

ADSORPTION OF HYDROGEN SULPHIDE ON NICKEL CATALYSTS

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Sorption of hydrogen sulphide on Ni/Al₂O₃ and Ni/Cr₂O₃ catalysts has been studied at temperatures of -78, 0, 20, 55 and 100°C and on a nickel catalyst without promotor at 55°C. Total surface area of the catalysts was determined by means of argon adsorption using the BET method. The number of nickel surface centers was determined by means of oxygen chemisorption at 20°C. Comparison of the number of nickel surface centers with the amount of hydrogen sulphide sorbed showed that at all temperatures except -78°C sulfur is incorporated into the nickel lattice. During sorption of hydrogen sulphide hydrogen was released into the gaseous phase in amounts depending on the extent of incorporation.

The degree of incorporation increases with increasing temperature. At 55°C its value is highest for the nickel catalyst without promotor and lowest for the Ni/Al₂O₃ catalyst.

In final purification of hydrogen or its mixtures, as *e.g.* the nitrogen-hydrogen mixture in the synthesis of ammonia, iron methanation catalysts have been recently substituted by more efficient nickel catalysts with Al₂O₃ and Cr₂O₃ promotors. Hydrogen prepared by conversion of water gas or from hydrocarbons contains also traces of sulphur compounds. Organic sulphur compounds are catalytically hydrogenated to hydrogen sulphide which is bound to the catalyst causing its desactivation.

Hitherto little attention has been paid to the chemisorption of hydrogen sulphide on nickel. Most of the studies were carried out only at higher temperatures when already a real chemical reaction takes place. The first paper to deal with chemisorption of hydrogen sulphide on nickel at low temperatures was that of Saleh, Kemball and Roberts¹ who studied adsorption of hydrogen sulphide on nickel films in the temperature range -80-100°C. They suggested a dissociative mechanism of hydrogen sulphide adsorption, assuming the formation of -Ni-SH and -Ni-H bonds. Den Bensten and Selwood² who carried out the adsorption of hydrogen sulphide on a Ni/SiO₂ catalyst at room temperature, assume total dissociation of hydrogen sulphide molecule under the formation of two -Ni-H and one -Ni-S-Ni- bond. More papers were devoted to the study of the effect of hydrogen sulphide and of further sulphur compounds on the poisoning of a nickel catalyst. *E.g.* Maxted and Evans³ followed the effect of hydrogen sulphide and of some sulphur compounds on the poisoning of the Ni/kieselgur catalyst and they found the following toxicity sequence:

hydrogen sulphide < carbon disulphide < thiophene < cysteine.

Ljubarskij and coworkers⁴⁻⁶ investigated the chemisorption of thiophene and carbon disulphide on nickel catalysts with promoters, both with respect to catalyst poisoning and with the aim to determine, by means of selective chemisorption, the surface area of the nickel component in multi-component catalysts. Šolc and coworkers⁷⁻⁹ who studied the poisoning of a Ni/Cr₂O₃ catalyst with hydrogen sulphide found that at 22°C hydrogen sulphide is bound only to the nickel component, whereas at 165°C also to Cr₂O₃.

The subject of the present work was to study the extent and the mechanism of hydrogen sulphide chemisorption and the way it is effected by the presence of different promoters.

EXPERIMENTAL

Adsorption of hydrogen sulphide was followed in a vacuum apparatus with two quartz helices. The extension of the helices (75 windings, wire diameter 300 μm) was determined by means of a cathetometer KM 6 (USSR). The amount of hydrogen released into the gaseous phase during adsorption of hydrogen sulphide was then determined volumetrically.

Catalyst Ni/Al₂O₃ was prepared by precipitation from the solutions of nickel nitrate and sodium aluminate, Ni/Cr₂O₃ catalyst by precipitation from a mixture of nickel nitrate and chromium(III) nitrate. In both cases the precipitate was dried, calcinated and pressed into tablets with graphite added. The catalysts were further reduced by hydrogen and after cooling in nitrogen they were passivated by controlled oxygen chemisorption. Prior to measurement the passivated catalysts were reduced with hydrogen at the temperature of 350°C. The Ni/Al₂O₃ catalyst contained in the reduced state 57.8 w% of Ni and the Ni/Cr₂O₃ catalyst 62.4 % of Ni. Samples of nickel catalyst without promoter were obtained by reduction of nickel oxide prepared by precipitation from a solution of nickel nitrate.

Measurement of the nickel surface area was carried out by means of oxygen chemisorption. Oxygen of medicinal purity was taken from steel flasks and purified by passing through a purifier with KOH. Electrolytic hydrogen was also taken from steel flasks and purified by passing over KOH, CaCl₂, Deoxo catalyst and again CaCl₂. Hydrogen sulphide was prepared by the reaction of 10% sulphuric acid with sodium sulphide in a special apparatus. It was purified by passage through a purifier with CaCl₂ and through a freezing trap immersed into a bath of solid carbon dioxide in ethanol. The hydrogen sulphide condensed in liquid nitrogen was purified in the adsorption apparatus by repeated evacuation. The apparatus was then evacuated also prior to each measurement. Argon for measuring the surface area was taken from glass ampoules supplied by fa Dusíkárny, Ostrava. Adsorption of hydrogen sulphide on both catalysts was measured at -78, 0, 20, 55 and 100°C.

RESULTS

Ni/Al₂O₃ Catalyst

To determine the extent of adsorption it is necessary to know the number of nickel surface centers. The method of selective chemisorption was employed to this purpose, using oxygen as adsorbate. $10 \cdot 10^{20}$ molecules were adsorbed on 1 g of the catalyst at 20°C. The determination of the number of active nickel centers was carried out

under the assumption that in the adsorption one oxygen molecule corresponds to one surface nickel particle^{10,11}. In this case the number of adsorbed oxygen molecules represents the number of nickel active centers.

When studying chemisorption on one component of a multicomponent catalyst it is always necessary to find to what extent the adsorption on the remaining components takes place. Therefore first of all we determined the extent of hydrogen sulphide adsorption on the Al_2O_3 promotor at all the above mentioned temperatures. At 55 and 100°C the amount of strongly bound hydrogen sulphide was so small that no correction for the sorption on Al_2O_3 was necessary in the measurements of hydrogen sulphide adsorption on the $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst. However, at -78 to 20°C the amount of strongly bound hydrogen sulphide was already so high that an appropriate correction proved necessary. Moreover, at -78°C, physical adsorption occurred in addition to pure chemisorption. To obtain the value of the chemisorbed hydrogen sulphide at this temperature, the catalyst was evacuated to constant weight after adsorption. After correction for the amount of hydrogen sulphide adsorbed on the Al_2O_3 promotor it was found that $4.3 \cdot 10^{20}$ hydrogen sulphide molecules were adsorbed on the nickel component per 1 g of the catalyst. The portion of physical adsorption was 42% of the total amount adsorbed. Only 5% of hydrogen of the total amount of sorbed hydrogen sulphide was released into the gaseous phase during measurement. At higher temperatures, 0, 20, 55 and 100°C the amount of sorbed hydrogen sulphide and the amount of hydrogen released into the gaseous phase increased whereas the

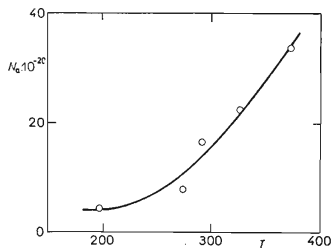


FIG. 1

Temperature Dependence of the Amount of Hydrogen Sulphide Sorbed on $\text{Ni}/\text{Al}_2\text{O}_3$ Catalyst

N_a Sorbed Amount in molecules per 1 g catalyst.

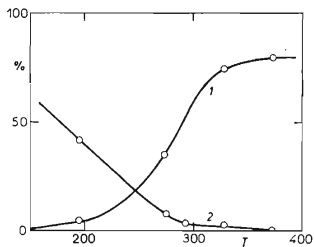


FIG. 2

Temperature Dependence of the Fraction of Hydrogen Released into the Gaseous Phase in Adsorption of Hydrogen Sulphide (1) and of the Fraction of Physical Adsorption (2) on $\text{Ni}/\text{Al}_2\text{O}_3$ Catalyst

percentage of physical adsorption diminished (Figs 1 and 2). At all these temperatures the portion of the released hydrogen was lowest in adsorption on a pure catalyst surface, *i.e.*, when the first charge was adsorbed. With increasing coverage the percentage of hydrogen released into the gaseous phase increased. Only 20% of hydrogen sulphide could be removed by reduction and evacuation at 300°C from the surface of the catalyst which was saturated with hydrogen sulphide at 55°C. However, reduction of a catalyst on which oxygen was sorbed at 20°C led to a complete removal of all oxygen.

Ni/Cr₂O₃ Catalyst

Similar as with the above mentioned Ni/Al₂O₃ catalyst also in the case of Ni/Cr₂O₃ the first step was to determine the number of nickel surface active centers. $4.8 \cdot 10^{20}$ oxygen molecules were chemisorbed per 1 g of the catalyst. Assuming that one oxygen molecule corresponds to one surface nickel the found number of oxygen molecules represents also the number of nickel centers.

Experimental results of the adsorption of hydrogen sulphide on Cr₂O₃ promotor showed that when the adsorption on a Ni/Cr₂O₃ is measured at 55 and 100°C, no correction is necessary for the amount of hydrogen sulphide chemisorbed on promotor Cr₂O₃. At low temperatures, -78 and 20°C this amount cannot be neglected any more and an appropriate correction is necessary.

The portions of hydrogen released into the gaseous phase were at -78, 0, 20, 55 and 100°C 5, 15, 40, 84 and 90%, respectively and the corresponding amounts of physical adsorption attained the values 42, 19, 9, 2 and 0%.

Nickel Catalyst without Promotor

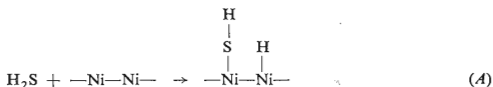
The total surface area of the sample determined from the physical adsorption of argon using the BET method was found to be $6.6 \text{ m}^2/\text{g}$. $1.1 \cdot 10^{20}$ oxygen molecules were sorbed per 1 g of the same catalyst at 20°C. Provided that one oxygen molecule corresponds to one surface nickel, $1.1 \cdot 10^{20}$ surface centers per 1 g were present on this catalyst. If we assume that the surface is composed of approximately equal amounts of the principal crystal planes, then the mean surface area per one nickel is 6.7 \AA^2 . Hence the total surface area of the nickel catalyst without promotor was $7.3 \text{ m}^2/\text{g}$. Adsorption of hydrogen sulphide was measured only at 55°C and $32.2 \cdot 10^{20}$ molecules of H₂S were found to be adsorbed on 1 g of nickel.

DISCUSSION

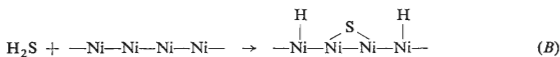
The course of the temperature dependence of hydrogen sulphide sorption with both types of catalysts shows that the amount of hydrogen sulphide sorbed increases distinctly with increasing temperature. From the comparison of the number of sorbed

hydrogen sulphide molecules with the number of surface centers it is then evident that at higher temperatures sulphur is incorporated into the bulk of nickel.

It has been already mentioned that in adsorption of hydrogen sulphide the percentage of hydrogen released into the gaseous phase is at all temperature lowest in the case of adsorption on the non-covered, clean surface. With increasing coverage this amount increases. The release of hydrogen into the gaseous phase is an evidence that hydrogen sulphide adsorption on both catalysts proceeds *via* the dissociation mechanism. This is in agreement with the hitherto published data^{1,2}. In the first of the papers Saleh and coworkers¹ suggest the following mechanism



Den Bensten and Selwood² presume the adsorption of hydrogen sulphide to proceed in the following way:



The first of the mechanisms was suggested on the basis of volumetric measurements, whereas the other one is based on magnetic measurements.

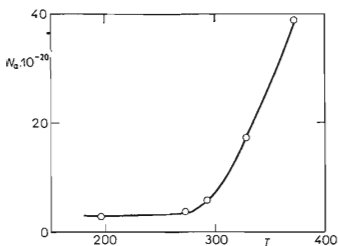


FIG. 3

Temperature Dependence of the Amount of Hydrogen Sulphide Sorbed on Ni/Cr₂O₃ Catalyst

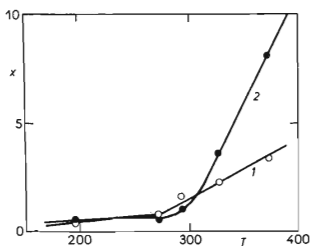


FIG. 4

Temperature Dependence of the Parameter of Bulk Sulphidation

X Number of sulphur atoms corresponding to one surface nickel particle. 1 Ni/Al₂O₃ catalyst, 2 Ni/Cr₂O₃ catalyst.

From the results found in the present paper no unambiguous decision can be made between the two mechanisms. Comparison of the number of adsorption centers with the amount of sorbed hydrogen sulphide in the initial stages of adsorption (at all temperatures) supports rather the mechanism of the first type, *i.e.* the formation of —Ni—SH and Ni—H bonds. The existence of —Ni—SH bond is also confirmed by the results of thermal desorption (300°C) which was carried out on the $\text{Ni/Al}_2\text{O}_3$ catalyst after adsorption of hydrogen sulphide at 55°C . No hydrogen was found in the gaseous phase which indicates that it is after adsorption of hydrogen sulphide very strongly bound to the surface. The same result, *i.e.* the stability of the bonding of hydrogen which remained on the surface after adsorption of hydrogen sulphide, was also reported in the above cited papers^{1,2}.

At higher temperatures sulphur is incorporated into the bulk of both catalysts. However, the temperatures at which this process starts to take place under the conditions of our experiment cannot be defined exactly. The incorporation obviously involves the release of always one hydrogen molecule per one molecule of the sorbed hydrogen sulphide. Incorporation into the bulk of the catalyst will evidently result in the expansion of the nickel surface layers. However, this expansion does not lead to any change in the number of adsorption sites for oxygen, since it has been found¹² that preadsorption of hydrogen sulphide on the surface of both $\text{Ni/Al}_2\text{O}_3$ and $\text{Ni/Cr}_2\text{O}_3$ catalysts does not influence the subsequent oxygen adsorption which is the same as on a clean surface.

To compare the behaviour of both types of catalysts the number of sulphur atoms corresponding to one surface nickel was plotted in dependence on temperature (Fig. 4). This parameter (X) is actually a measure of the bulk sulphidation of nickel. Thus it is evident from Fig. 4 that at temperatures above *c.* 20°C a deeper sulphidation takes place with the $\text{Ni/Cr}_2\text{O}_3$ catalyst.

The results obtained in measuring the interaction of hydrogen sulphide with a nickel catalyst without promotor indicate that a deep bulk sulphidation occurs. Of all the studied catalysts this one is thus the least stable against sulphidation. The stability of nickel in different nickel catalysts against sulphidation at 55°C decreases in the sequence: $\text{Ni/Al}_2\text{O}_3 > \text{Ni/Cr}_2\text{O}_3 > \text{Ni}$. From the comparison of the extent and the course of oxygen and hydrogen sulphide adsorption it is evident that the extent of hydrogen sulphide adsorption on the nickel catalyst without promotor is much greater than that of oxygen. On the catalyst $\text{Ni/Al}_2\text{O}_3$ at 20°C oxygen adsorption is faster and proceeds to a greater extent than hydrogen sulphide adsorption.

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