

## STUDIES OF MAGNETIC CHANGES IN A Ni/Al<sub>2</sub>O<sub>3</sub> CATALYST IN THE ADSORPTION OF HYDROGEN AND HYDROGEN SULPHIDE

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Adsorption of hydrogen and hydrogen sulphide and the changes in the magnetization of the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst have been studied. Adsorption of both gases was followed at room temperature. In both cases relative magnetization decreases with increasing amount of the adsorbed gas. In hydrogen adsorption this decrease is linear. The magnetic isotherm of hydrogen sulphide consists of two linear parts, the first one having the slope twice as high as that of hydrogen and the second one of the same slope as in the case of hydrogen. Comparison of the slopes of magnetic isotherms of hydrogen and hydrogen sulphide confirms the assumption that chemisorption of hydrogen sulphide on a Ni/Al<sub>2</sub>O<sub>3</sub> catalyst proceeds *via* a dissociative mechanism. In the first stage, *i.e.* in adsorption on a clean surface, hydrogen sulphide is bound to the catalyst by four bonds. Further sorption results in incorporation of sulphur under the formation of two bonds, while hydrogen is released into the gaseous phase.

Previous papers<sup>1,2</sup> were devoted to the investigation of hydrogen sulphide adsorption on nickel catalysts. The results obtained, however, do not allow to draw any more detailed conclusions on the adsorption mechanism. It was therefore necessary to try to find a further, independent method, which could throw new light upon this problem. For this reason we chose to measure the mutual relation of adsorption and magnetic properties, a method, for which the nickel catalysts are especially suitable.

In chemisorption electrons of the chemisorbed substance interact with electrons of the metal in *d*-orbitals. Since the unpaired electrons are responsible for the magnetic properties, chemisorption is accompanied by a change of magnetic susceptibility. These changes are measurable only if the adsorbent has a great specific surface area, *i.e.*, when the ratio of surface atoms to the total number of atoms<sup>9</sup> is at least 10%. This is just the case with nickel catalysts on carriers or with promoters, on whose surface nickel is very finely dispersed. Very small ferromagnetic particles form separate domains, differing in their behaviour from compact ferromagnetic substances; they are denoted as superparamagnetic substances.

Measurement of magnetic properties was employed to study the sorption<sup>4-8</sup> of H<sub>2</sub>, O<sub>2</sub>, CO, H<sub>2</sub>S.

### EXPERIMENTAL

Magnetic and adsorption isotherms were measured on a Ni/Al<sub>2</sub>O<sub>3</sub> catalyst prepared as described previously<sup>1</sup>. The catalyst, whose total surface area was 170 m<sup>2</sup>/g catalyst, contained in the re-

duced state 50-2% Ni. Prior to measurement the catalyst was reduced with hydrogen at 400°C for 30 h. After reduction the sample was evacuated at 400°C to  $10^{-4}$ – $10^{-5}$  Torr.

Hydrogen and hydrogen sulphide were taken from steel flasks and were purified as described earlier<sup>1</sup>. Isotherms were measured with a volumetric vacuum apparatus. Magnetic properties were measured by means of an AC permeameter, similar to that employed in the work of Geus and coworkers<sup>7</sup>. The instrument consisted of two primary coils (1000 windings of Cu wire, diameter 2 mm). Secondary coils (400 windings of Cu wire, diameter 0.1 mm) were placed inside these coils. Primary coils were supplied with alternative stabilized voltage 24 V (50 cycles). The induced voltage was measured with a selective voltmeter Tesla 12 XN 016, connected in series to the secondary coils. The sample of the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst to be studied was placed into one of the secondary coils so as to obtain the maximum deflection of voltage  $U$ . This deflection was then compensated by inserting a compensation sample (a reduced and evacuated sample of the same composition) into the other secondary coil. After finding the minimum voltage deflection  $U_0$  (0.02–0.05 mV), the change in voltage caused by adsorption,  $\Delta U$ , was measured. Since the voltage induced in the secondary coils is directly proportional to the magnetization<sup>3</sup>  $M$ , the found value  $\Delta U/U$  is equal to the change of relative magnetization  $\Delta M/M$ .

## RESULTS

### *Adsorption of Hydrogen*

Adsorption of hydrogen was carried out in portions about  $0.5 \cdot 10^{20}$  molecules/g. Final equilibrium pressure was 15–30 Torr. Simultaneously with the adsorption isotherm also the magnetic isotherm was measured. Total amount of the adsorbed hydrogen was  $2.9 \cdot 10^{20}$  molecules/g of the reduced catalyst. A part of hydrogen was sorbed reversibly. Irreversible adsorption was  $2.3 \cdot 10^{20}$  molecules, the reversible portion amounted  $0.6 \cdot 10^{20}$  molecules/g.

Adsorption of hydrogen is accompanied by a decrease in the relative magnetization. The dependence of  $\Delta M/M$  on the adsorbed amount is linear, with the slope  $0.032 \cdot 10^{-20}$ . Total decrease of the relative magnetization after adsorption of the mentioned total amount of hydrogen was 10% on the average. After evacuation of the reversible portion the magnetization increased by 3%. When a new portion of hydrogen was admitted after evacuation, the magnetization decreased again to the value before evacuation. Like all other results also the reversible change of magnetization was very well reproducible. In order to obtain more information on the reversibly bound hydrogen, repeated adsorption and evacuation of hydrogen was carried out under simultaneous measurement of the magnetization changes. Up to about  $4.8 \cdot 10^{20}$  molecules of hydrogen adsorbed, the evacuation did not cause any change in magnetization. Reversible adsorption was observed only after adsorption of further portions.

### *Adsorption of Hydrogen Sulphide*

As with hydrogen, adsorption of hydrogen sulphide was studied at room temperature. The course of magnetization changes is more complicated than in the case of hydrogen

adsorption. Even here magnetization decreased with the adsorbed amount. The magnetization isotherm is at the beginning linear with the slope  $0.080 \cdot 10^{-20}$ . When c.  $1.7 \cdot 10^{20}$  molecules are adsorbed a break appears with a new linear branch, having the slope  $0.042 \cdot 10^{-20}$ . The slope of the first part is approximately twice as high as in the case of hydrogen, that of the second part is nearly the same as with hydrogen. Up to the value of c.  $1.7 \cdot 10^{20}$  molecules of adsorbed hydrogen sulphide the adsorption was complete. When a further portion was adsorbed, hydrogen was released into the gaseous phase. Fig. 1 shows the magnetic isotherm as well as the dependence of the amount of released hydrogen on the amount adsorbed.

The results of hydrogen adsorption clearly indicate that there exists a part on the catalyst surface where hydrogen is reversibly bound. In the adsorption of hydrogen sulphide a balance has to be carried out of hydrogen released into the gaseous phase and for this reason it was necessary to know whether this reversible adsorption takes place also in the case of hydrogen sulphide adsorption. First of all,  $1.2 \cdot 10^{20}$  molecules of hydrogen sulphide were adsorbed in portions on the catalyst surface. The subsequent evacuation caused no change in magnetization. Hydrogen was then admitted onto the catalyst and the change in magnetization was measured. The procedure and the results obtained are presented in Table I.

### Interaction Experiments

The results obtained in interaction of hydrogen with hydrogen sulphide preadsorbed on a part of the surface were described above. In a further series of experiments hydrogen sulphide was adsorbed on the whole surface. No irreversible adsorption takes place in this case, but reversible adsorption of hydrogen is observed. Its extent

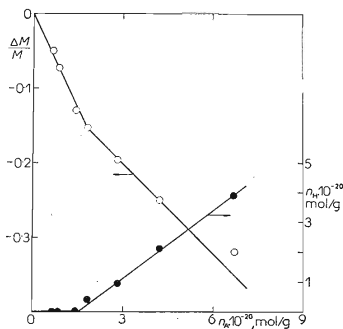


FIG. 1

Dependence of the Changes of Relative Magnetization,  $\Delta M/M$ , on the Amount of Adsorbed Hydrogen Sulphide ( $n_A$ ) and the Dependence of the Amount of Hydrogen, Released into the Gaseous Phase ( $n_H$ ) on the Amount of Adsorbed Hydrogen Sulphide

depends on the amount of the sorbed hydrogen sulphide, decreasing with its increase. When approximately  $5 \cdot 10^{20}$  molecules of hydrogen sulphide are adsorbed even the reversible adsorption of hydrogen disappears.

Interaction of hydrogen sulphide with preadsorbed hydrogen was investigated in two kinds of experiments:

1) Hydrogen was adsorbed on a part of the catalyst surface ( $0.7 \cdot 10^{20}$  molecules). Adsorption of hydrogen sulphide was measured after evacuation. Magnetic isotherm consisted, as in the case of clean surface, of two parts. The first, linear part had the slope  $0.082 \cdot 10^{-20}$ , the second part was also linear, with the slope  $0.040 \cdot 10^{-20}$ . The presence of preadsorbed hydrogen was reflected in the amount of adsorbed hydrogen sulphide at which the break on the magnetic isotherm appeared. This value was  $1.2 \cdot 10^{20}$  hydrogen sulphide molecules. At the same time hydrogen was released into the gaseous phase. The value of the adsorbed amount at which the break on the magnetic isotherm appears, is lower in this case than on a clean surface. The presence of preadsorbed hydrogen evidently shifts the value of the adsorbed amount on the isotherm break towards lower values. With increasing amount of preadsorbed hydrogen this value further decreases.

2) In the second series of experiments the whole surface of nickel was covered with hydrogen which was followed by evaluation at room temperature. Hydrogen sulphide was then admitted in portions onto the nickel surface with preadsorbed hydrogen. After the first portion had been adsorbed, only 60% of hydrogen of the adsorbed hydrogen sulphide was released into the gaseous phase. Adsorption of further portions of hydrogen sulphide was accompanied by a practically complete release of hydrogen from the adsorbed hydrogen sulphide. Magnetization decreased linearly, the slope of the isotherm being  $0.040 \cdot 10^{-20}$ . The isotherm does not inter-

TABLE I

Adsorption of Hydrogen Sulphide and of Hydrogen on the Ni/Al<sub>2</sub>O<sub>3</sub> Catalyst and the Change of Relative Magnetization

Procedure	Adsorbed amount $10^{20}$ molecules/g catal.	$\Delta M/M, \%$
Hydrogen sulphide	1.2	11.2
Evacuated	—	11.2
Hydrogen	0.6	13.3
Evacuated	—	11.6
Hydrogen	0.4	13.6
Evacuated	—	11.6

sect the origin which is obviously due to the fact that the part of hydrogen, released in adsorption of the first portion of hydrogen sulphide, is immediately bound to sites, accessible only to reversible hydrogen adsorption. Since this kind of adsorption is connected with a decrease in magnetization, the decrease related to one molecule is higher in the first portion of adsorbed hydrogen sulphide than in further adsorption where all hydrogen is released into the gaseous phase.

## DISCUSSION

### *Adsorption of Hydrogen*

As shown above, magnetization decreased during the whole process of hydrogen adsorption. This is in accordance with the earlier findings of Selwood<sup>3</sup> and other authors<sup>6-8</sup>. Selwood derived a relation<sup>9</sup> describing the change of relative magnetization in hydrogen adsorption

$$\Delta M/M = -\frac{2n_H\epsilon\beta}{n\mu} + \left[\frac{n_H\epsilon\beta}{n\mu}\right]^2,$$

where  $\Delta M/M$  is the change of relative magnetization in adsorption,  $n_H$  is the number of adsorbed hydrogen atoms,  $\beta$  is Bohr's magneton,  $\mu$  is the magnetic moment of a volume nickel atom,  $\epsilon$  is the change of atomic magnetic moment of nickel caused by adsorption of one hydrogen atom and  $n$  is the number of nickel atoms in the sample. As the second term can be neglected (it can cause a deviation only at high coverages with samples having great surface areas), the relation (1) shows evidently the linear decrease of relative magnetization on the amount of adsorbed hydrogen.

The results demonstrate that irreversible adsorption of hydrogen is followed by reversible adsorption. Reversible adsorption of hydrogen on nickel was found even by other authors<sup>10-12</sup>. *E.g.*, Brocker and Wedler<sup>11</sup> found the reversibly adsorbed hydrogen from the reversibility of the resistance and heats. Suhrman<sup>12</sup> describes the increase of the resistance of nickel film after evacuation of 15% of hydrogen. The slow reversible adsorption is explained by dissolving hydrogen atoms in nickel. Evacuation leads to their recombination and desorption from the surface.

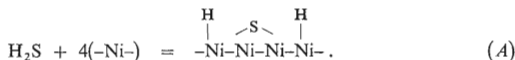
From all the magnetic data obtained it can be concluded that the adsorption mechanism is the same both for reversible and irreversible adsorption. Assuming that hydrogen is chemisorbed on nickel under dissociation into two atoms, this mechanism remains unchanged in reversible adsorption.

The value of the change in magnetic moment of nickel atom in adsorption of hydrogen,  $\epsilon$ , can be calculated from the changes of relative magnetization during adsorption according to relation (1) (the second term is omitted). The value found for  $\mu = 0.606^{13}$  was 0.26. Wosten and coworkers<sup>6</sup> give the values 0.39 and 0.52. They assume that

the lower value of  $\epsilon$  as compared with the magnetic moment of nickel atom is caused by the fact that surface nickel atoms have in small particles a lower moment than the internal ones. This problem will be discussed later in connection with the interaction of hydrogen sulphide with nickel catalyst which is accompanied by volume sulphidation.

### Adsorption of Hydrogen Sulphide

From the course of the magnetic isotherm in adsorption of hydrogen sulphide it can be concluded that hydrogen sulphide is sorbed on the catalyst by two different mechanisms. Selwood<sup>3</sup> proposed a method for determining the number of adsorption bonds. This method is based on the comparison of the slope of magnetic isotherm of the studied gas with that of the hydrogen. If, *e.g.*, the slope is twice as high as with hydrogen, it can be judged that one molecule of the sorbate is bound by twice as many bonds as the hydrogen molecule. In view of the fact that the mechanism of hydrogen adsorption is known (one atom is bound to one nickel)<sup>14</sup> it is possible to determine that four bonds per one molecule are formed in the first stage of hydrogen sulphide adsorption, whereas in the second stage two bonds are formed. The first of these mechanisms proceeds till  $1.7 \cdot 10^{20}$  hydrogen sulphide molecules are present on the surface. Up to this amount no hydrogen is released into the gaseous phase. The results support the following mechanism

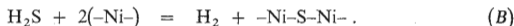


Adsorption of  $1.7 \cdot 10^{20}$  hydrogen sulphide molecules would correspond to the coverage of  $6.8 \cdot 10^{20}$  active centers. The determination of the number of centers for hydrogen sulphide adsorption was performed using the value of total hydrogen adsorption, *i.e.* including the reversible portion. The result is  $5.8 \cdot 10^{20}$  centers on the surface. The value is lower than the number of centers occupied in hydrogen sulphide adsorption. This difference is discussed in more detail in the paper in preparation<sup>15</sup>.

To the same conclusion on the mechanism of adsorption arrived also Den Bensten and Selwood<sup>5</sup> on the basis of magnetic measurements. However, they did not observe the break on the magnetic isotherm, differing the surface chemisorption and incorporation, eventhough the amount of sorbed hydrogen sulphide in the final step was so high that it could not be bound only to surface according to mechanism (A). The number of centers necessary for bonding such amount of adsorbed hydrogen sulphide exceeded by far the number of centers as determined by hydrogen adsorption.

The second part of magnetic isotherm has the same slope as the magnetic isotherm of hydrogen. Accordingly, in this process two bonds are formed per one hydrogen

sulphide molecule. Since hydrogen is released into the gaseous phase, the results confirm the following mechanism



In these bonds sulphur is incorporated.

The used magnetic method makes it possible to detect even changes resulting from incorporation of sulphur into deeper sub-surface layer. If the surface nickel atom had a lower magnetic moment than the internal one, then the incorporation would necessarily be accompanied by a greater change in magnetization than was found experimentally. On the basis of these results it can be concluded that the low value of  $\epsilon$  is not due to the difference between the magnetic moment of the nickel atoms inside and on the surface, as it was assumed by Wosten and coworkers<sup>6</sup>.

### *Interaction Experiments*

Interaction of hydrogen with a catalyst on which hydrogen sulphide was adsorbed to various extent, yields information above all on the reversibly bound hydrogen. The results indicate that this reversibly bound hydrogen is bound to sites which are not accessible to sulphur. Incorporation of sulphur causes changes in the surface layers and consequently the portion of reversibly adsorbed hydrogen decreases.

In contrast to hydrogen sulphide adsorption on a clean catalyst surface the magnetic isotherm in the case of hydrogen sulphide adsorption on the surface with pre-adsorbed hydrogen did not show two branches. The slope of the linear dependence was in this case the same as that of the hydrogen isotherm. Hydrogen sulphide molecule is adsorbed on the surface with preadsorbed hydrogen under the formation of two bonds, belonging to sulphur since hydrogen is released into the gaseous phase. Sulphur was expected to displace hydrogen in this kind of interaction, occupying itself the empty sites. If this last mechanism were valid magnetization would necessarily have remained constant, since no new nickel atoms would have entered the interaction. However, the experimentally found decrease of magnetization since the very beginning of adsorption confirms that new bonds with nickel are formed which evidently is in contradiction with the above mentioned assumption on hydrogen displacement. Hydrogen which was preadsorbed on the catalyst remains bound even after hydrogen sulphide adsorption. Sulphur enters the interaction with further nickel atoms and is probably bound above the layer of the initially adsorbed hydrogen.

Concluding it can be said that the study of magnetic changes in adsorption of hydrogen and hydrogen sulphide gave the following information: 1) Mechanism of hydrogen sulphide adsorption and of the subsequent incorporation of sulphur was elucidated. 2) It was found that in the coverage of the surface with hydrogen sulphide there exists a part of the catalyst where hydrogen is reversibly bound.

3) Preadsorption of hydrogen leads to a change in the mechanism of hydrogen sulphide adsorption and to total release of hydrogen into the gaseous phase.

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