisorption. Saturation layers of various catalysts.

Table 2 and Fig. 2 show results from sulfur uptake of the saturation layers (called s_0) of the four catalysts. It should be noted that the measurements on Catalyst D are subject to great uncertainty. From the data in Table 2 it may be concluded that the sulfur uptake was independent of the amount of sulfur added, which amounted to 1.3 to 30 times that which was retained. In addition to this, the sulfur uptake is not correlated with the H_2S/H_2 ratios applied, which were varying from 2×10^{-6} to 27×10^{-6}. Hence, the measured amounts of sulfur that have been retained are assumed to represent the saturation layers.

TABLE 1
ISOTHERMS AT 550°C AND 645°C—CATALYST A[a]

Mg S/hr	Mole H_2/hr	Mole A/hr	$r \times 10^6$ [b]	s (wt ppm)
		Isotherm at 550°C		
0.067	4.0	0	0.53	410
0.110	4.1	0	0.84	520
0.016	4.3	0	0.12	150
0.100	2.0	0	1.56	515
0.004	4.5	0	0.03	96
0.016	1.2	1.9	0.43	395
0.011	2.5	1.9	0.14	222
0.374	3.8	0	3.08	543
0.045	2.2	0	0.64	515
0.034	2.0	0	0.53	470
		Isotherm at 645°C		
0.144	3.9	0	1.16	440
0.100	2.0	0.9	1.56	455
0.104	1.9	2.4	1.73	520
0.110	1.5	1.9	2.34	559
0.078	1.4	0	1.74	492
0.020	4.9	0	0.13	140
0.311	1.3	0	7.84	545
0.130	2.0	1.9	2.02	545
0.044	2.0	1.9	0.69	437
0.028	4.5	0	0.20	227
0.061	4.2	0	0.45	420
0.054	3.9	0	0.48	420

[a] 0.5 g of catalyst used in each experiment. Duration more than 50 hr.

[b] $r = p_{H_2S}/p_{H_2}$.

Scanning experiments showed that an abrupt increase in the sulfur uptake occurs when the H_2S/H_2 ratio exceeds the value for formation of bulk sulfide predicted from the thermodynamics (*1*). Thus, depending on the duration of the experiment, Catalyst

TABLE 2
SATURATION LAYERS OF VARIOUS CATALYSTS[a]

Catalyst amount (g)	Duration (hr)	H_2S flow (mg S/hr)	H_2S addition (mg S/g cat)	$r \times 10^6$ [b]	s_0 (wt ppm)
			Catalyst B		
10	18½	0.97	1.8	15.1	705
10	21	0.63	1.3	9.8	675
10	45	1.04	4.7	16.2	685
5[c]	42	1.70	7.2	26.6	723
10	66	0.87	5.7	13.5	738
			Catalyst C		
10	44	0.77	3.4	12.0	235
5	43½	0.80	6.9	12.5	267
5	66	0.43	5.7	6.7	288
5	42	0.91	7.6	14.2	263
5	42½	0.86	7.3	13.4	310
			Catalyst D		
10	88	0.74	6.5	11.6	1045
10	44	0.59	2.6	9.2	1125
10	47	0.36	1.7	5.6	1270
10	45	0.81	3.7	12.7	923
5[c]	42	1.70	7.2	26.6	983

[a] Temperature: 550°C; H_2 flow, 2 mole/hr.
[b] $r = p_{H_2S}/p_{H_2}$
[c] Same experiment.

B contained about 0.1 to 2.7 wt % sulfur after treatment at 550°C with H_2S/H_2 in a ratio of about 10^{-3}. Ni_2S_3 was identified by X-ray analysis, as expected from the data of Rosenqvist (*1*).

Finally, it should be mentioned that the carrier impregnated with a potassium compound did not show any sulfur uptake at 550°C and with $H_2S/H_2 = 2.5 \times 10^{-6}$. This means that potassium apparently does not influence the results from Catalyst A.

2. Hydrogen Chemisorption

Typical isotherms are shown in Fig. 3, one of which shows incidentally a measurement for $p = 0$ mm Hg placed just where the linear extrapolation intersects the ordinate axis. This may support the validity of the procedure of calculation of the area on the basis of this extrapolation to low pressures. It should be noted that this result is not in accordance with the extrapolation suggested by Sinfelt (*11*).

By leaving the sample overnight, the effect of the activated hydrogen adsorption is observed (Fig. 4). However, the rate of hydrogen uptake has been too small to influence the determinations of the areas that are shown in Table 3. Again the measurements on Catalyst D are subject to relatively great uncertainty.

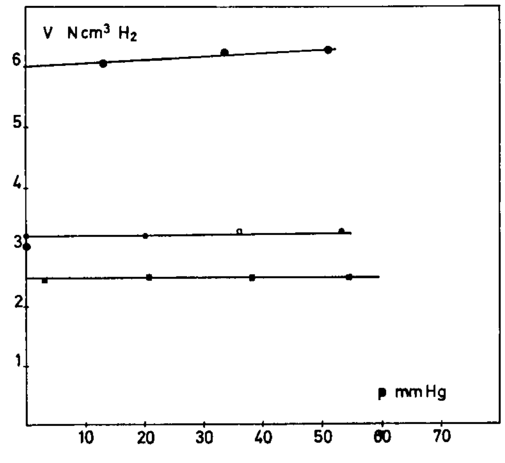


FIG. 3. H_2 chemisorption. Isotherms at −72°C.

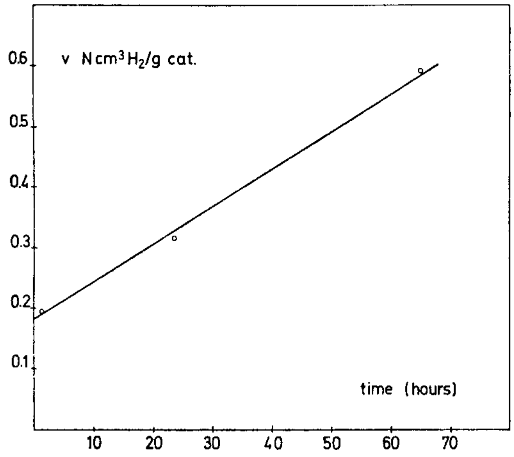


FIG. 4. H_2 chemisorption. Influence of the activated chemisorption. The hydrogen uptake has been followed by a decrease in pressure from 32 to 8 mm Hg.

TABLE 3
RESULTS FROM MEASUREMENTS OF NICKEL AREAS BY MEANS OF HYDROGEN CHEMISORPTION AT −72°C

Catalyst	H_2 uptake (Ncm^3/g red. cat.)	Ni area (m^2/g red. cat.)	Number of measurements	Est. variance of mean $\times 10^4$
A	0.224	0.78	2	16
B	0.348	1.21	8	4
C	0.143	0.50	3	11
D	0.454	1.58	6	88

DISCUSSION

Corresponding values of sulfur uptake (s) and $r = p_{H_2S}/p_{H_2}$, which are plotted in Fig. 1, show a correlation resembling a Langmuir isotherm. It has therefore been attempted to correlate the results by an expression of the form

$$s = \frac{ar^n}{1 + br^n} \qquad (2)$$

where a, b, and n are constants.

In order to estimate n, the expression is rearranged to

$$\log \frac{s}{s_0 - s} = n \log r + \log b \qquad (3)$$

where $s_0 = a/b$.

The plot of log $(s/s_0 - s)$ against log r is shown in Fig. 5. The value of s_0 has been determined as the mean of the measured s values for r above 2×10^{-6}. By linear regression analysis the slope n is estimated to be 1.1.

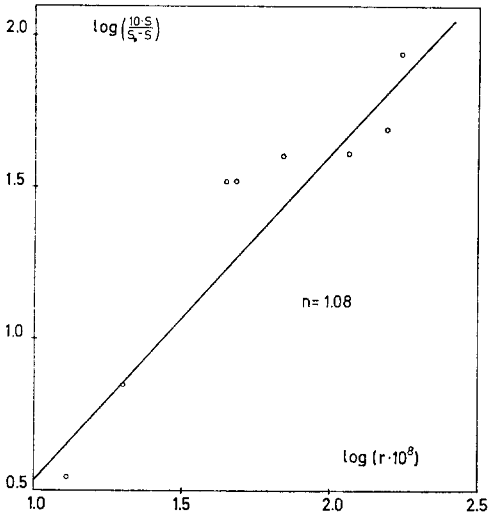


FIG. 5. Estimation of n in $s = ar^n/1 + br^n$ by plotting log $(s/s_0 - s) = n \log r + \log b$, where $s_0 = a/b$. Data from isotherm at 645°C.

Assuming $n = 1$ linear regression of r/s on r fitting the well known linear form of the isotherm

$$\frac{r}{s} = \frac{b}{a} r + \frac{1}{a} \qquad (4)$$

yields at 550°C

$$s = \frac{3.1 \times 10^9 r}{1 + 5.3 \times 10^6 r} \text{ wt ppm S} \qquad (5)$$

and at 645°C

$$s = \frac{2.5 \times 10^9 r}{1 + 4.4 \times 10^6 r} \text{ wt ppm S} \qquad (6)$$

By weighted regression analysis of the form

$$\frac{1}{s} = \frac{1}{ar} + \frac{b}{a} \qquad (7)$$

where the variables are separated, the obtained results do not deviate significantly from these expressions.

Calculated values of the expressions have formed the basis of the curves shown in Fig. 1, and it is obvious that the estimated expressions can be looked upon only as a guidance.

It is well known that it is questionable whether it is possible to conclude from an analytical expression, which covers an experimentally obtained isotherm, anything about the mechanism of the adsorption. The fact that a certain theory turns out to be in agreement with experimental data, need not be a proof of its assumptions.

However, it should be mentioned that $n = 1$ after Langmuir's assumptions represents the following mechanism including occupation of one nickel site:

$$H_2S\ (\text{gas}) + Ni = Ni{-}S + H_2\ (\text{gas}) \quad (8)$$

By similar analysis Muller and Gibert found from their data from low temperatures (*4*) that $n = \frac{1}{2}$, which was related to the dissociation of hydrogen sulfide involving occupation of two sites.

Another method of illustrating how sulfur may be adsorbed at the nickel surface is to compare the respective saturation layers with respect to their contents of sulfur and hydrogen. This has been done for the four catalysts in Fig. 6 where the number of sulfur atoms retained per gram of catalyst has been plotted as a function of the number of hydrogen atoms chemisorbed per gram of catalyst. There appears to be a linear dependency and by weighted regression analysis fitting a straight line through the origin, the slope is determined to be 0.74 for hydrogen capacity as independent variable. Moreover, statistical analysis indicates a high correlation factor. In other words, the surface may have nearly three-fourths of a "sulfur site" per "hydrogen site."

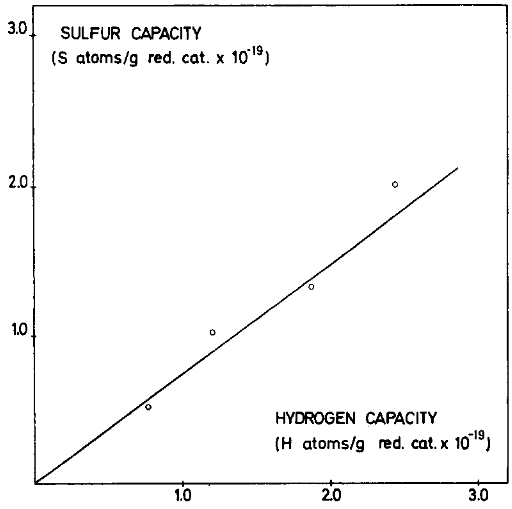


Fig. 6. Correlation between hydrogen and sulfur uptake.

Now, it should be possible to estimate, in principle, the atomic ratio of sulfur and nickel in the saturation layer, which in itself may give an idea of the atomic arrangement. This implies knowledge of the atomic ratio of hydrogen and nickel at the surface after the fast chemisorption at −72°C; it also implies that the surfaces may be considered identical under the different conditions of the two measuring methods and that the sulfur and hydrogen atoms are occupying the same type of "sites."

The latter assumption is made probable by the observation that no measurable chemisorption of hydrogen took place on a catalyst which was saturated beforehand with sulfur. Since in the two measuring methods the catalysts have very similar pretreatments, and as no correlation has been observed between sulfur capacity and time of sulfidation (i.e., no sintering effects), it would be reasonable to assume that the same amount of "sites" have been involved in the two measuring methods.

According to the general assumption that one hydrogen atom per nickel atom is chemisorbed at the conditions used here, there ought to be chemisorbed 0.8 sulfur atom per nickel atom, in the saturation layer. However, as a consequence of what was previously mentioned about the criticism of this assumption proposed by Knor and Ponec (*4*), one should rather use a hydrogen capacity of 6.5/8.9 = 0.73 hydrogen atom per nickel atom, which will result in a sulfur capacity of 0.54 sulfur atom per nickel atom.

These calculations are of course very uncertain, but the result seems reasonable in relation to the size of the sulfide ion (about 10 Å^2), which hardly allows a coverage above 0.5 sulfur atom per nickel atom. Stable surface layers containing free metal atoms have also been observed in the chemisorption of hydrogen sulfide on silver by Bénard *et al.* (*18*), an observation probably corresponding to the observations made by means of the LEED technique on the chemisorption of oxygen on nickel (*19*). As no hydrogen uptake was observed on a catalyst saturated with sulfur, it may be presumed that the sulfur atoms of the saturation layer are concealing the free nickel atoms.

The idea of the composition of the saturation layer which has been suggested above, is somewhat different concerning the role of hydrogen, from what is inferred in the literature (*2*, *3*, *4*) from results obtained at low temperatures. At low temperatures the hydrogen originating from hydrogen sulfide is at least partly retained at the surface, whereas the mechanism discussed above involves no chemisorption of hydrogen. This may well be ascribed to the different temperatures applied, the sulfur displacing the hydrogen from the surface when the temperature is increased. The discrepancies concerning the number of bonds formed when a sulfur atom is chemisorbed, will not be discussed because it must be conceded, again, that the argument on the basis of the isotherm cannot be conclusive.

CONCLUSION

The sulfur capacity of the saturation layer observed in the chemisorption of hydrogen sulfide on nickel at temperatures about 550°C may be related to the nickel area as measured by hydrogen chemisorption. A mechanism involving a single bound sulfur atom and no chemisorption of hydrogen, seems possible but, probably owing to the size of the sulfide ion, the sulfur capacity is less than one sulfur atom per nickel atom. It may be reasonable then to consider the atomic arrangement of the surface phase instead of considering the adsorption complex. This requires further studies by means of another technique.

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