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## STUDY OF MAGNETIC CHANGES IN THE INTERACTION OF HYDROGEN, OXYGEN AND HYDROGEN SULPHIDE ON A Ni/Al<sub>2</sub>O<sub>3</sub> CATALYST

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Received March 15th, 1974

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Interactions of oxygen with hydrogen sulphide, of oxygen with hydrogen and of hydrogen sulphide with hydrogen were studied at laboratory temperature on a Ni/Al<sub>2</sub>O<sub>3</sub> catalyst and parallel changes in magnetization were followed. In the adsorption of oxygen on the surface of a catalyst with preadsorbed hydrogen sulphide the adsorbed amount is nearly the same as on a clean catalyst surface. Magnetization decreases from the beginning of adsorption process. Adsorption of hydrogen sulphide on a catalyst with preadsorbed oxygen has approximately the same course as on a clean surface. Magnetization at first remains constant and later decreases. Preadsorption of hydrogen results in a slight decrease of the amount of oxygen adsorbed. Hydrogen is not adsorbed on a surface with preadsorbed oxygen. In the interaction of hydrogen with preadsorbed hydrogen sulphide, the amount of hydrogen adsorbed depends on the quantity of preadsorbed hydrogen sulphide. If only the surface is covered with hydrogen sulphide, hydrogen is adsorbed reversibly on the catalyst. With increasing extent of sulphidation the amount of reversibly adsorbed hydrogen gradually decreases to zero.

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In the preceding communication<sup>1</sup> interactions of oxygen at 20°C and of hydrogen sulphide at 55°C were followed gravimetrically. These experiments have shown that oxygen is bound to the surface of the catalyst with preadsorbed hydrogen sulphide to a nearly the same extent as on a clean surface. In a reverse interaction, *i.e.* that of hydrogen sulphide with preadsorbed oxygen, water was formed. It was not possible, on the basis of adsorption data only, to discuss the problems of adsorption and interaction mechanism. For this reason in the present paper the changes of magnetization were followed parallel to adsorption measurements to make possible a better elucidation. Another aim of the work was to yield at least a partial answer to the question of the mutual influence of hydrogen and oxygen chemisorption with hydrogen sulphide in order to explain the differences between the surface area of nickel as determined by chemisorption of the mentioned gases in the preceding paper<sup>3</sup>.

## EXPERIMENTAL

All adsorption data as well as the changes in magnetization were measured in a static vacuum apparatus at room temperature. The Ni/Al<sub>2</sub>O<sub>3</sub> catalyst was prepared by continuous precipitation of a solution of nickel(II) nitrate with sodium aluminate. After drying and calcination the catalyst was reduced in hydrogen at 425°C and then it was passivated by regulated chemisorption of oxygen. The sample prepared in this way was, prior to measurement, again reduced in hydrogen for 30 h at 400°C. Evacuation was carried out at 420°C up to 10<sup>-4</sup> to 10<sup>-5</sup> Torr. In the reduced state the catalyst contained 50.2% Ni. Its total surface area was 160 m<sup>2</sup> per 1 g of the reduced catalyst (further, all results will be related to 1 g of the reduced catalyst). The surface area of nickel was 2.34 m<sup>2</sup>/g.

All gases were taken from steel flasks and were purified as described earlier<sup>2</sup>. Changes of magnetization were measured with an A.C.-permeameter the scheme of which was described in our previous paper<sup>2</sup>.

## RESULTS

*Interaction of hydrogen sulphide with preadsorbed oxygen.* Oxygen was first adsorbed on the catalysts surface at room temperature (average 8.3.10<sup>20</sup> molecules). After evacuating the gaseous phase hydrogen sulphide was adsorbed in portions. The course of adsorption was the same as on a clean surface, i.e. at first it took place instantaneously, but later the rate of adsorption decreased. Up to the amount of approximately 6.10<sup>20</sup> hydrogen sulphide molecules adsorbed no hydrogen was released into the gaseous phase. Only after this amount had been adsorbed the release of hydrogen into the gaseous phase was observed. An example is shown in Fig. 1: only 2.14 . 10<sup>20</sup> (i.e. 16%) hydrogen molecules were released into the gaseous phase when the amount of adsorbed hydrogen sulphide was 13.4 . 10<sup>20</sup> molecules.

During adsorption of hydrogen sulphide at room temperature no water was released. Only after heating the catalyst to 50°C water is released into the gaseous phase. Water from the gaseous phase could be completely condensed in a bath of solid carbon dioxide and ethanol. Magnetization remains constant at the beginning of hydrogen sulphide adsorption, at more than 6.10<sup>20</sup> molecules adsorbed it slowly decreases. The beginning of the decrease in magnetization depends on the amount of oxygen adsorbed. The less oxygen is adsorbed on the surface, the shorter is the phase of constant magnetization. For example, when only 5.3 . 10<sup>20</sup> oxygen molecules were adsorbed on the surface the decrease in magnetization began already at 3 . 10<sup>20</sup> molecules of hydrogen sulphide adsorbed.

*Interaction of oxygen with preadsorbed hydrogen sulphide.* The extent as well as the character of oxygen adsorption on the surface of a catalyst with preadsorbed hydrogen sulphide are nearly the same as on a clean surface. In the average 7.8 . 10<sup>20</sup> oxygen molecules were adsorbed. All oxygen is bound irreversibly, its amount being independent of the amount of preadsorbed hydrogen sulphide. Magnetization decreases from the start, with the slope of the linear part of its isotherm 0.04 (Fig. 2).

*Interaction of hydrogen sulphide with preadsorbed hydrogen.* In one series of these experiments hydrogen was preadsorbed only on a part of the surface and the changes in adsorption and magnetization properties of hydrogen sulphide were followed in comparison with those on a clean surface. In the latter case the course of adsorption was as follows: the adsorption proceeded completely, up to  $1.7 \cdot 10^{20}$  molecules adsorbed in further adsorption hydrogen was released into the gaseous phase. Magnetic isotherm consisted of two linear parts, the first one with the slope 0.080, the second with the slope 0.042. The break in the slope occurred, when the value of the amount adsorbed reached the value  $1.7 \cdot 10^{20}$  hydrogen sulphide molecules. Partial preadsorption of hydrogen causes a shift of the value of the adsorbed amount at the point of break on the magnetic isotherm towards lower values. If, e.g.,  $0.8 \cdot 10^{20}$  hydrogen molecules were preadsorbed, the break on magnetic isotherm appeared at the value  $1.3 \cdot 10^{20}$  molecules of adsorbed hydrogen sulphide. At the same moment the release of hydrogen into the gaseous phase appeared.

In another series of experiments hydrogen was adsorbed on the whole surface and after evacuation the adsorption of hydrogen sulphide was followed. The corresponding magnetic isotherm is shown in Fig. 3. The slope of the linear part of the isotherm is 0.04. Upon adsorption of the first portion only 60% hydrogen of the adsorbed hydrogen sulphide was released into the gaseous phase. With further portions all hydrogen was released into the gaseous phase.

*Interaction of hydrogen with preadsorbed hydrogen sulphide.* Adsorption of hydrogen on a surface, covered only partially with hydrogen sulphide, proceeded

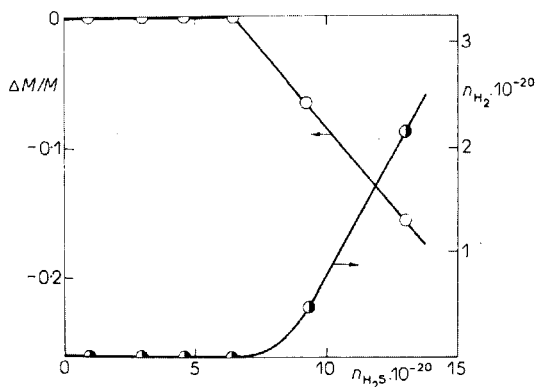


FIG. 1

Dependence of Relative Magnetization  $\Delta M/M$  and of the Amount of Released Hydrogen on the Amount of Adsorbed Hydrogen Sulphide in a Catalyst with Preadsorbed Hydrogen

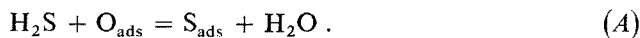
irreversibly. When the coverage with preadsorbed hydrogen sulphide was complete, *i.e.* at about  $1.7 \cdot 10^{20}$  molecules, no more irreversible adsorption was observed. However, reversible adsorption still proceeded on this surface. The amount of this reversible adsorption decreased with increasing amount of the hydrogen sulphide adsorbed. When the coverage attained about  $5 \cdot 10^{20}$  molecules of hydrogen sulphide adsorbed the adsorption of hydrogen stops entirely.

*Interaction of oxygen with preadsorbed hydrogen.* Hydrogen was admitted onto the catalyst up to full saturation and afterwards the gaseous phase was evacuated. Oxygen was then admitted in portions onto the catalyst and the dependence of the changes in relative magnetization on the adsorbed amount was measured. Magnetization decreases linearly with increasing amount of oxygen adsorbed, with the slope 0.046, which is less than in adsorption on a clean surface<sup>2</sup> (0.06). Also the total adsorbed amount was lower ( $7.3 \cdot 10^{20}$  molecules) as compared with adsorption on a clean surface ( $8.3 \cdot 10^{20}$  molecules). Oxygen was sorbed irreversibly and even heating to 200°C did not lead to its desorption.

No hydrogen was adsorbed on a catalyst surface where  $8.3 \cdot 10^{20}$  oxygen molecules were adsorbed.

## DISCUSSION

*Interaction of hydrogen sulphide with preadsorbed oxygen.* In the interaction of hydrogen sulphide at 55°C with oxygen preadsorbed at 20°C water was released into the gaseous phase during hydrogen sulphide adsorption. Its formation indicates unambiguously the reaction



When, however, the interaction was followed at room temperature, no water was released into the gaseous phase during hydrogen sulphide adsorption. Only thermal desorption leads to its removal from the catalyst. Obviously, interaction of hydrogen sulphide with preadsorbed oxygen at room temperature proceeds according to reaction (A), but, because of the low temperature, water remains to be bound to the catalyst. Also the results of measurement of the changes in magnetization support the mentioned mechanism. The constant value of magnetization supports the assumption that in this interaction no new bonds are formed in the initial phases of adsorption between sulphur and nickel and sulphur only replaces nickel in the nickel lattice. In this manner the adsorption proceeds as long as the value of the amount of hydrogen sulphide adsorbed is lower than about  $6 \cdot 10^{20}$  molecules. In further adsorption hydrogen sulphide evidently interacts with further nickel atoms which were not bound to oxygen. This can be seen from the decrease of magnetization as well as from the release

of hydrogen into the gaseous phase. However, comparison of the amount of released hydrogen with the decrease in magnetization suggests the assumption that both reactions, *i.e.* reaction (A) and sulphidation of further nickel atoms, proceed simultaneously.

*Interaction of oxygen with preadsorbed hydrogen sulphide.* To explain the initial course of the adsorption of oxygen on a catalyst with preadsorbed hydrogen sulphide three alternative types of oxygen bonding can be considered. 1) Oxygen is bound in the surface layer of sulphides, 2) oxygen is bound to nickel atoms, either through the sulphide layer (diffusion of oxygen atoms inward) or above the sulphide layer (diffusion of nickel atoms to the surface), 3) both processes, *i.e.* binding to sulphides and to free nickel atoms, take place.

The first possibility is opposed by the found decrease of magnetization which indicates interaction with further nickel atoms. The second alternative is improbable, too, since according to the published data<sup>4,5</sup> oxygen is easily adsorbed on sulphide. The third possibility seems to be the most probable one. According to it first a dissociative adsorption takes place on the sulphide layer which is then followed by diffusion of oxygen atoms below the sulphide layer.

*Interaction of hydrogen sulphide with preadsorbed hydrogen.* As mentioned above, in the interaction of hydrogen sulphide with hydrogen preadsorbed on the whole surface of the catalyst only 60% of hydrogen of the total amount of hydrogen

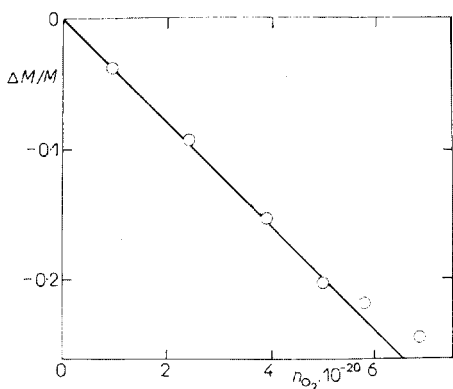


FIG. 2

Dependence of Relative Magnetization  $\Delta M/M$  on the Amount of Adsorbed Oxygen on a Catalyst with Preadsorbed Hydrogen Sulphide

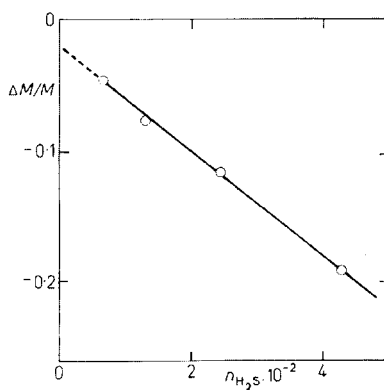


FIG. 3

Dependence of Relative Magnetization  $\Delta M/M$  on the Amount of Adsorbed Hydrogen Sulphide on a Catalyst with Preadsorbed Hydrogen

sulphide adsorbed were released in the first portion, whereas in further portions all hydrogen is released. The lower amount of the released hydrogen in the first portion can be explained so that only the irreversible hydrogen was adsorbed on the surface and the sites for reversible hydrogen remained free. In the adsorption of hydrogen sulphide part of the released hydrogen is bound just to these sites, accessible to reversible hydrogen adsorption. This is also the reason, why the magnetic isotherm does not go through the coordinates origin. The section, cut by the extrapolated part of magnetic isotherm on the axis of relative magnetization, represents the decrease of relative magnetization caused only by reversible adsorption of hydrogen released from the adsorbed hydrogen sulphide. The slope of linear magnetic isotherm was the same as in the case of hydrogen which means, according to Selwood's method<sup>6</sup>, that two bonds per one molecule are formed. Consequently, we can assume that sulphur is bound independently of hydrogen present on the surface. If sulphur were bound to hydrogen, *e.g.* under the formation of S-H bonds, then obviously magnetization would remain constant. The same assumptions are valid for the adsorption of hydrogen sulphide on the surface of a catalyst covered partially with preadsorbed hydrogen. Part of the surface is occupied by hydrogen sulphide bound in the same way as on a clean surface, *i.e.* under the formation of four bonds. For the part of the surface on which hydrogen is preadsorbed the same holds as in the preceding paragraph.

*Interaction of hydrogen with preadsorbed hydrogen sulphide.* After the surface is covered by hydrogen sulphide and after evacuation reversible adsorption of hydrogen on the catalyst takes place. The sites for reversible adsorption of hydrogen are evidently not occupied by hydrogen sulphide. If a greater amount of hydrogen sulphide is adsorbed on the catalyst than would be necessary for complete coverage of the surface, the sites for reversible hydrogen adsorption gradually disappear.

*Interaction of oxygen with preadsorbed hydrogen.* From the comparison of the number of atoms of preadsorbed hydrogen ( $\sim 5 \cdot 10^{20}$ ) with that of sorbed oxygen ( $\sim 15 \cdot 10^{20}$ ) we can assume that only one third of the adsorbed oxygen can interact with hydrogen, while the remaining atoms must be adsorbed as if no hydrogen were present. The comparison of the slopes of magnetic isotherm with that of adsorption on a clean surface clearly shows that the surface interaction of oxygen with hydrogen occurs simultaneously with the oxidation of further nickel atoms. The amount of oxygen adsorbed on a catalyst with preadsorbed hydrogen was less than on a clean surface, by 12%. From this we can conclude that the remnants of hydrogen which could remain on the surface after reduction, would affect only very little the following amount of adsorbed oxygen.

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Translated by V. Čermáková.